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THERMODYNAMICS OF MIXING AND FINAL STATE OF A MIXTURE FORMED BY THE DILUTION OF ANHYDROUS HYDROGEN FLUORIDE WITH MOIST AIR

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Thermodynamics of mixing and final state of a mixture formed by the dilution of anhydrous hydrogen fluoride with moist air

by

P. N. Clough, D. R. Grist and C. J. Wheatley

SUMMARY

In predicting the dispersion behaviour of a cloud of hydrogen fluoride following an accidental release to the atmosphere, it is necessary to know certain properties of hydrogen fluoride mixtures with moist air, particularly the temperature and density. Pure anhydrous hydrogen fluoride (AHF) is highly associated at ambient pressure, and dissociation reactions which occur on dilution with air tend to cool the mixture. However, hydrogen fluoride associates strongly with water vapour in an exothermic process. In moist air, this interaction promotes formation of a condensed aerosol phase, and also tends to heat up the mixture, leading to a possibility of buoyancy.

This work describes a chemical thermodynamic treatment of mixtures of AHF with varying quantities of moist air which enables the final equilibrium state of the mixture to be defined, subject to an assumption of adiabaticity. The treatment has been incorporated in a computer code, WETAHF, which can calculate various properties of the mixture such as temperature, density, and fraction of HF in aerosol form, as a function of air mixing ratio and relative humidity. The code has been applied to a number of starting conditions which might be associated with accidental releases of bulk-stored AHF. The results show that for most starting conditions, the HF-water vapour interaction strongly influences the properties of mixtures for mixing ratios in the range 10 to 1000. In particular, aerosol is predicted to be a significant contributor to the total HF present, and the mixtures are predicted to be buoyant within specific ranges of mixing ratio. The implications of these results with respect to the toxicological and dispersion properties of hydrogen fluoride clouds in the atmosphere are discussed.

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1. INTRODUCTION

Anhydrous hydrogen fluoride (AHF) has a number of applications in the chemical process and nuclear industries notably as an alkylating agent in the petrochemical industry. Bulk storage of the liquid at approximately ambient pressure on a scale up to several tens of tons is practised at several sites, and in plant operation substantial quantities may be maintained at temperatures above the normal boiling point (19·54°C) in pressurised storage. The high toxicity of hydrogen fluoride means that accidental releases of this compound present a significant hazard, and that some assessment of the potential hazard from use and storage is necessary. In a release of liquid AHF to the atmosphere, even at temperatures below the normal boiling point, a substantial vapour fraction is expected to form rapidly, and vaporization will continue as ambient air becomes mixed with the initially released material. The dispersion behaviour of the resulting air/AHF cloud is extremely important with respect to hazard assessment. Various properties of the cloud as a function of the extent of dilution with air must be established as a necessary input to the modelling of the dispersion. Of these, the temperature and buoyancy are the most important.

This report describes an analysis of the thermodynamic equilibrium state and resulting cloud properties after mixing AHF with varying amounts of air containing realistic quantities of water vapour derived from the atmospheric humidity. Water vapour and hydrogen fluoride exhibit a strong chemical interaction which promotes the formation of a liquid phase, the latter being manifest in the form of aerosol in the cloud. The interaction has a number of important consequences in influencing the dispersion and hazard of the cloud, as compared with the situation of mixing in dry air. The reaction of AHF with water is strongly exothermic, so that the condensation of aerosol is associated with heat release which tends to increase the buoyancy of the cloud. Conversely, the formation of a liquid phase itself tends to increase the average cloud density, and so reduce the buoyancy. These effects impact directly on the dispersion behaviour. A secondary effect arises from the deposition of aerosols from the cloud onto the ground, which will occur at a different rate from the deposition of gaseous AHF. The influence of the aerosol also arises in the toxicity properties of the cloud, since the exposure/dose relationship for the gaseous and aerosol forms of HF are expected to differ.

This study centres on a detailed treatment of the thermodynamics of the interaction of HF and water vapour in air, directed towards defining the equilibrium state after mixing. The mixing process is assumed to be adiabatic, so that external heat sources such as the ground are excluded. The chief products of the work are incorporated in a computer code, WETAHF, which can calculate the final state and associated properties for a wide range of selected starting conditions. Perfect mixture is assumed. This work is viewed as an input to the modelling of the dispersion behaviuor of a cloud of AHF taking proper account of the role of water vapour. Only qualitative consideration is given here to the significance of the aerosol formation with respect to dispersion. In some respects, the AHF-water system represents one of the most difficult to handle, since the complications of treating the condensation behaviour have superimposed on them the complexities of the polymerisation behaviour of AHF. However, the approach to solving the final state of the system in terms of the binary phase properties developed is quite general, and should be readily applicable to simpler gaseous-water vapour systems such as SO_3 and NH_3.

2. OUTLINE OF APPROACH

2.1 Scope

The computer code WETAHF, described in outline below, was developed to perform calculations of the thermodynamic equilibrium state of anhydrous hydrogen flouride (HF) after mixing with air of realistic temperature and relative humidity. The thermodynamic equilibrium state following an adiabatic HF/air mixing process at specified mixing ratios was investigated. At these mixing ratios the treatment provides a full description of the state of the mixture and is an essential first step in undertaking analyses allowing simultaneous modelling of dispersion and chemical processes. The criterion of chemical equilibrium assumed for the adiabatic, isobaric system was that the overall enthalpy change, written as a function of temperature ($\Delta H(T)$) should be zero.

Principal input parameters include masses, specific heats, HF and air initial temperature, relative humidity and HF: air mass mixing ratio. The most important output data are the final cloud temperature, density and the presence or absence of an aerosol phase.

2.2 Principal assumptions

To make analysis of the HF/air system feasible certain assumptions are required. These are noted and their validity discussed below.

(a) An adiabatic mixing process is assumed. Brief investigation of the effect of an arbitrary heat transfer to or from the surroundings suggests that such additional inputs to the heat balance (most likely from the ground) are small in relation to other factors. Deposition is not initially considered.

(b) The system is assumed to be well mixed and homogeneous. In reality, in a dispersing cloud localised inhomogeneities and turbulence are likely to lead to regions higher or lower than bulk density. Such effects are outside the scope of the present work.

(c) Supersaturation of vapours is not allowed. As soon as saturation conditions are attained, it is assumed that a liquid phase is formed and a vapour/liquid equilibrium established. In reality, the presence of adventitious nuclei in the atmosphere makes this a plausible assumption.

(d) The chemical behaviour of HF and formation of small polymeric species (oligomers), is assumed to be adequately described by considering 'macroscopic' or observable bulk HF vapour behaviour in terms of a mixture of monomer, dimer and hexamer, each of which behaves as an ideal gas. Interconversion of components is used to describe the observed non-ideal behaviour of HF. The chemical model is described in greater detail in Appendix 2.

(e) The partial pressures of HF and H_2O above a liquid phase of specified temperature and composition and the heat of mixing are derived from interpolation methods described in Reference 1. These may be viewed as fundamentally based on the Duhem-Margules equation or derived from vapour pressure correlation expressions for the pure components, with empirical correction factors to express mixture behaviour.

(f) The kinetics of HF oligomerisation and aerosol condensation are not treated explicitly. These processes are assumed to be near-instantaneous. Elementary reaction kinetics and heat/mass transfer considerations suggest that at the concentrations treated here (mixing ratio $\leqslant 10^3$) these assumptions are well-justified.

2.3 Factors influencing the density of an HF/air cloud

The dispersion behaviour of any gas cloud will depend on the buoyancy of the cloud and hence on the density and temperature of the released gas and ensuing gas/air clouds. The formula weight of HF or the molecular weight of the monomer $\simeq$ 20 and is thus less than the molecular weight of air ($\sim$ 29) Monomeric HF would thus be expected to be buoyant, but the oligomerisation reactions and the thermochemistry of interaction with the atmosphere can drastically modify the behaviour. For anhydrous HF dispersing in air, a considerable number of factors will influence the temperature and density of any resulting cloud. The self-association of HF monomer to form oligomeric species, described by the monomer, dimer, hexamer or 1, 2, 6 chemical model discussed in Appendix 2, could be expected simply to increase the density of an HF/air cloud though further investigation reveals considerably more complex behaviour.

As the hydrogen fluoride partial pressure is reduced the degree of association will decrease, reducing the cloud density. The dissociation reactions, however, are significantly endothermic, thus reducing the cloud temperature and hence increasing the cloud density. If HF is initially released in the liquid phase, the presence of any liquid HF, probably as droplets of sufficiently small size to remain airborne for a significant time, will increase the cloud density. Latent heat, required to evaporate the droplets will cool the cloud and thus increase the density. The strong chemical affinity will lead to interaction of HF and H_2O promoting formation of a liquid aerosol phase. Solution of HF in water droplets is, however, a strongly exothermic reaction which will tend to reduce the cloud density. These interacting processes affect the cloud density through their influence on the cloud volume and temperature in a way indicated by the following scheme:-

Process	Volume effect	Heating effect
Evaporation of initial liquid HF present	d	i
Monomer formation from oligomers	d	i
Aerosol formation	i	d

i = increasing cloud density
d = decreasing cloud density

2.4 Outline of solution technique

Full details of the solution technique are given in Appendices 1 and 2 and a brief outline is presented here. Consideration of the unknown quantities to be determined, such as final temperature, masses of HF and H_2O liquid, oligomer mole fractions, etc. and the available expressions linking known and unknown quantities, shows that the final cloud temperature pervades many of the equations developed and partly determines many of the unknowns. It is apparent that the most convenient approach would be to treat the temperature as the independent variable and attempt to express other unknowns as a function of temperature. For an adiabatic, isobaric system, the criterion of equilibrium is that the overall enthalpy change should be zero:

$$\Delta H = H(\text{final}) - H(\text{initial}) = 0$$

The most promising approach is thus to obtain equations and models whereby the overall expression for ΔH as a function of temperature, $\Delta H(T) = 0$, may be expressed in terms of known parameters and solved. As many of the parameters, such as partial pressures, extents of dissociation, or oligomerisation reactions have complex dependencies on temperature, an iterative approach to the evaluation of zeros of the function $\Delta H(T) = 0$ is necessary. A further advantage of this approach is that a direct solution can be obtained for each HF: air mixing ratio; it is not necessary to use the results of previous mixing ratio evaluations, add further air and investigate the resulting changes. Such step-wise approaches can easily lead to significant errors building up by compounding minor errors in each mixing step.

The first step in the overall solution is to determine all the parameters needed to provide a full description of the initial state of the system. The assumed HF initial state is that of a cloud of pure HF at 1 atmosphere pressure and at a temperature and initial liquid phase fraction specified by the input data. The enthalpy change associated with depressurisation, discharge from a vessel or fragmentation of liquid is thus ignored. The initial state of oligomerisation, and hence the apparent hydrogen fluoride molecular weight, may be determined given the initial temperature and the combined partial pressure of the oligomers (equal to atmospheric pressure for the assumed initial state). The initial state of the air is defined by the temperature and the relative humidity.

The next stage is to evaluate the enthalpy change as a function of temperature. The enthalpy change ensuing, ΔH, may be expressed as

$$\Delta H = \Delta U + P\Delta V$$

and the contributions to each term may be split into

$$\Delta H = \Delta U_{air} + \Delta U_{HF} + \Delta U_{H_2O} + \Delta U_{mix} + P\Delta V$$

where ΔU_{air}, ΔU_{H_2O} may be readily obtained from the evaluated temperature change using appropriate specific and latent heat values. The enthalpy of formation of HF/H_2O solutions is considered using separate contributions for the vapour and liquid phase of each component, and a heat of mixing of pure HF liquid with pure H_2O liquid thus

$$\begin{tikzcd}
\text{Vapour phase HF} \arrow[r, "\Delta U_1"] & \text{pure HF liquid} \arrow[dr, "\Delta U_3"] & \\
 & & \text{HF/H}_2\text{O solution} \\
\text{Vapour phase H}_2\text{O} \arrow[r, "\Delta U_2"] \arrow[urr, bend right, "\Delta U_4"'] & \text{pure H}_2\text{O liquid} \arrow[ur] &
\end{tikzcd}$$

where

$$\Delta U_4 = \Delta U_1 + \Delta U_2 + \Delta U_3$$

To evaluate $\Delta H(T)$, it is necessary to have a criterion to determine whether a liquid phase will form. Two different but related routes to evaluating the enthalpy change are used according to whether a liquid phase is or is not present. The phase test employs the continuous algorithms describing the HF and H_2O partial pressures above mixtures at specified temperature and composition discussed in Reference 1. The solution technique adopted initially assumes that no liquid phase is present, then tests the evaluated P_{HF} and P_{H_2O} to determine whether the combined saturation vapour pressure is exceeded. As no allowance is made for supersaturation, if the evaluated pressure is below the SVP no liquid phase is assumed to be present, if above, the condition is found where sufficient liquid of appropriate composition is condensed to achieve saturation of both vapours. A convenient algorithm is of considerable value as the iterative approach to solution necessitates repeated checks on the phases present. The two approaches, for vapour only cases or for vapour and liquid phase present cases, will now be considered in turn.

2.5 Establishing equilibrium with only vapour phase present

At chemical equilibrium, the total HF partial pressure may be related to the partial pressures of the oligomers, and the total number of moles of HF may also be related to the partial pressures of the oligomers. It is thus possible to establish two equations which may be manipulated to obtain an expression in which

$$P_{HF} = f(P_1, T)$$

where P_{HF} = total partial pressure, P_1 = monomer partial pressure. At given T, this equation may be solved, initially for P_1/P_{HF}. The individual oligomer pressures and thus the HF composition may be obtained subsequently. Once the partial pressures and HF composition have been established it is then necessary to evaluate the enthalpy change.

2.6 Establishing equilibrium with both vapour and liquid phases present

If it is determined that a liquid phase will be present, it is necessary to proceed via a distinct route from the single phase case until the overall enthalpy change is determined. The approach to defining the final state is based on mass conservation of both HF and water in the cloud. At a given temperature, the equilibrium vapour pressures of HF and H_2O above the liquid phase can be expressed as a function of the mass fraction XM_{HF} of HF in the liquid. Each value of XM_{HF} corresponds to a single value of P_{HF}, which in turn corresponds to a given mass of HF vapour in the cloud if the volume is known. The latter can be determined from the behaviour of the dry air component in the cloud. The mass of HF in the liquid phase then follows from mass conservation, leading to the mass of water in the liquid phase, since the water mass fraction $XM_{H_2O} = (1 - XM_{HF})$. A check on the water mass balance then determines whether the residual water in the vapour phase is consistent with the required equilibrium vapour pressure of water above the liquid phase. This latter requirement is met by a unique value of XM_{HF}, which defines the equilibrium state of the system at temperature T, and this must be obtained by an iterative method. The HF oligomeric composition in the vapour is uniquely determined by the total pressure P_{HF} and the temperature.

2.7 Final determination of enthalpy change and cloud parameters

Once parameters such as partial pressures, and composition variables have been established, the enthalpy balance may be performed. At a certain final cloud temperature this will be zero and at this point thermodynamic equilibrium will have been attained.

Once the thermodynamic equilibrium state is established, the final cloud parameters may be readily evaluated.

3. RESULTS AND DISCUSSION

3.1 General survey

A wide range of conditions could exist immediately after an accidental release of AHF to the atmosphere, encompassing temperatures of the AHF cloud above or below the normal boiling point, and the presence or absence of an initial liquid phase. For this reason, a matrix of case runs of the code WETAHF has been investigated, designed to cover most likely situations, and to test aspects of the code and the impact of different atmospheric conditions. The case studies have concentrated on an initial HF temperature of 19·54°C, the normal boiling point, which would apply for a release of stored liquid. Various properties of the mixture as a function of the mass ratio of admixed air have been examined. Of these, the most important with respect to dispersion and hazard are the temperature, the density (which determines the buoyancy), and the fraction of HF in the aerosol phase. The complete matrix of initial conditions and output properties examined is shown in Table 1, which provides a key to the figures in which the various properties are graphically represented. Several other features of the mixture are output by the code, such as the volume, partial pressures of HF and water vapour, and state of oligomerisation of HF. However, since these are of no direct importance as far as dispersion is concerned, they have not been included in the results presented here. An upper limit on air mass mixing ratio of 1000 has been employed. It must be borne in mind that the detailed results presented here are based on the data described in Appendix 3. Some of these data, particularly those relating to the phase properties of the HF-H_2O system, involve selection or extrapolation, and are subject to non-negligible uncertainties. Sensitivity analysis of such uncertainties has not been undertaken, but they are judged to be sufficiently small as to have insignificant impact on the main conclusions.

Figures 1 - 3 immediately illustrate the marked impact of water vapour on the properties of the mixture, for starting conditions of saturated HF vapour at the normal boiling point mixed with air at 20°C and various relative humidities (RH). In all cases, the temperatures (Fig. 1) initially fall during the early stages of dilution, because the endothermic dissociation of HF oligomers is the dominating effect. As the dilution continues, and mixing ratios (MR) exceed about 5 - 10, the sensible heat contributed by the admixed air counteracts this cooling effect and temperatures begin to rise again. For dry air, this rising region tends monotonically towards ambient temperature, but for moist air, the importance of the exothermic HF-water interaction is evident from the existence of a mixing region in which the temperature significantly exceeds ambient. At very high dilutions, all properties of the mixture tend towards those of the air. Direct evidence of the importance of the HF-water interaction is provided in Fig. 3, which shows the aerosol-borne fraction of the total HF mass in the mixture. Some aerosol is predicted to be formed almost immediately on admixing small amounts of moist air. For relative humidities 50% and 95%, the aerosol fractions show maxima at intermediate mixing ratios, which represent substantial proportions of the total HF. The persistence of the aerosol on further dilution is strongly dependent on RH. For a RH of 50%, aerosol has completely disappeared at MR $\geqslant$ 1000, and the properties of the mixture thereafter are negligibly affected by the presence of moisture. However, for RH = 95%, the aerosol and its influence on other properties persist to much higher mixing ratios. The impact of these temperature and phase separation effects on overall mixture density is shown in Fig. 2. The density of a dry-air mixture falls monotonically with dilution, asymptotically towards the ambient air density (1·204 kg m^{-3}). By contrast, mixtures involving air of 50% or 95% RH show density minima at intermediate mixing ratios corresponding to buoyancy. The detailed predictions of buoyancy for these and other initial conditions are summarised in Table 2.

Figures 4 - 8 illustrate the effects of initial air temperature on properties of the mixture when single phase saturated AHF at its boiling point (19·54°C) is released into air at 50% RH. All of these mixtures exhibit temperatures above ambient (Fig. 4) and slight buoyancy (Fig. 5, Table 2) for specific ranges of MR towards the upper end of the range investigated. Because the mass fraction of water vapour in the admixed air falls steeply with temperature at constant relative humidity, major effects of HF-water interaction are evident in successively higher ranges of MR as the initial air temperature is reduced. This is particularly clear in Fig. 6, which shows that the MR corresponding to the maximum fraction of HF in aerosol form shifts steadily upwards as the initial air temperature declines, peaking beyond MR = 1000 for an air temperature of − 10°C. In all cases, aerosol represents a significant fraction of the total HF mass over the MR range 30 - 3000. The aerosol composition is shown in Fig. 7. The mass fraction of HF declines steadily as more and more water vapour becomes available in the admixed air. The high mass fraction of HF at low mixing ratios reflects a remarkable feature of the HF-H_2O phase diagram. Only a small fraction of water is required in the liquid phase to bring about a marked reduction in the vapour pressure of HF relative to that of the pure liquid, so strong is the chemical affinity of these compounds.

Moreover, at low mixing ratios, essentially all of the water in the cloud becomes condensed in the aerosol. For example, for an air temperature of 20°C at RH = 50%, more than 99% of the water present in the cloud exists in the aerosol phase for mixing ratios up to 20. The mass fraction of HF present in aerosol form and the aerosol composition are important parameters for assessing the exposure/dose properties of the cloud. A further parameter important for dispersion assessment is the aerosol mass density, shown in Fig. 8. This refers to the total mass of aerosol particles per unit volume of cloud, and it is the principle parameter needed for estimating the rate of aerosol agglomeration and settling in the cloud. The significance of the values derived is discussed further in Section 3.2 below.

Figures 9 - 13 show the same cloud properties as Figs 4 - 8, but here for admixed air of 95% RH. All of the effects and trends apparent at 50% RH due to the HF-water vapour interaction are now even more obvious. Most notably, distinct buoyancy of the clouds is predicted in the higher range of mixing ratios as shown in Fig. 10 and in Table 2. Also, the fractions of HF present in aerosol form (Fig. 11) are significantly larger than that at RH = 50%, and in fact for air temperatures of 0 and − 10°C aerosol becomes the predominant form of HF in certain MR ranges. The aerosol composition (Fig. 12) shows similar trends to the results for 50% RH, but for corresponding conditions the water mass fraction in the aerosol is somewhat higher than before. The aerosol mass densities (Fig. 13) are everywhere higher. For mixing ratios below 5, the aerosol mass densities scale roughly according to the relative humidity, which follows from the fact that almost all the water is present in the aerosol phase in this mixing range.

In Figs 14 - 18, the effects of including a 0·5 liquid fraction in the initially released AHF at the normal boiling point are examined, for air at 95% relative humidity and various temperatures. The main influence of the liquid on cloud temperature, comparing Figs 14 and 9, is at MR less than about 20, where cooler clouds are predicted with liquid AHF initially present. There is very little effect for MR in the range 100 - 1000. Correspondingly, although the cloud density is markedly higher for low mixing ratios, Fig. 15 and Table 2 show that the initial two phase release results in buoyant clouds of similar density to a single phase release at higher mixing ratios. In this case, the initial aerosol fraction of HF falls steeply corresponding to evaporation of the initial 50% liquid, before rising again at higher MR values, due to the increasing role of the water in the condensed phase (Fig. 16). The aerosol composition (Fig. 17) is everywhere richer in HF than for the analogous situations when no liquid is initially present, although at low MR essentially all of the water is still present in aerosol form. A steep decline in the aerosol mass density over the MR range 0·1 to 1 is predicted (Fig. 18), again due to the evaporation of the initially release liquid AHF. Unlike the cases previously examined the aerosol mass density here shows no maximum, but decreases monotonically with increasing MR.

The final group of figures, Figs 19 - 21, show three cloud properties for a release of AHF, initially at 41°C into air at 20°C and varying RH. The HF temperature was chosen to give an initial density of the HF at one atmosphere very close to the air density. The effect of relative humidity on buoyancy is then clearly apparent. Figure 20 shows that for dry air, the cloud density is always greater than the air density. However, at 50% RH buoyancy develops at MR $\sim$ 10, and at 95% RH the exothermic HF-water interaction becomes dominant, resulting in buoyancy of the mixture over most of the mixing range. The heating effect of the HF-water vapour interaction is evident in Fig. 19. Figure 21 shows that even under the high temperature conditions of release chosen here, aerosol is formed immediately moist air mixes into the AHF, and that aerosol will play a substantial role over much of the mixing ratio range examined.

3.2 Properties of the aerosols formed

It is not possible to predict with certainty the average size or the size distribution of the aerosol droplets formed as a result of the HF-water vapour interaction. Such information is, however, needed for assessing the dispersive properties of the cloud, and the role of aerosol deposition in modifying these. It is also important with respect to the hazard from the cloud, since gaseous HF and HF aerosols when inhaled would be expected to exhibit different toxicological properties. This is discussed below.

The most important output parameter for estimating the aerosol properties is the aerosol mass density. Results for this are shown in Figs 8, 13 and 18 for a range of initial conditions. For mixing ratios greater than 1, which are expected to be attained very rapidly following an accidental release, aerosol mass densities less than 0·1 kg m^{-3} are predicted in all cases. This implies that the aerosols formed are not so dense as to settle out rapidly. At intermediate dilutions of 10 to 100, which will be reached fairly quickly, the densities lie roughly in the range 0·05 to 0·01 kg m^{-3}, and at high dilutions are below 0·01 kg m^{-3}. General modelling studies of aerosol settling behaviour(2) show that, provided the particles are not very large (< 50 μm), aqueous aerosols in this density range will take at least an hour, and more usually several hours, to settle out appreciably.

The aerosol mass densities predicted also provide some guidance on the likely particle sizes, at least when no liquid AHF phase is initially present. Figures 8 and 13 show the mass densities peaking in the range 0·05 to 0·01 kg m^{-3} for MR $\sim$ 1 in seven out of eight cases. These densities are only compatible with mean droplet diameters greater than about 0·1 μm, since smaller particles would agglomerate extremely rapidly up to this size range due to the very high number densities of smaller particles required to accommodate the mass densities. It seems reasonable to assume, therefore, that the aerosol size distribution will range from 0·1 μm upwards. As already noted, particles of size greater than about 50 μm will settle out from the atmosphere quite rapidly, so this places a rough upper limit on the range of transported particles. Further guidance is available from data on naturally-formed fogs and mists(3) although it must be recognised that the mechanisms for formation of these may differ significantly from those of the HF aerosols considered here. Natural mists typically have mass densities of around 10^{-4} kg m^{-3}, and so are probably not relevant to the present situation. Clouds, with mass densities of 10^{-2} - 10^{-3} kg m^{-3}, appear more appropriate. Although different cloud types have characteristic particle size distributions, the peaks in the number density distributions lie in the vicinity of 10 μm, with broad distributions extending from a few microns up to 40 - 50 μm. The mass distribution is weighted towards larger particle sizes.

In summary, it seems likely that the aqueous HF aerosols will be of a size range which persists for some hours without substantial settling out. A broad range of particle sizes is likely, but most of the aerosol mass will be associated with particles of diameter 10 μm and upwards. Clearly, some dependence on the air temperature and RH is to be expected, but this is hard to predict.

With regard to the toxicological impact of aerosol formation, the physiological effect of aerosol once it has contacted tissue will be identical to that of gaseous HF. Only in the context of inhalation might the difference in retention efficiencies of the gas and the aerosol be of significance. The human respiratory system acts as an effective fractionator for aerosol particles, the larger particles (> 5 μm) being mainly deposited in the nose and upper respiratory tract by inertial impaction, and only small particles in the size range 0·1 to 1 μ penetrating into the lung. The retention efficiency in the lung for such particles is quite low, and typically more than 70% will be exhaled. That fraction of the HF aerosol in the 0·1 to 1 μm size range will thus probably give a lower lung dose than a corresponding amount of gaseous HF. However, if the arguments concerning the most probable aerosol sizes above are correct, the largest part of the HF aerosol is likely to be deposited in the nose and upper respiratory tract. The overall effect of the presence of aerosol will thus be to shift the location of inhalation damage somewhat towards the upper regions of the respiratory tract. It must be borne in mind that in almost all of the case studies here, less than 50% of the total HF will be present in aerosol form in the cloud under any conditions of dilution. It follows that the overall exposure/dose properties of the cloud cannot be greatly modified by the presence of aerosol.

3.3 Implications for dispersion modelling

It has been found that the density of a mixture of HF and air is strongly affected by adsorption of heat due to conversion of HF to the monomer, and by emission of heat due to condensation of HF with water vapour to form an aqueous phase. In the early phases of dilution the former dominates and causes the mixture to become denser. In the later phases of dilution the latter dominates and causes the mixture to become less dense and even buoyant in moist atmospheres. Consideration is given to whether these density effects significantly affect the atmospheric dispersion behaviour, and as a consequence the hazardous effect, of an HF vapour cloud and implications for modelling this behaviour.

During the early states of dispersion the cloud will be denser than the surrounding air. This affects dispersion in two ways: the cloud will spread horizontally due to gravity forces, becoming low-lying and broad; and, the cloud will form a stable layer with vertical mixing suppressed by the stable density gradient.

The significance of horizontal spreading and suppressed vertical mixing in relation to dilution without density effects can be quantified in terms of a 'layer' Richardson number defined by

$$Ri = g \frac{\Delta\rho H}{\rho_a u_*^2} \qquad \Delta\rho = \frac{\rho - \rho_a}{\rho_a} \qquad \ldots (3.1)$$

where

$\Delta\rho/\rho_a$ is the relative density excess of the cloud with respect to the ambient atmosphere,

g is acceleration due to gravity,

H is the height of the stable layer, and

u_* is the friction velocity.

For horizontal spreading due to gravity to be more rapid than horizontal mixing due to ambient turbulence the following relation must be satisfied

$$Ri \geqslant 1 \qquad \ldots (3.2)$$

turbulent

For vertical mixing to be significantly suppressed compared to passive vertical mixing the relation is slightly different

$$Ri \geqslant \frac{w'^2}{u_*^2} \qquad \ldots (3.3)$$

where w' is the ambient vertical turbulence velocity. In neutral atmospheres w'^2/u_*^2 is of order unity. In stable atmospheres w'^2/u_*^2 is $\sim$ 1/5 and in unstable atmospheres w'^2/U_*^2 is $\sim$ 2. Density effects therefore persist longest in stable atmospheres and by inserting values for the parameters u_* and $(w'/u_*)^2$ and with $H \sim 3$ m, typical for a 2 tonne release of heavy vapour, we find

$$\frac{\Delta\rho}{\rho_a} \geqslant 0{\cdot}2 \times 10^{-3} \qquad \ldots (3.4)$$

A corresponding upper limit for $\Delta\rho/\rho_a$ occurs in neutral atmospheres when u_* is larger:

$$\frac{\Delta\rho}{\rho_a} \geqslant 8{\cdot}0 \times 10^{-3} \qquad \ldots (3.5)$$

Using these bounds, inspection of Figs 2, 5, 10, 15 and 20 reveals the following results with regard to the effects of excess density on dispersion:

(i) In dry air, excess density effects are significantly enhanced due to cooling of the cloud by formation of the HF monomer. Significant density effects extend up to mass mixing ratios greater than 10^3 in stable conditions and of order 10^3 in neutral conditions.

(ii) In moist air with relative humidity 50 - 95% (encompassing typical values in the UK) the enhanced density effects due to formation of the monomer are less significant. Most importantly, the range of mass mixing ratios over which excess density effects are important is reduced by roughly two orders of magnitude.

To summarise, it has been found that moist air reduces the significance of the enhanced density effects caused by formation of HF monomer and causes a very large reduction in the mass mixing ratio range over which dispersion is effected by excess density. It therefore follows that it is essential that the effects of humidity be incorporated in any model for dispersion of HF, otherwise the effect of excess density will be overestimated and predictions will be unrealistic.

The effects of enhanced density increase the hazardous range of the cloud upwind and crosswind as a direct consequence of increased horizontal spreading. The effect on the downwind hazardous range is however, less clear. Suppressed vertical mixing causes the rate of dilution of the cloud to be reduced. This is opposed by the increased surface area of the cloud over which mixing takes place and by the slower speed of travel of the cloud. In most cases this results in a net reduction of the maximum centre-line concentration at a given point downwind of the release point. The hazardous effect depends on exposure time as well as concentration. For continuous releases this is not strongly affected but for puff releases the exposure time is increased because the path length through the cloud is larger and the speed of the cloud is smaller. Thus, no general conclusion on reduction in downwind hazard ranges is possible; each case has to be considered individually.

It has been found that the heat released due to aqueous aerosol formation in moist air causes the cloud to become buoyant in the later stages of dilution. The mass mixing ratio range over which this occurs is shown in Table 2. The buoyancy may be sufficient to cause two possible effects:

(i) Coherent lift-off of the cloud as a whole in the form of a rising thermal.

(ii) Enhanced vertical mixing caused by localised thermal effects.

Not surprisingly, the parameter which determines whether (i) occurs in preference to mixing by ambient turbulence is the layer Richardson number defined above, which must satisfy

$$Ri \geqslant \left(\frac{w'}{u_*}\right)^2 \qquad \ldots (3.6)$$

Dimensional arguments suggest that the parameter relevent to (ii) is again the layer Richardson number, but it is not apparent what determines whether (ii) takes place in preference to (i) or vice versa.

The results found above for $\Delta\rho/\rho_a$ compared with values found from Table 2 show that the positive buoyancy is significant in most cases.

The modelling of positive buoyancy effects is new ground in the field of atmospheric dispersion of toxic and flammable substances. Clearly positive buoyancy when it occurs may drastically alter the process of dispersion and has the potential to lead to significant reductions in hazard ranges. It is known that transition from negative to positive buoyancy also occurs in ammonia and liquefied natural gas vapour clouds and so it is concluded that this topic is worthy of further study.

TABLE 1

Key to figures
(The entry in the table shows the Fig. No where the particular output variable is shown for the specified input conditions.)

Input				Output				
°C T_{HF}	HF liquid fraction	RH %	T_{Air}	T final	Cloud density	HF mass in aerosol	Aerosol composition	Aerosol density
19·54	0	0	20	1	2	3		
"	"	50	"	"	"	"		
"	"	95	"	"	"	"		
"	"	50	20	4	5	6	7	8
"	"	"	10	"	"	"	"	"
"	"	"	0	"	"	"	"	"
"	"	"	− 10	"	"	"	"	"
"	"	95	20	9	10	11	12	13
"	"	"	10	"	"	"	"	"
"	"	"	0	"	"	"	"	"
"	"	"	− 10	"	"	"	"	"
"	0·5	95	20	14	15	16	17	18
"	"	"	10	"	"	"	"	"
"	"	"	0	"	"	"	"	"
"	"	"	− 10	"	"	"	"	"
41	0	0	20	19	20	21		
"	"	50	"	"	"	"		
"	"	95	"	"	"	"		

TABLE 2

Comparison of minimum cloud density and ambient air density in cases where cloud buoyancy is predicted

T_{HF} °C	HF liquid fraction	RH %	T_{AIR} °C	Air density kg m^{-3}	Minimum cloud density kg m^{-3}	MR range of minimum	MR for onset of buoyancy
19·54	0	50	20	1·199	1·196	80 - 160	63
			10	1·244	1·240	200 - 250	126
			0	1·291	1·288	300 - 500	200
			− 10	1·341	1·339	600 - 1000	500
19·54	0	95	20	1·194	1·170	60 - 80	25
			10	1·241	1·220	120 - 130	40
			0	1·289	1·274	200 - 250	80
			− 10	1·340	1·331	300 - 1000	158
19·54	0·5	95	20	1·194	1·174	80 - 100	31
			10	1·241	1·223	150 - 170	50
			0	1·289	1·276	250 - 300	100
			− 10	1·340	1·332	400 - 800	200
41	0	50	20	1·199	1·176	30 - 40	12
		95	"	1·194	1·145	16 - 20	0·5

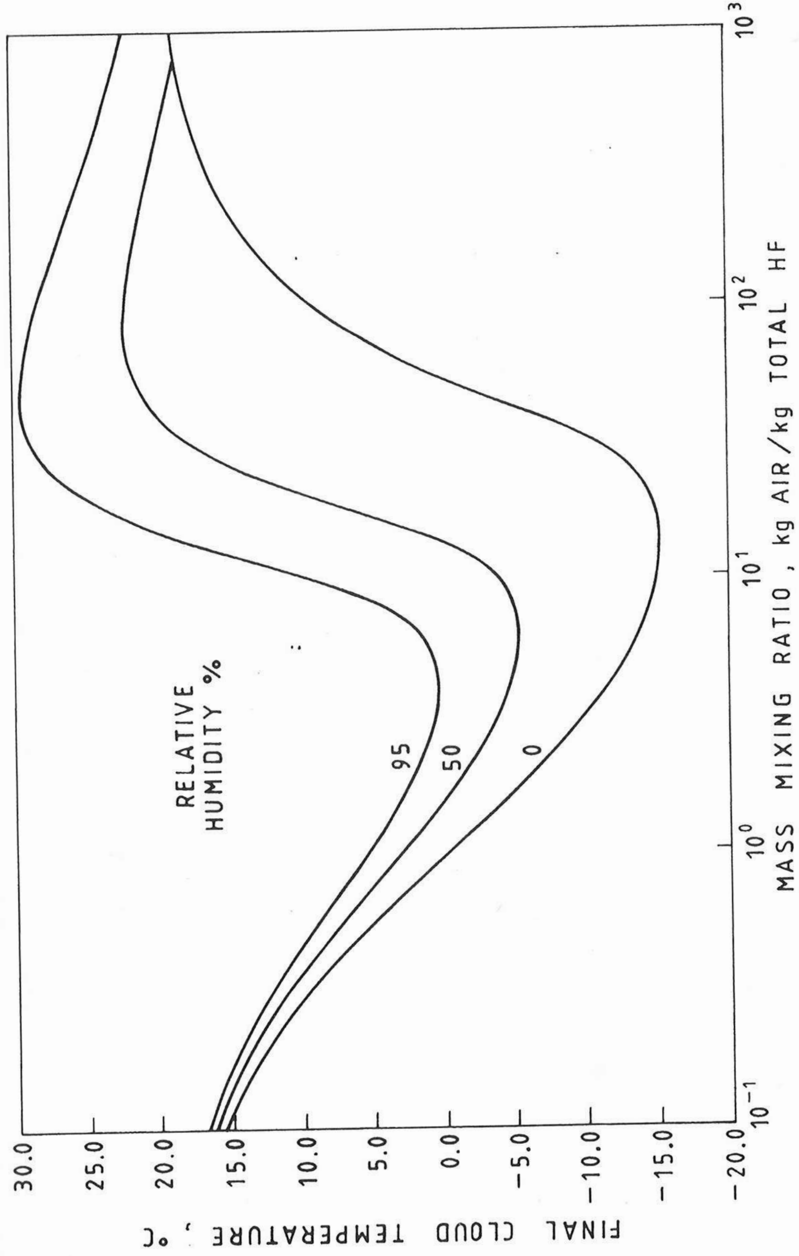

FIG.1 VARIATION OF FINAL CLOUD TEMPERATURE WITH RELATIVE HUMIDITY.
T_{HF} = 19.54°C, LIQUID FRACTION = 0. T_{AIR} = 20°C

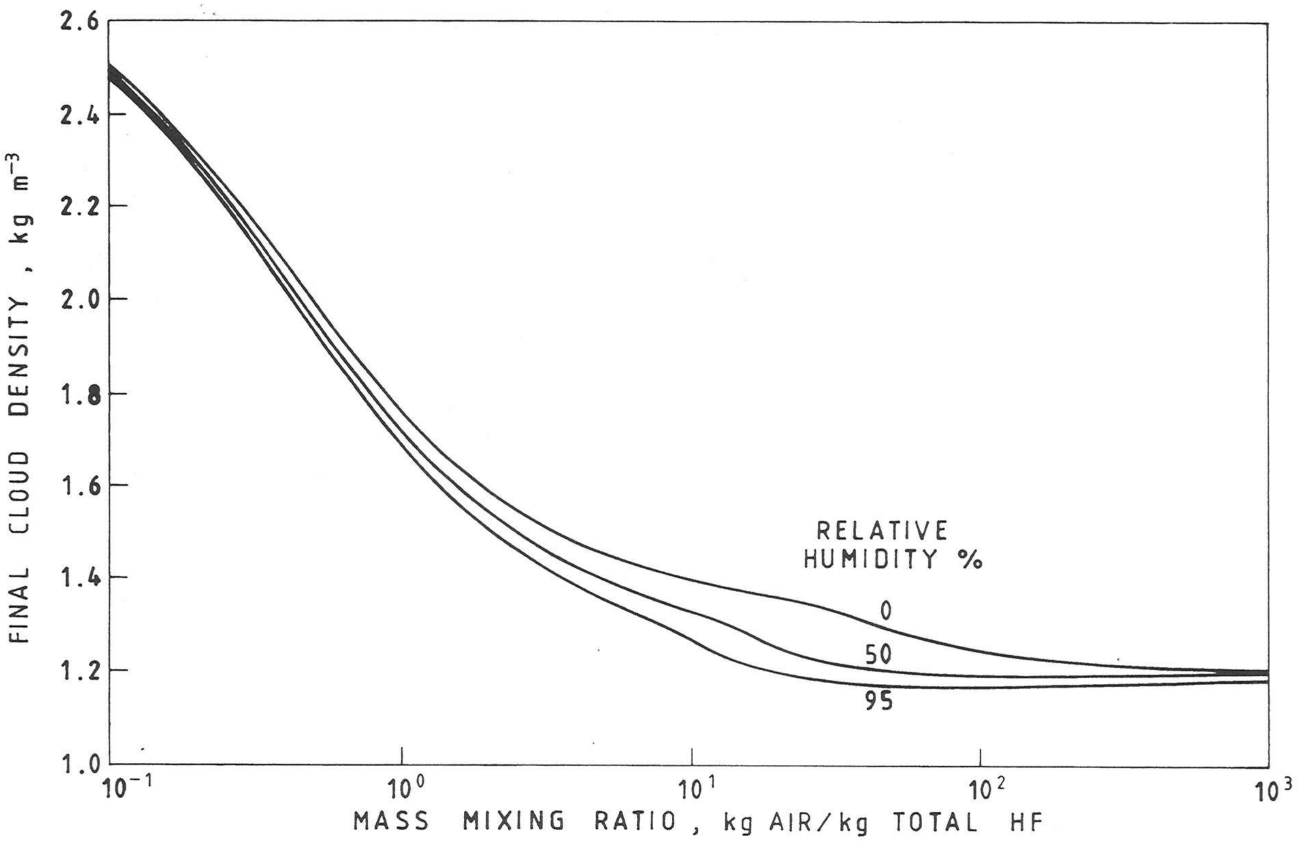

FIG. 2 VARIATION OF FINAL CLOUD DENSITY WITH RELATIVE HUMIDITY
T_{HF} = 19.54 °C , LIQUID FRACTION = 0. T_{AIR} = 20 °C

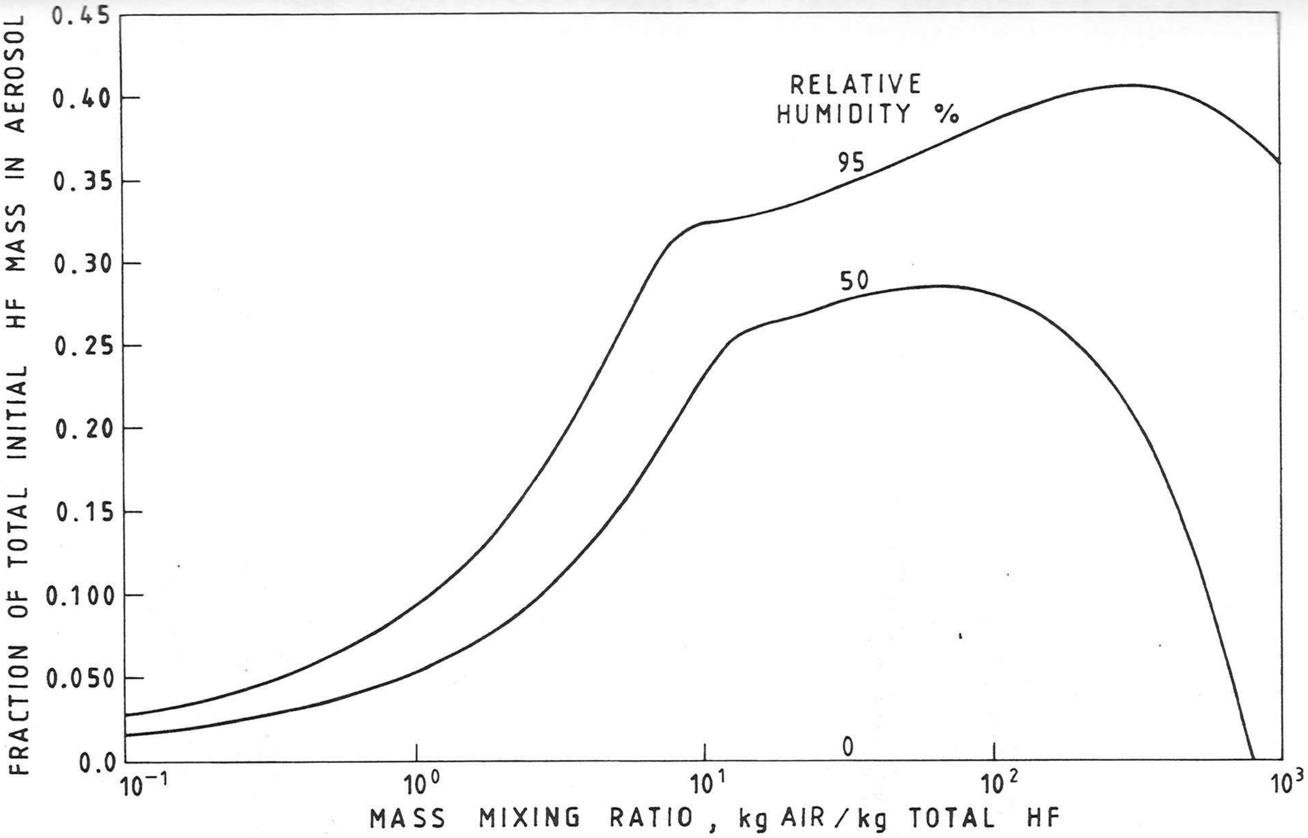

FIG. 3 VARIATION OF FRACTION OF HF MASS IN AEROSOL WITH RELATIVE HUMIDITY. T_{HF} = 19.54 °C , LIQUID FRACTION = 0. T_{AIR} = 20 °C

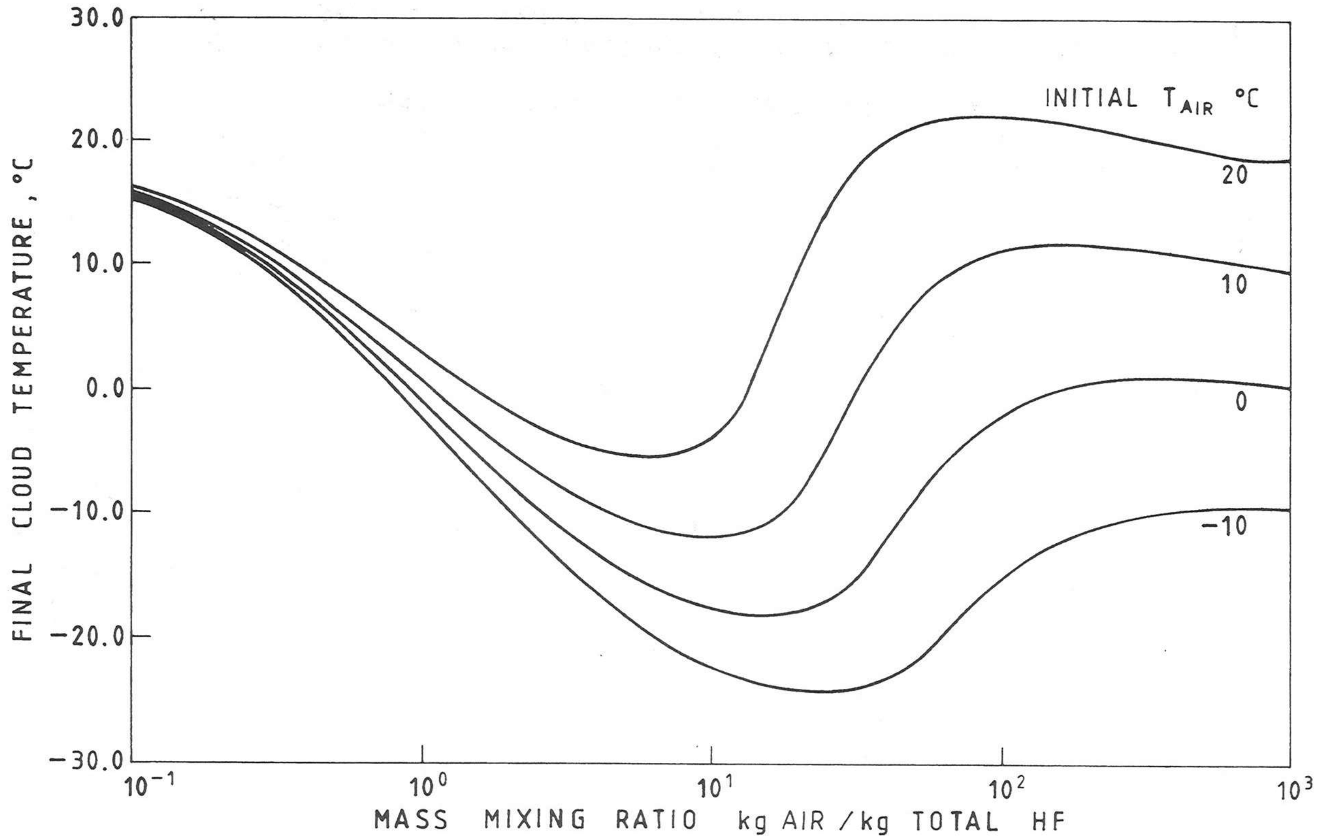

FIG. 4 VARIATION OF FINAL CLOUD TEMPERATURE WITH INITIAL AIR TEMPERATURE. $T_{HF} = 19.54$ °C, LIQUID FRACTION = 0. RH = 50%

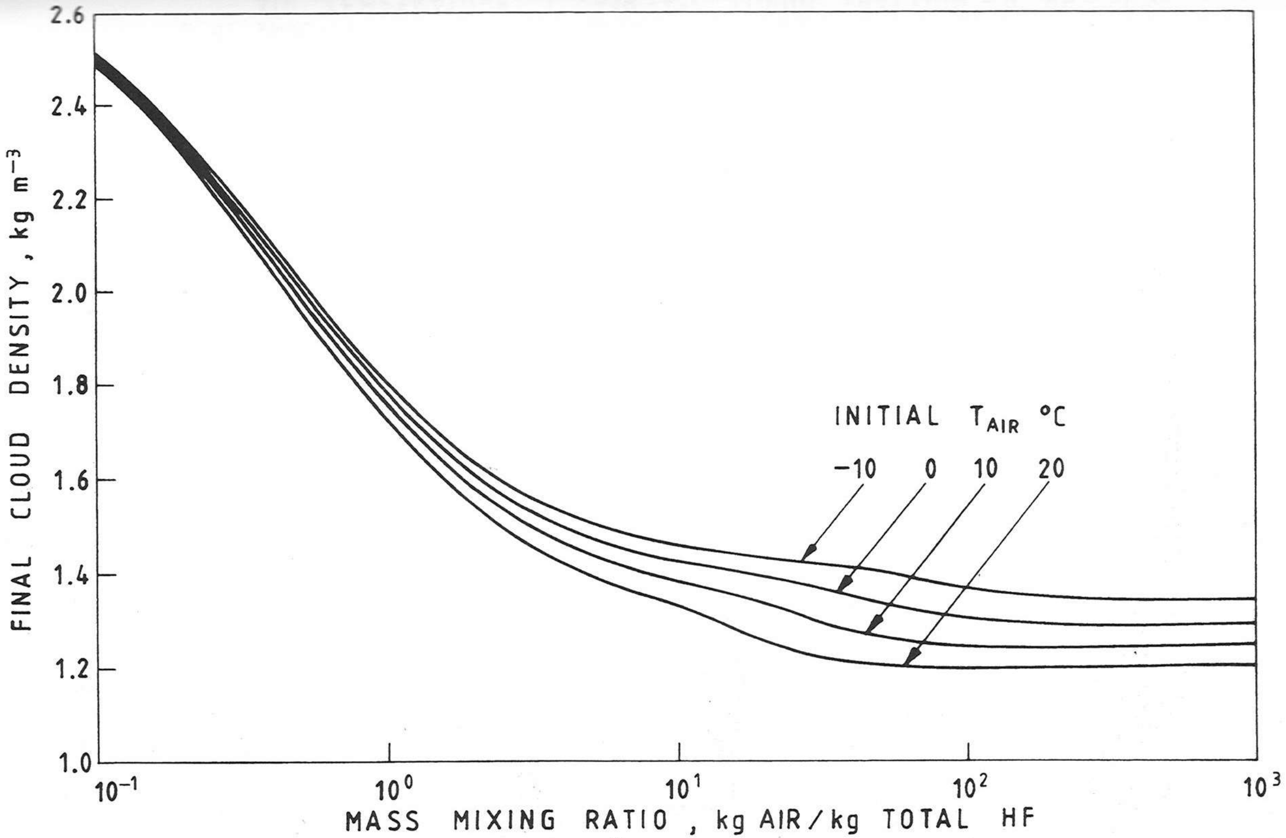

FIG. 5 VARIATION OF FINAL CLOUD DENSITY WITH INITIAL AIR TEMPERATURE. $T_{HF} = 19.54$ °C, LIQUID FRACTION = 0. RH = 50%

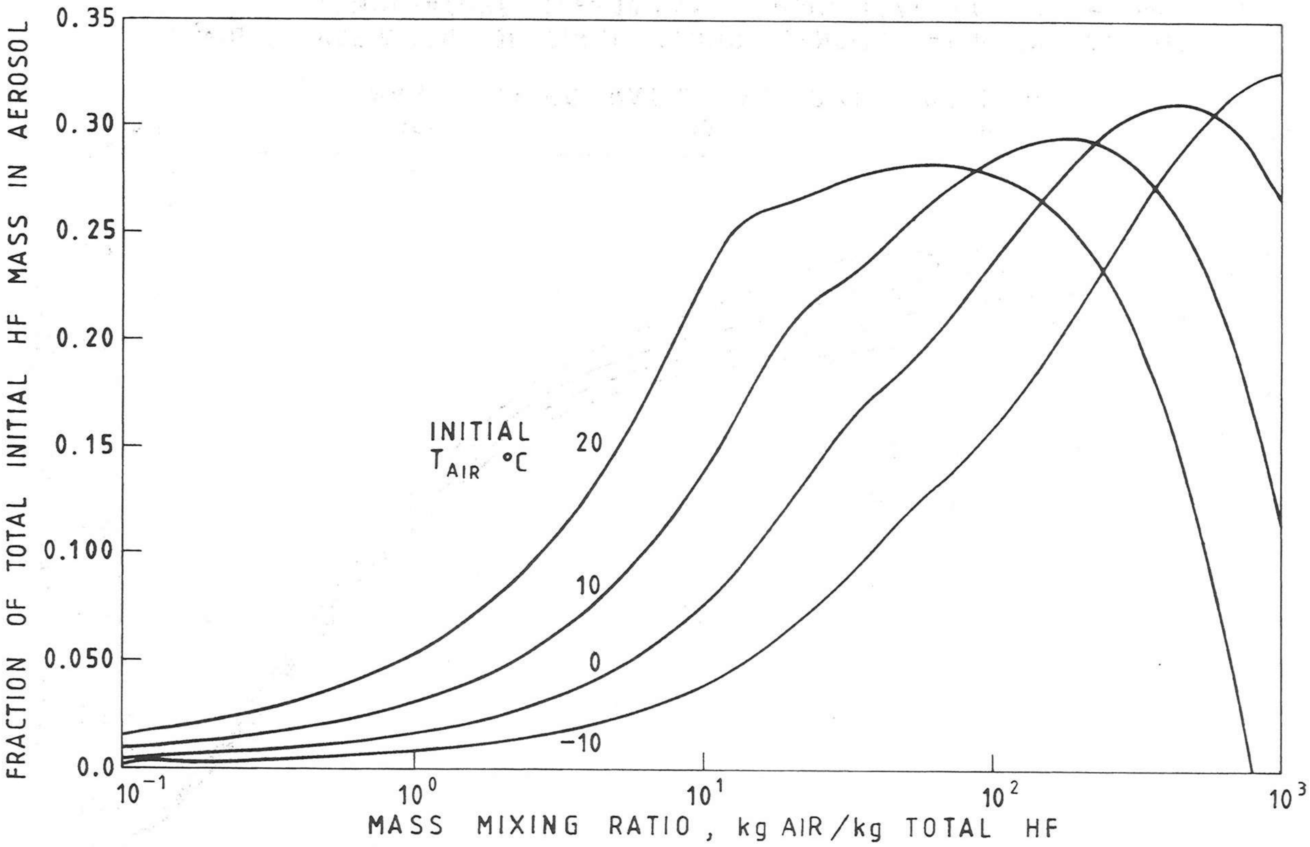

FIG. 6 VARIATION OF FRACTION OF HF MASS IN AEROSOL WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54°C, LIQUID FRACTION = 0. RH = 50%

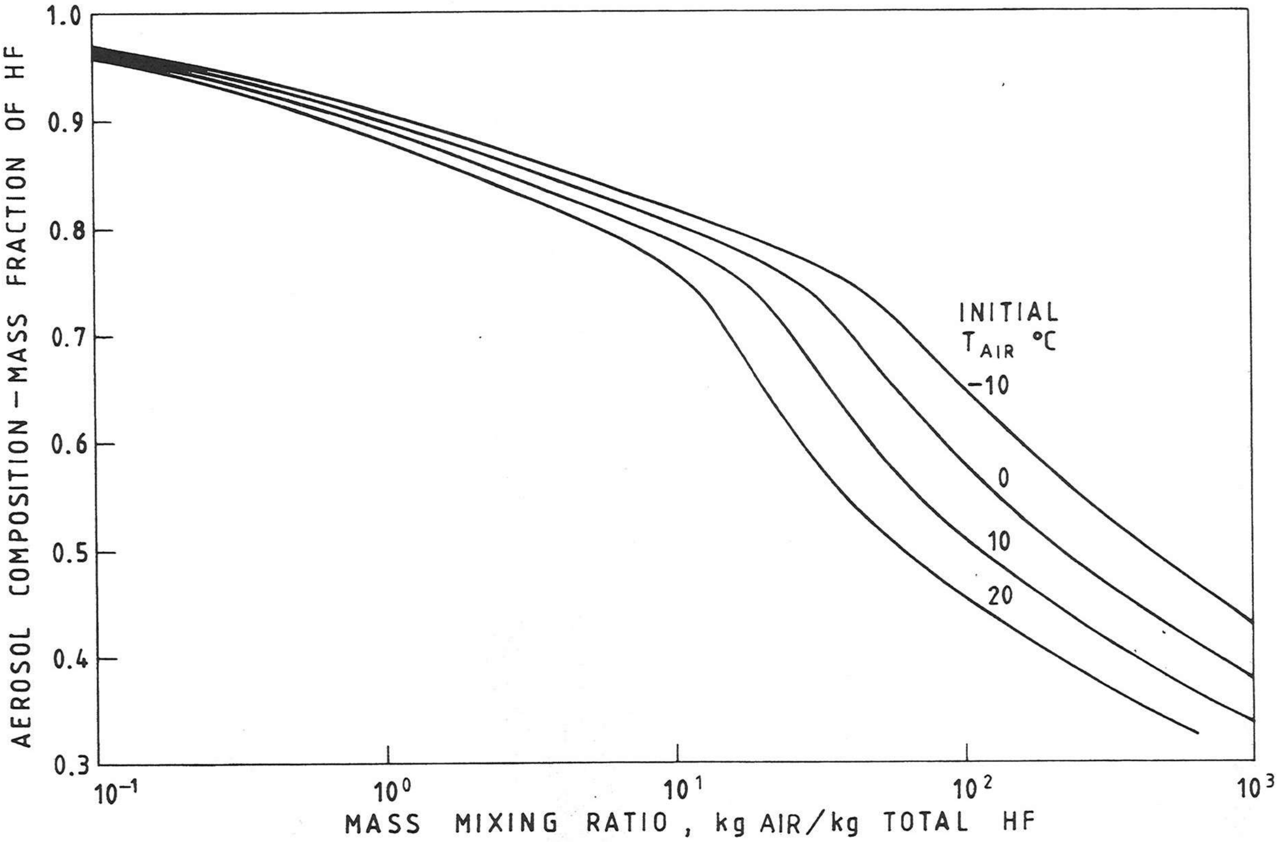

FIG. 7 VARIATION OF AEROSOL COMPOSITION WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54 °C, LIQUID FRACTION = 0. RH = 50%

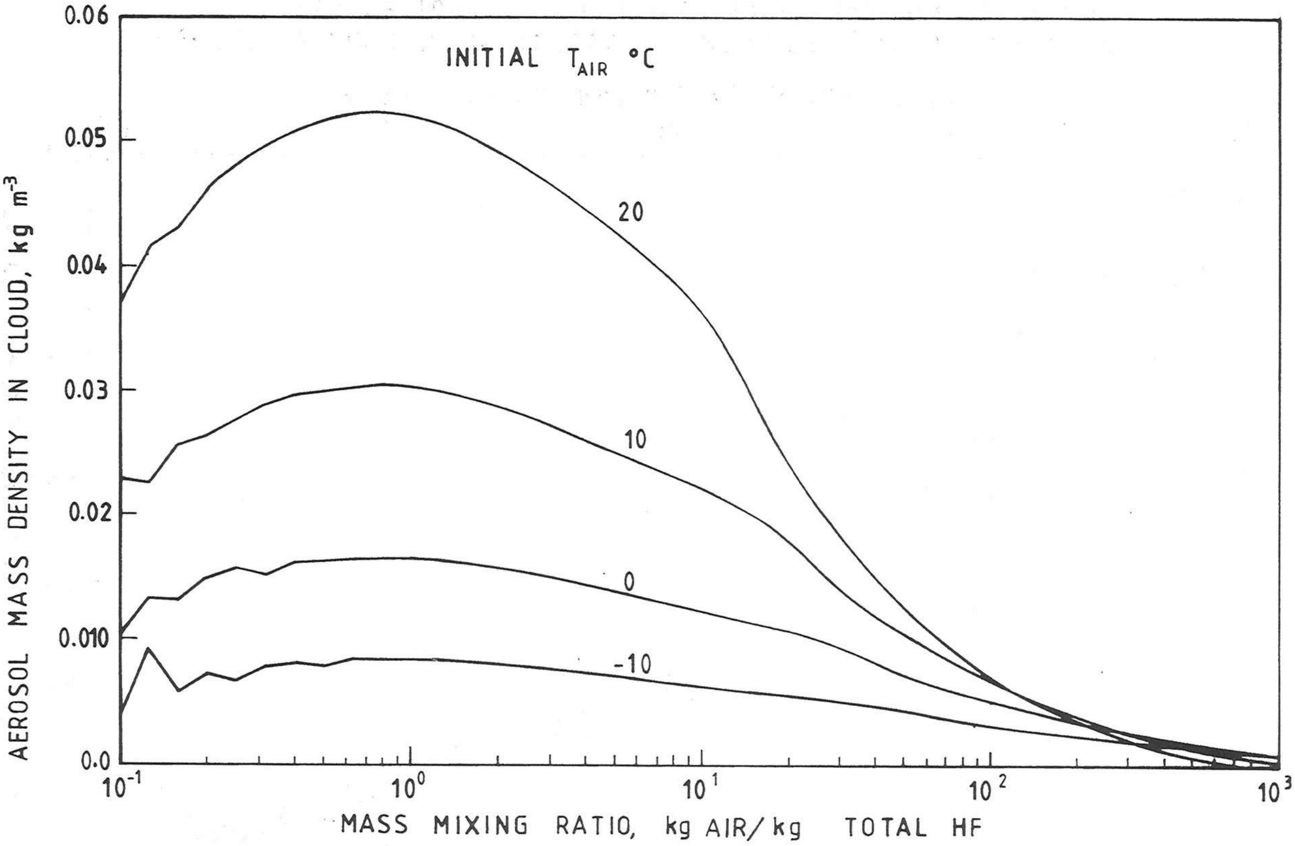

FIG. 8 VARIATION OF AEROSOL MASS DENSITY IN CLOUD WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54 °C, LIQUID FRACTION = 0. RH = 50%.

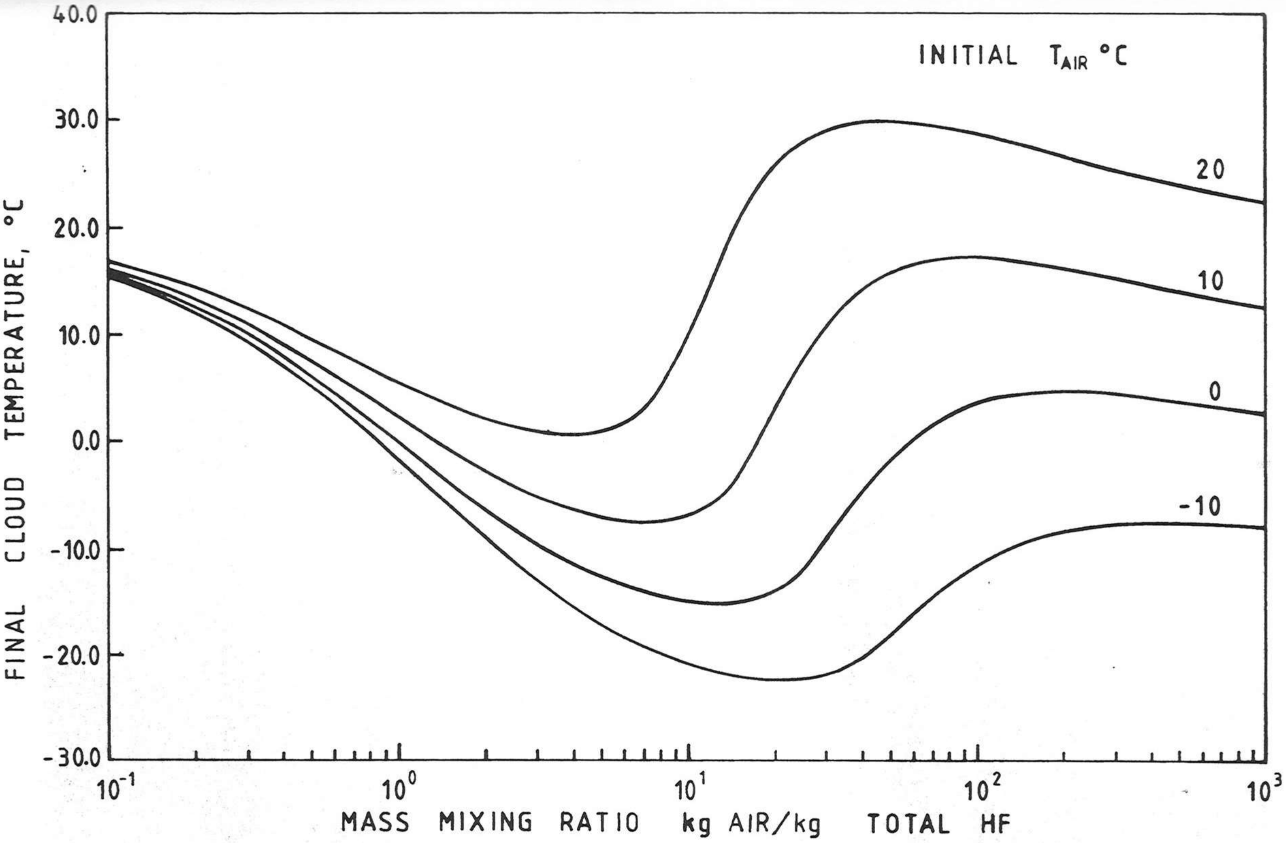

FIG. 9 VARIATION OF FINAL CLOUD TEMPERATURE WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54 °C LIQUID FRACTION = 0. RH = 95%

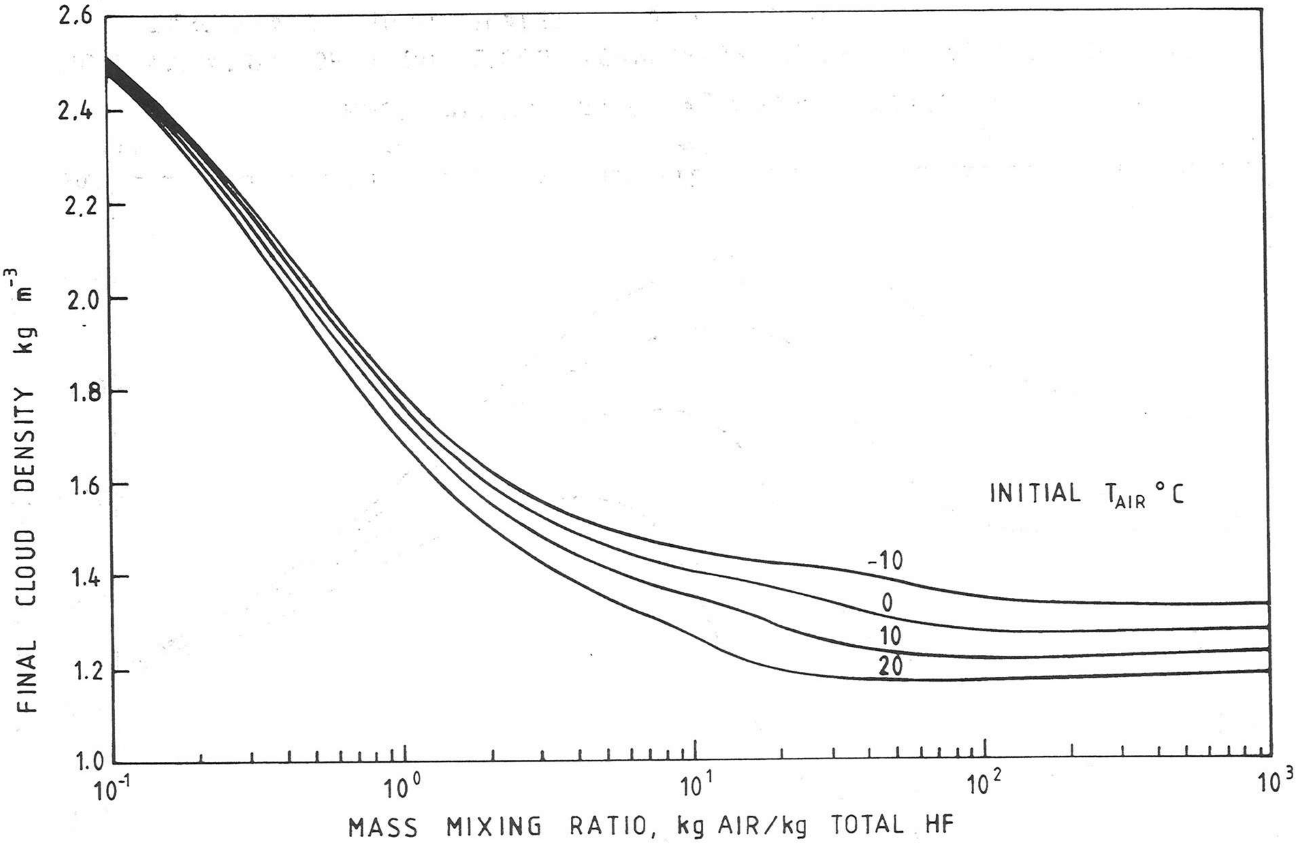

FIG. 10 VARIATION OF FINAL CLOUD DENSITY WITH INITIAL AIR TEMPERATURE T_{HF} = 19.54°C, LIQUID FRACTION = 0. RH = 95%

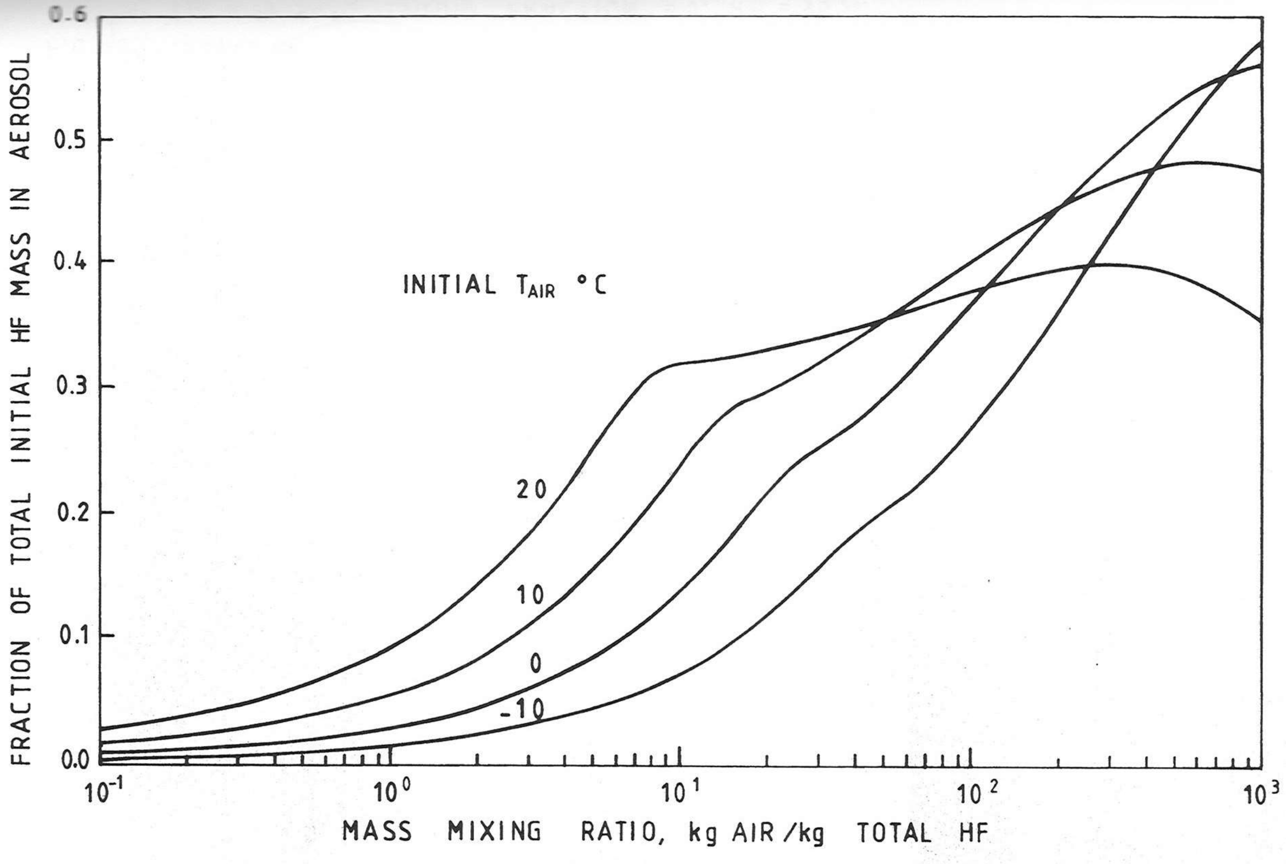

FIG. 11 VARIATION OF FRACTION OF HF MASS IN AEROSOL WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54°C, LIQUID FRACTION = 0. RH = 95%

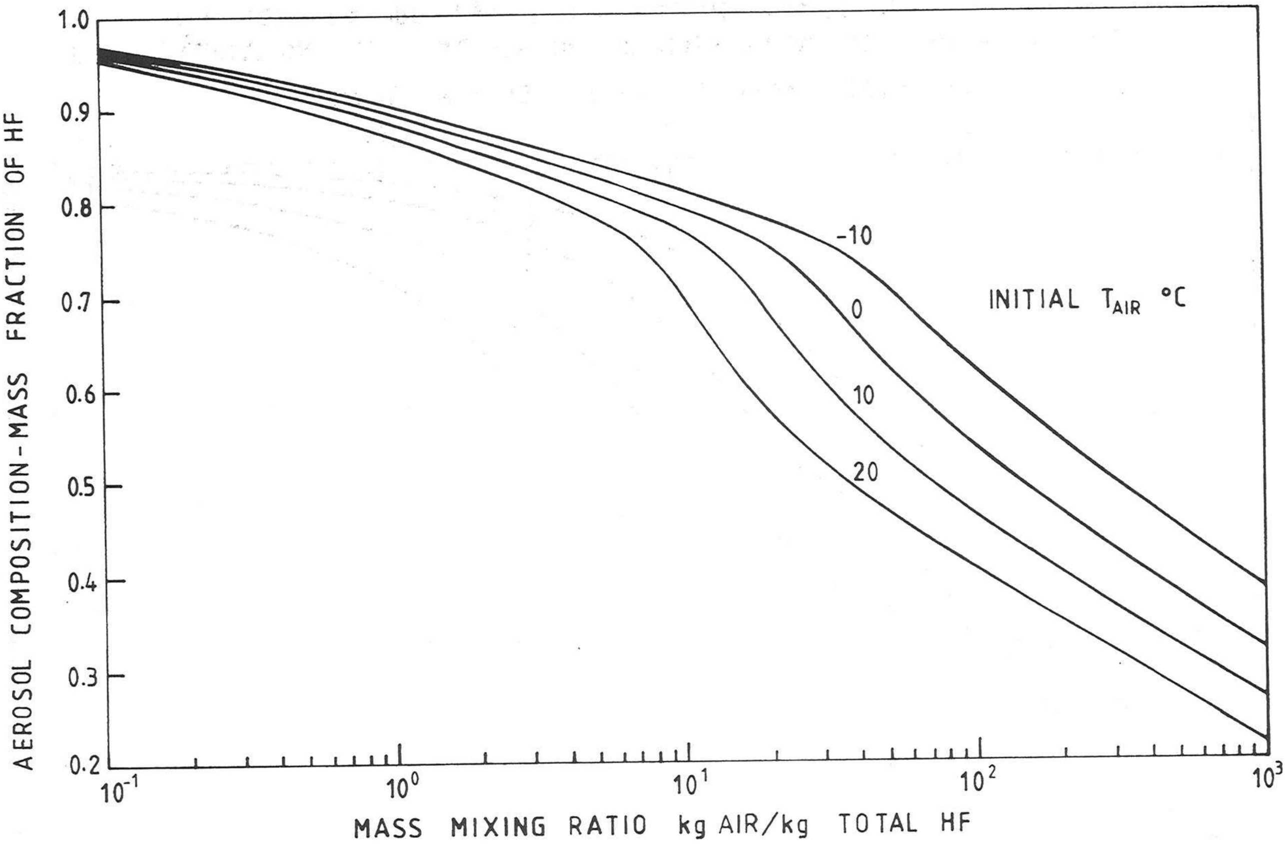

FIG. 12 VARIATION OF AEROSOL COMPOSITION WITH INITIAL AIR TEMPERATURE
T_{HF} = 19.54°C, LIQUID FRACTION = 0. RH = 95%

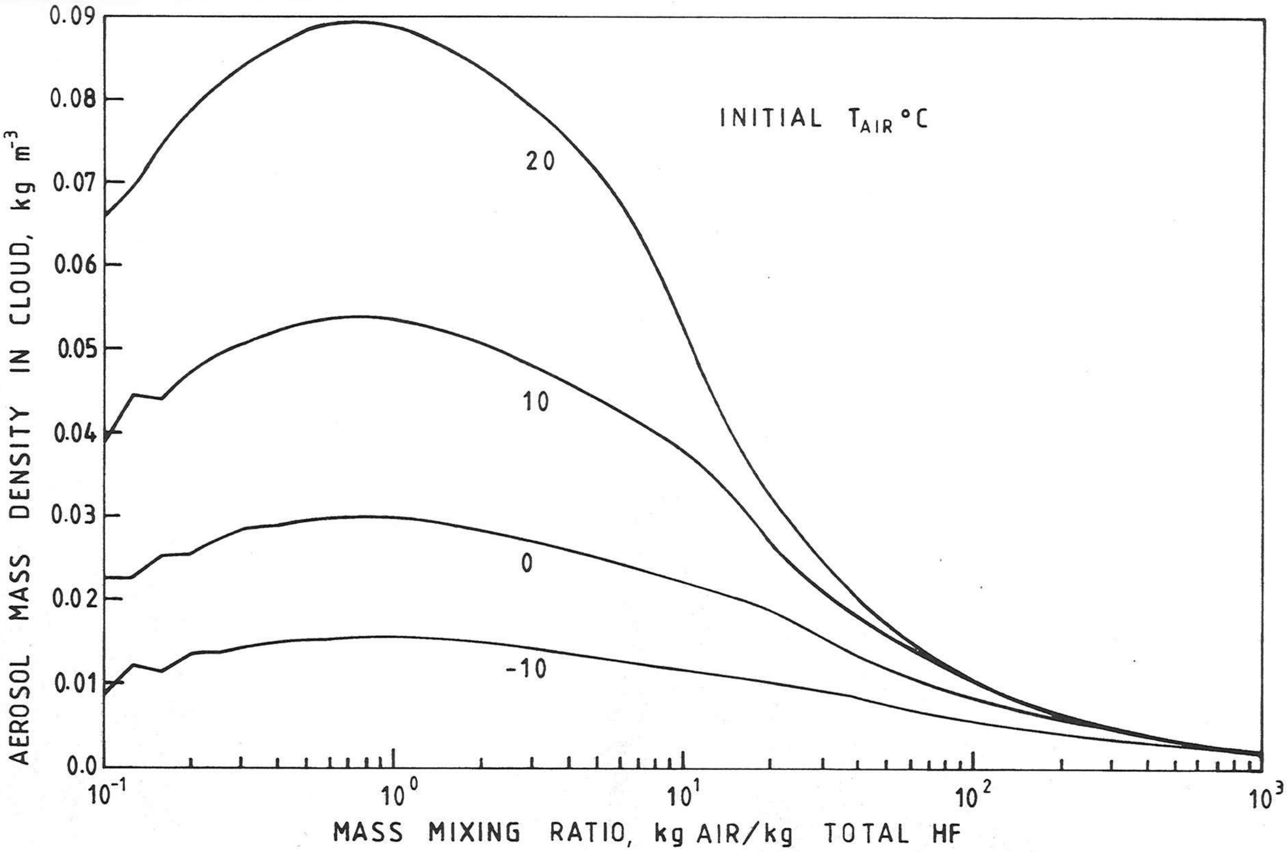

FIG. 13 VARIATION OF AEROSOL MASS DENSITY IN CLOUD WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54°C LIQUID FRACTION = 0. RH = 95%

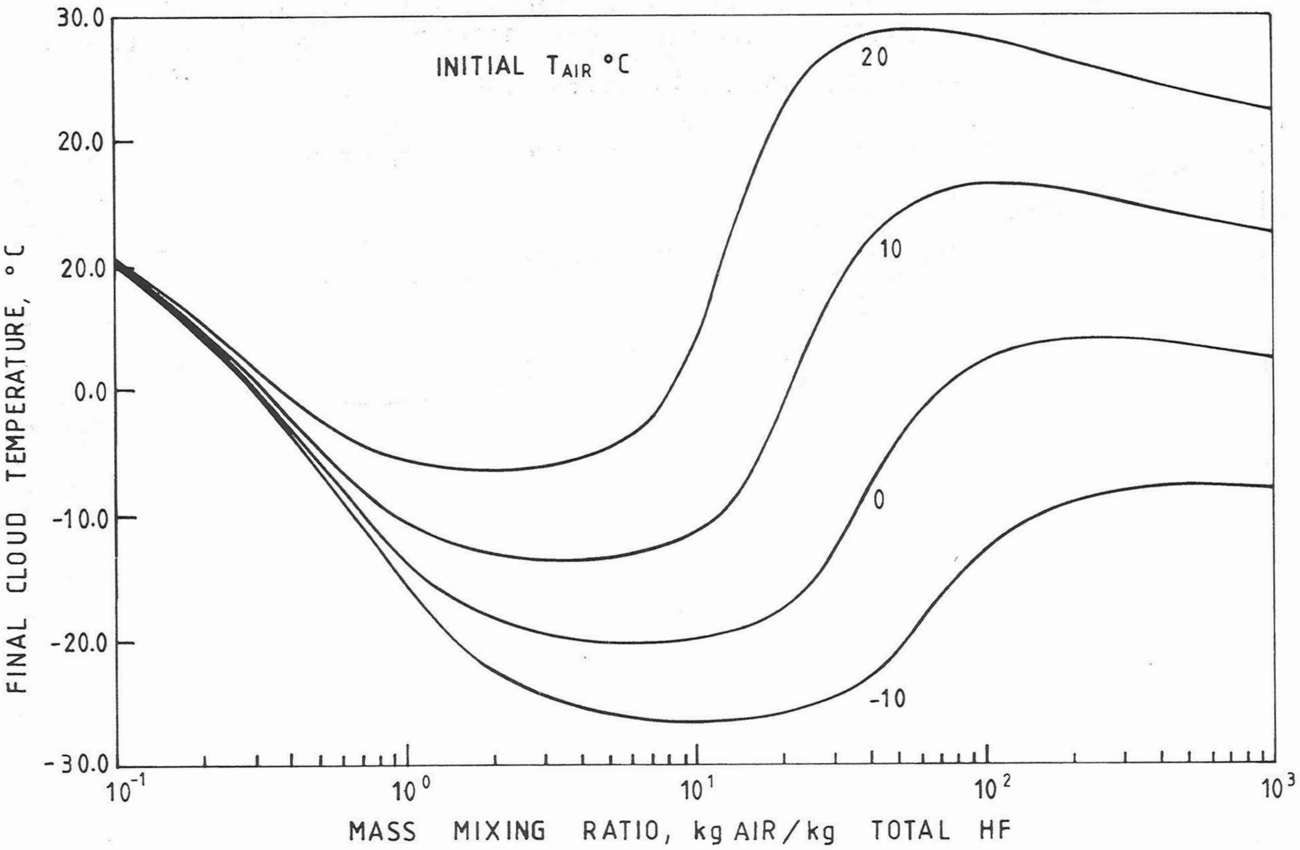

FIG. 14 VARIATION OF FINAL CLOUD TEMPERATURE WITH INITIAL AIR TEMPERATURE . T_{HF} = 19.54 °C, LIQUID FRACTION = 0.5. RH = 95 %

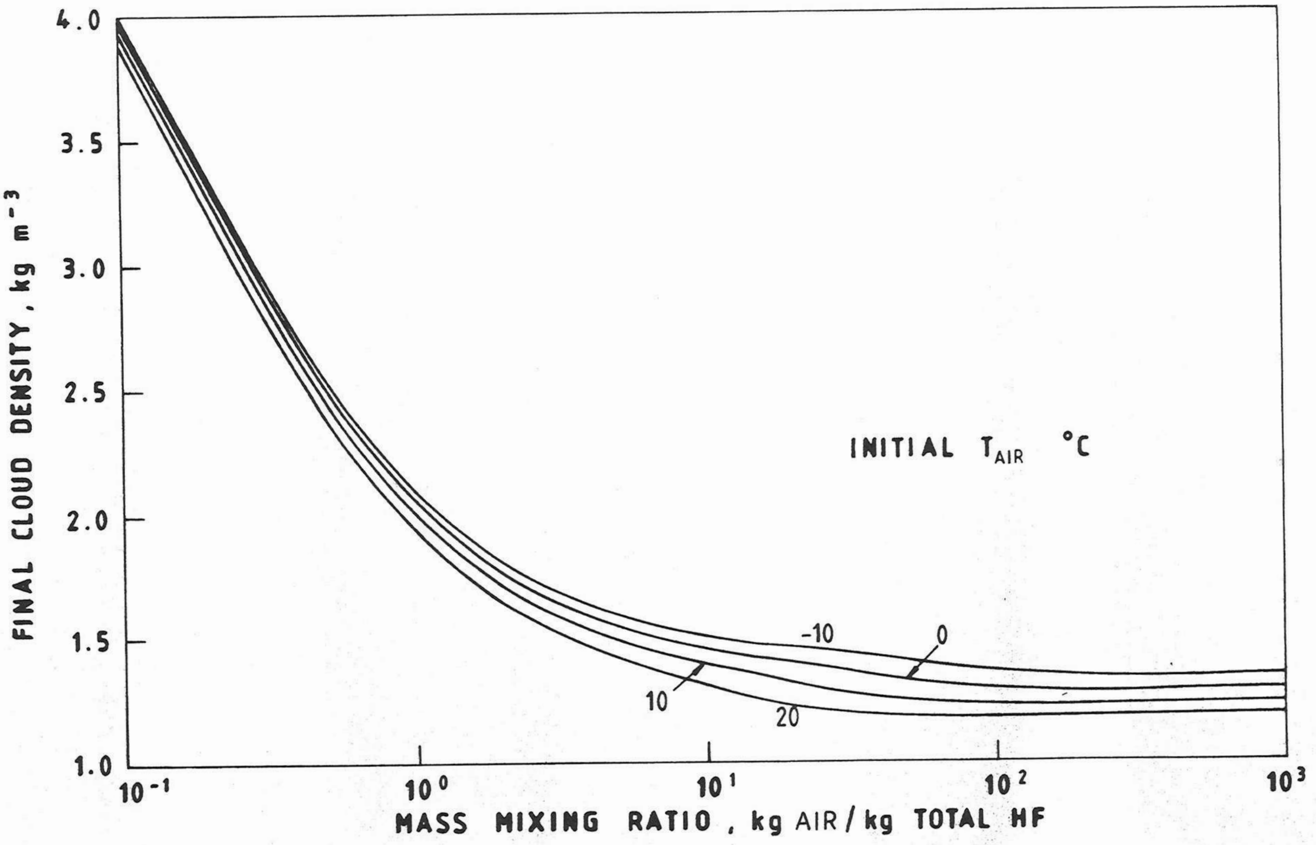

FIG.15 VARIATION OF FINAL CLOUD DENSITY WITH INITIAL AIR TEMPERATURE . T_{HF} = 19.54 °C, LIQUID FRACTION = 0.5 RH = 95 %

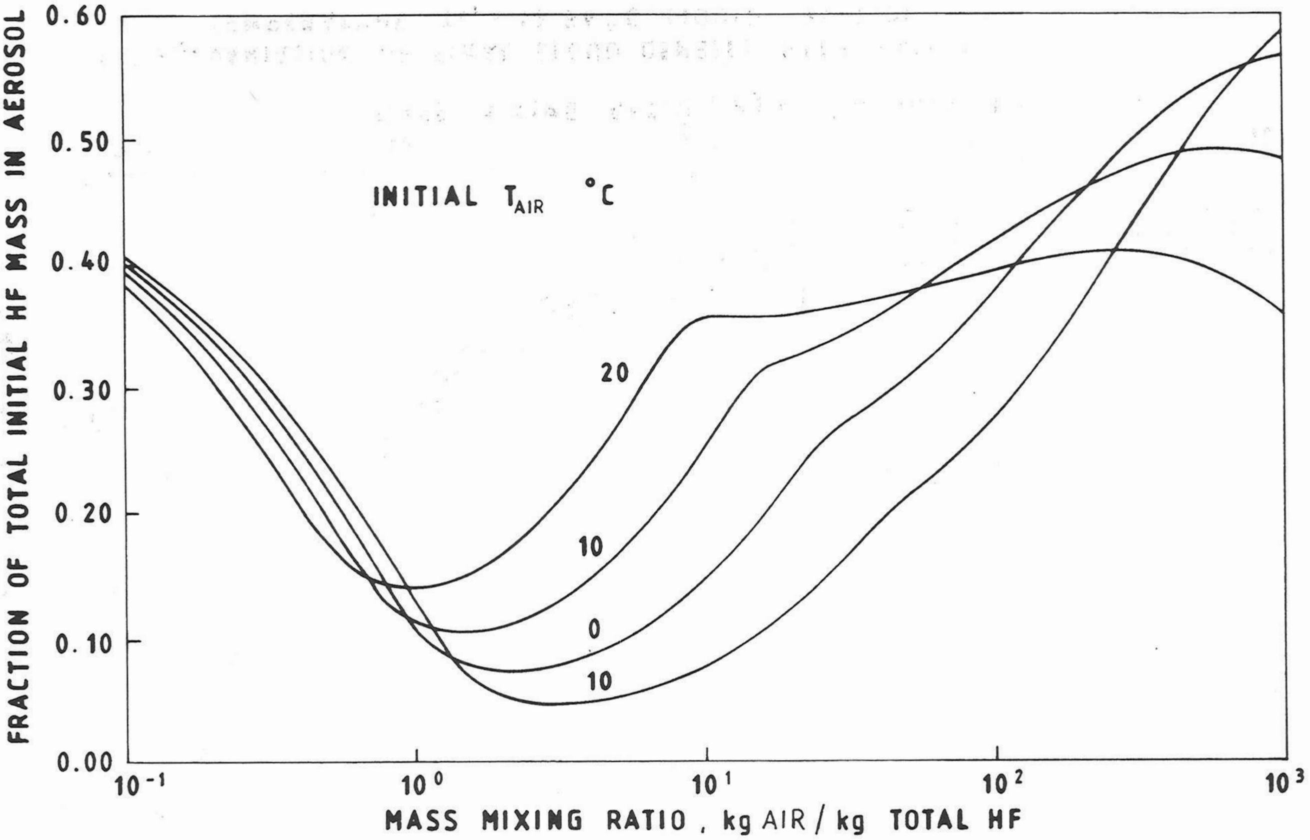

FIG.16 VARIATION OF FRACTION OF HF MASS IN AEROSOL WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54 °C, LIQUID FRACTION = 0.5. RH = 95%

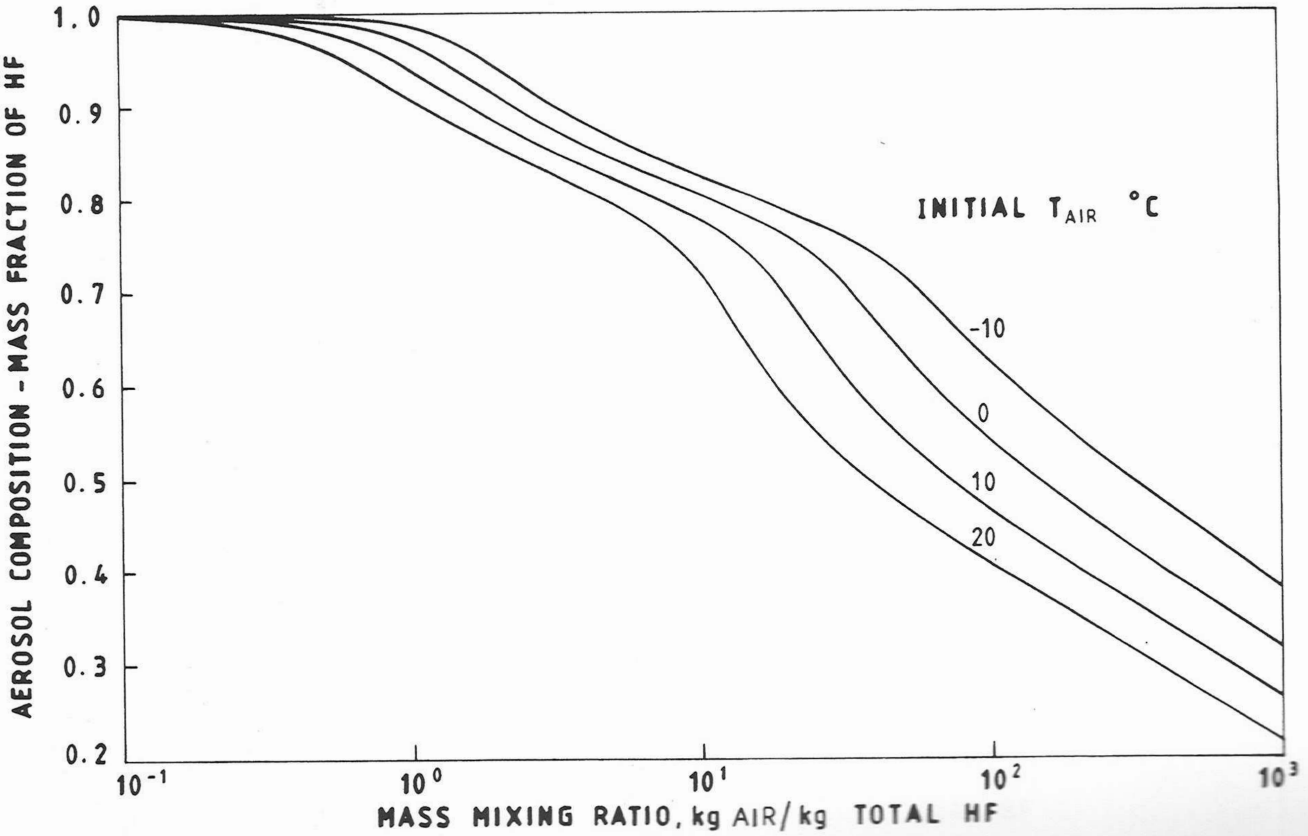

FIG.17 VARIATION OF AEROSOL COMPOSITION WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54 °C, LIQUID FRACTION = 0.5. RH = 95%

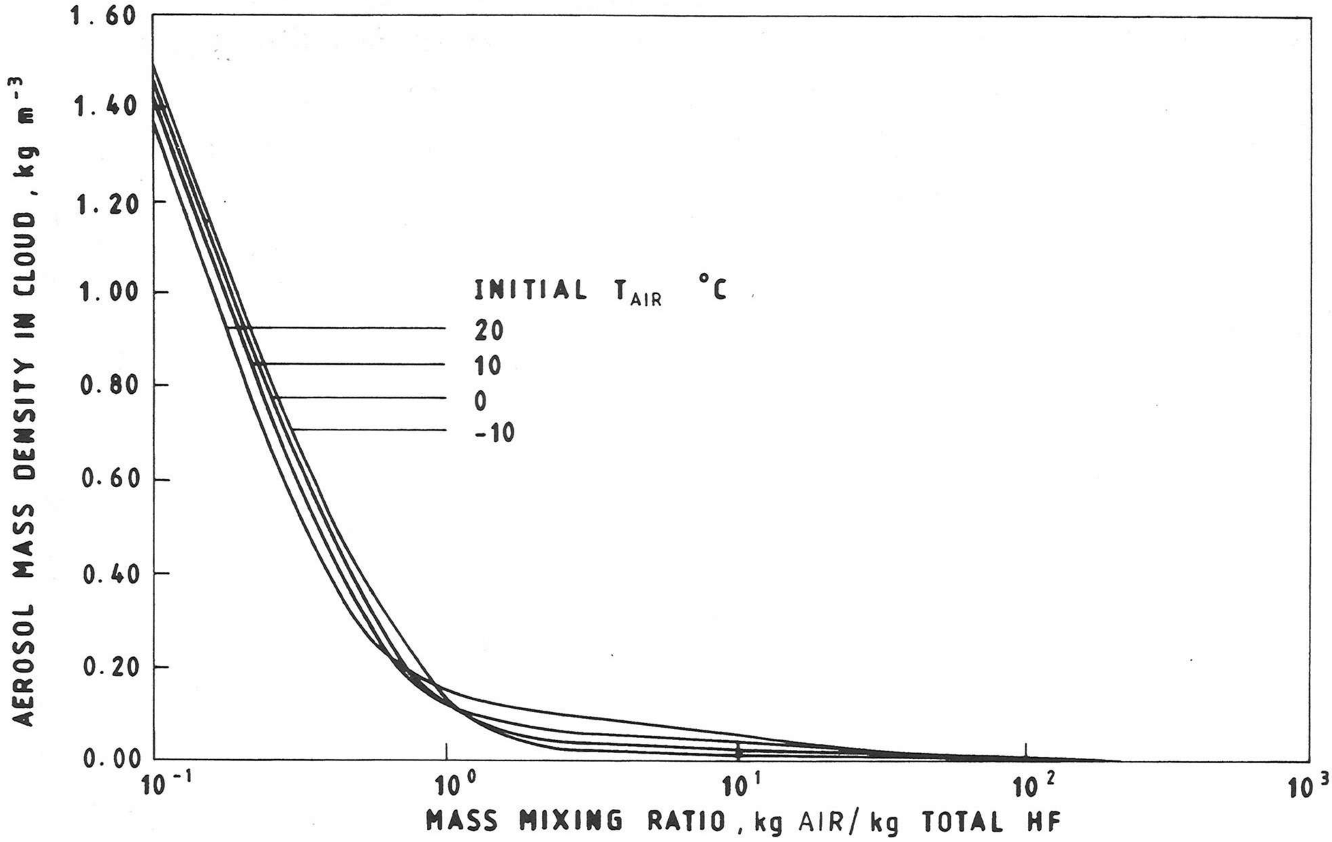

FIG. 18 VARIATION OF AEROSOL MASS DENSITY IN CLOUD WITH INITIAL AIR TEMPERATURE. T_{HF} = 19.54°C, LIQUID FRACTION = 0.5. RH = 95%

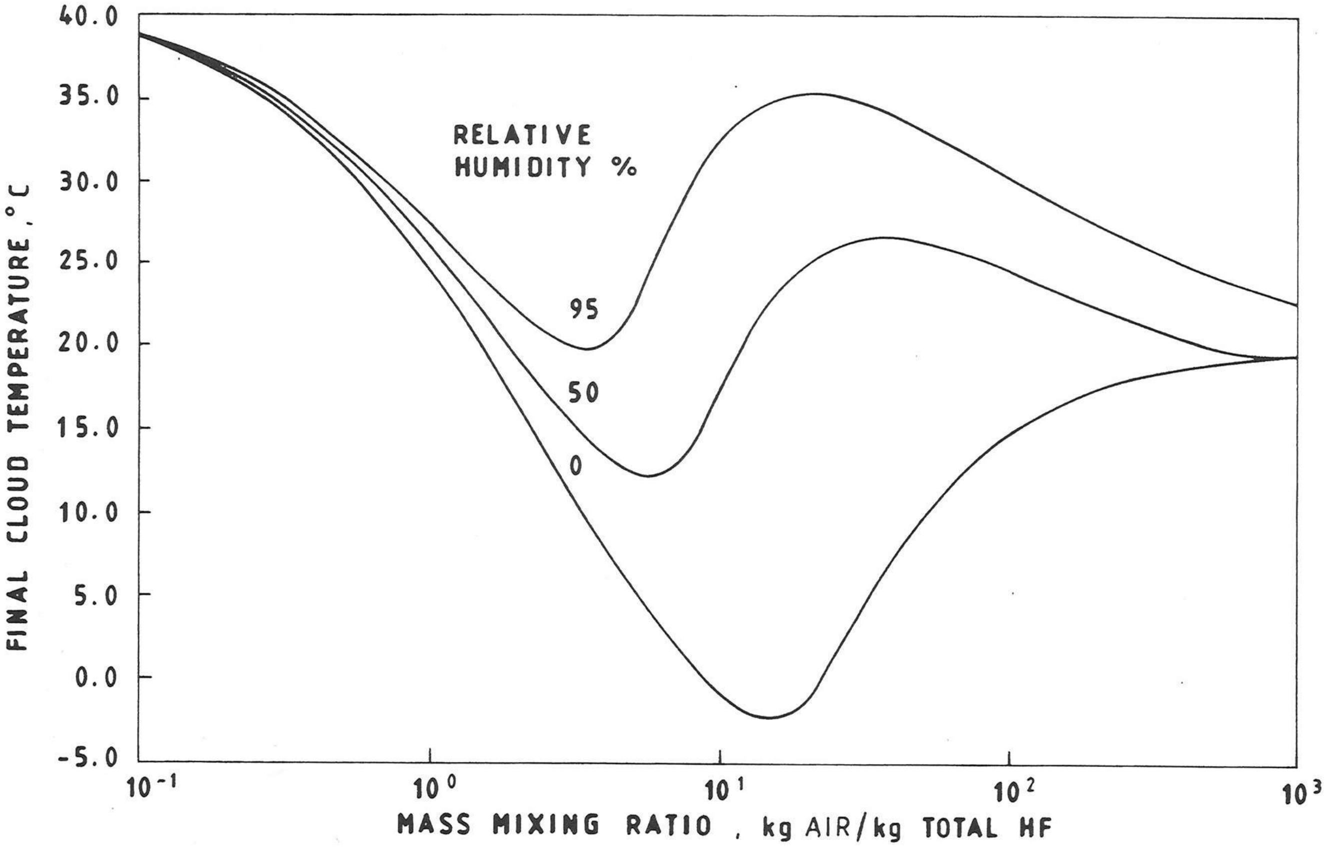

FIG. 19 VARIATION OF FINAL CLOUD TEMPERATURE WITH RELATIVE HUMIDITY. T_{HF} = 41°C, LIQUID FRACTION = 0. T_{AIR} = 20°C

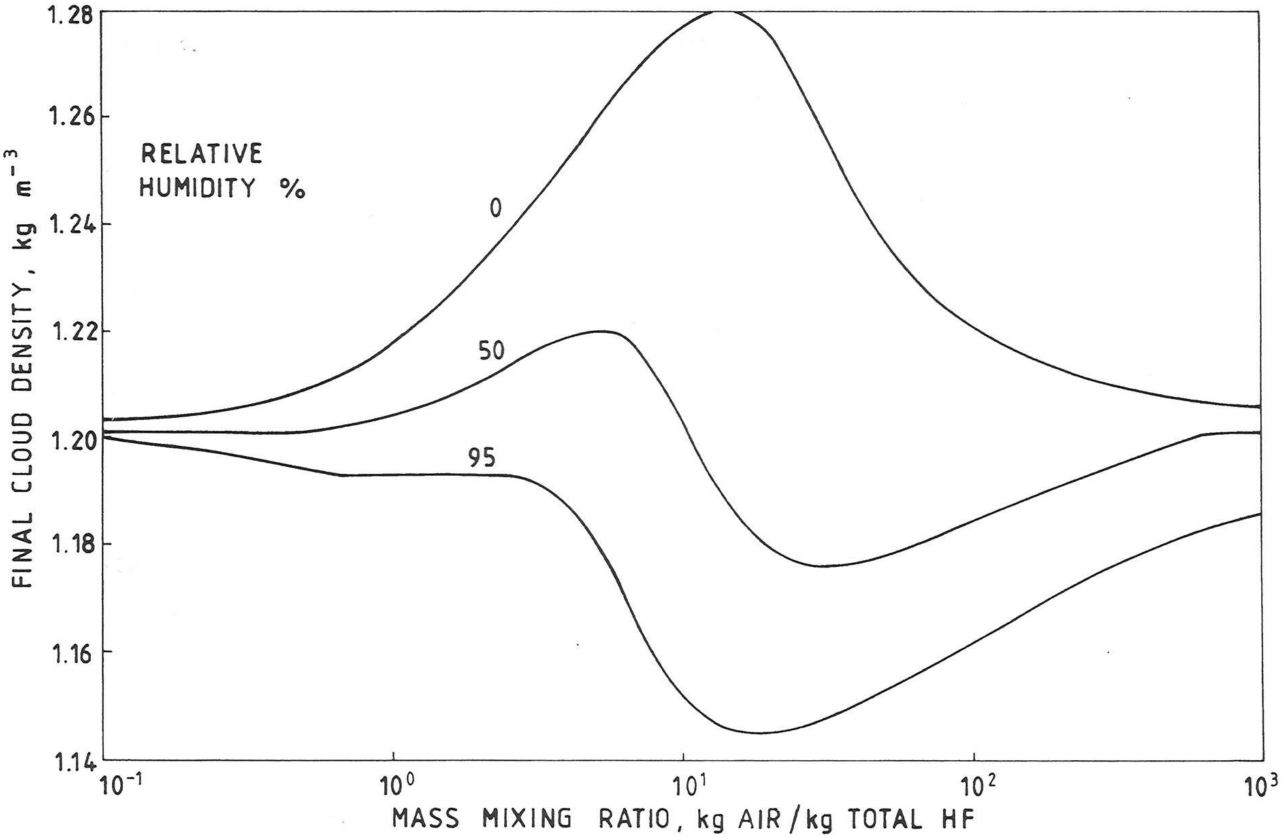

FIG. 20 VARIATION OF FINAL CLOUD DENSITY WITH RELATIVE HUMIDITY
T_{HF} = 41°C, LIQUID FRACTION = 0. T_{AIR} = 20°C

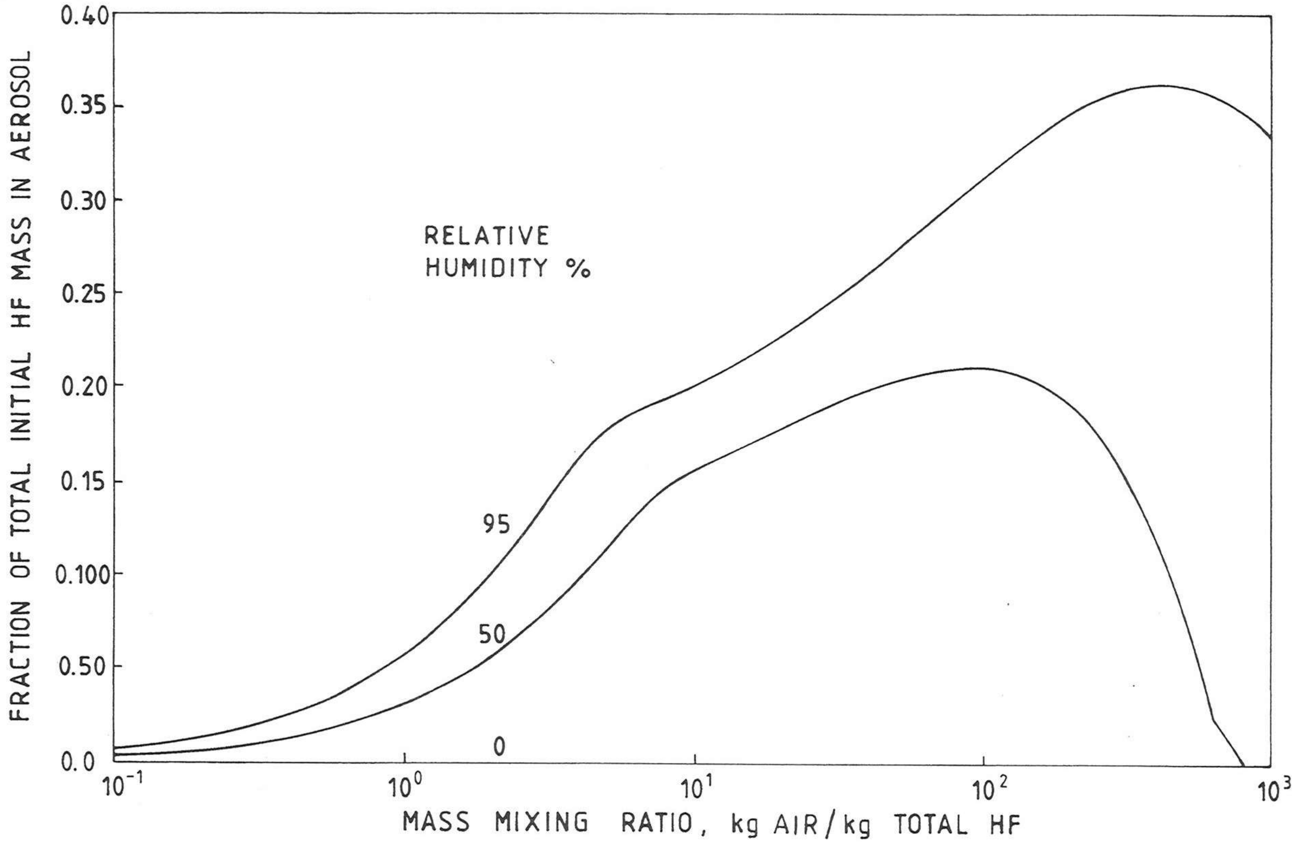

FIG. 21 VARIATION OF FRACTION OF HF MASS IN AEROSOL WITH RELATIVE HUMIDITY.
T_{HF} = 41°C, LIQUID FRACTION = 0. T_{AIR} = 20°C

4. APPENDIX 1

Details of solution technqiue

4.1 Introduction

This appendix elaborates on the outline description of the solution technique provided in the main text. Details of the thermodynamic and mathematical approach are given below.

4.2 Basic strategy

It is of value to consider the unknown quantities which need to be determined and to examine the dependencies between these parameters. The key unknowns are:

(1) Final temperature.

(2) Final volume and density of vapour phases.

(3) Mass of H_2O liquid (may be zero) and HF liquid (may be zero) and thus liquid phase composition.

(4) Mole fractions of monomer, dimer, hexamer.

(5) Partial pressure of HF vapour and of H_2O vapour.

As described in Appendix 2, (4) may be determined given the temperature and total HF partial pressure. (2) may be readily determined from (1), (5) and input data, and (3) and (5) are intimately dependent on temperature. The final temperature of the cloud thus appears in many of the equations developed and partly determines many of the unknowns. To reduce the number of variables it is obviously desirable to express certain parameters as functions of others.

For an adiabatic, isobaric system, the overall enthalpy change for the mixing and interaction of air with HF will be zero. $\Delta H = 0$ is thus used as the criterion of equilibrium, and efforts are made to obtain ΔH as a function of T. Solution of the equation $\Delta H(T) = 0$ is sought, recognising that there will be a discontinuity at the onset of a phase change.

Consideration of the available information and parameters that are readily obtained show that there are three principal difficulties unique to the HF problem.

(1) The ability to model the association behaviour of HF into oligomeric species (Appendix 2) is necessary. The mole fractions or partial pressures of individual oligomeric species will be determined by the total HF partial pressure and the temperature.

(2) There is a potential for occurrence of phase changes in the temperature and partial pressure ranges of interest. The ability to determine vapour pressures of both HF and water above a liquid for a continuum of composition and temperature is required.

(3) HF is one of the most non-ideal substances known. Reliable data for parameters such as vapour phase heat capacities are sparse, and the assumption of a constant value across the range of conditions of interest may be invalid.

The solution technique is actually implemented using a sub-routine that evaluates the enthalpy change on mixing air with HF and establishing thermodynamic equilibrium at a specified temperature, T. The enthalpy of this putative state is compared to that of the initial state, and values of T reselected so that after a reasonable number of iterations the overall equilibrium criterion $\Delta H(T) = 0$, is satisfied.

4.3 Evaluation of the enthalpy change at temperature T

The enthalpy change for an isobaric process may be rewritten as:

$$\Delta H = \Delta U + p\Delta V \qquad \ldots(4.1)$$

For the HF/moist air system the components will be

$$\Delta H = H^{\text{final}} - H^{\text{initial}} = \Delta U_{air} + \Delta U_{HF} + \Delta U_{mix} + p\Delta V \qquad \ldots(4.2)$$

Considering each term separately, the $p\Delta V$ term may be split and expanded as follows:

$$p\Delta V = pV^f - pV^i \qquad \ldots(4.3)$$

where

$$pV^i = RT^i_A\,(N_A + N^i_{WV}) + RT^i_{HF}\,(N^i_1 + N^i_2 + N^i_6) + \frac{M^i_{HFL}\,p}{\rho_{HFL}} \qquad \ldots(4.4)$$

where

T^i_A = initial air temperature
T^i_{HF} = initial HF temperature
M^i_{HFL} = initial mass of HF in liquid phase
N_A = number of moles of air
N^i_{WV} = initial number of moles of vapour phase water
N_1, N_2, N_6 = number of moles of each oligomer.

$$pV^f = RT^f\,(N_A + N^f_{WVf} + N^f_1 + N^f_2 + N^f_6) + \frac{(M^f_{HFL} + M^f_{WL})\,.\,p}{\rho_{liq}} \qquad \ldots(4.5)$$

where f denotes final states,

M^f_{WV}, M^f_{WL} = final number of moles of water in vapour, liquid phases
ρ_{liq} = solution density
T^f = final cloud tempreature

The ΔU air term may be simply evaluated from the thermal capacity of air:

$$\Delta U_{air} = C_{v,A}\,N_A\,(T^f - T^i_A) \qquad \ldots(4.6)$$

where $C_{v,A}$ = constant volume heat capacity of air.

For the ΔU_{H_2O}, ΔU_{HF} terms consideration needs to be given to the phase change. To determine the enthalpy changes, HF association/dissociation reactions, phase changes and the HF/H_2O reaction are all assumed to occur at reference temperatures.

Though the information on the temperature dependence of HF thermodynamic properties is rather sparse, the reference temperature for both phase changes and interaction with water is chosen to be the atmospheric pressure boiling point of HF, and the reference temperature for oligomerisation is taken as 0°C. The sources and data chosen for the less readily available data are discussed in Appendix 3.

The scheme shown in Fig. A1.1 may be used to illustrate the contributions to the overall ΔU term. In writing the full expressions for the ΔU terms it should be noted that the HF and H_2O contributions are retained separately until the HF and H_2O are in the correct phase and temperature. Thus, ΔU_{mix} refers solely to the heat of mixing and the subsequent change of the mixed liquid phase from the reference temperature T_s to the final temperature T^f.

Only the changes designated by steps 5, 6 and 7 in the scheme are thus included in ΔU_{mix}. The individual contributions to the remaining ΔU terms in expression (4.2) are then given as follows, where the numbers in parentheses under each term refer to the relevant steps in Fig. A1.1.

$$\begin{aligned}\Delta U_{HF} = {} & \underset{(15)}{(N_2^f - N_2^i)\,\Delta U_{1\to 2}} + \underset{(18)}{(N_6^f - N_6^i)\,\Delta U_{1\to 6}} \\ & + \underset{(11,\ 12,\ 16,\ 19)}{(N_{HF1}^i C_1 + N_{HF2}^i C_2 + N_{HF6}^i C_6)\,(T_S - T_{HF}^i)} \\ & + \underset{(14,\ 17,\ 20)}{(N_{HF1}^f C_1 + N_{HF2}^f C_2 + N_{HF6}^f C_6)\,(T^f - T_S)} \\ & + \underset{(12)}{C_1\,(M_{HFL}^i - M_{HFL}^f)\,(T_S - T_{HFBPT})/W_{HF1}} \\ & + \underset{(10)}{(M_{HFL}^i - M_{HFL}^f)\,.\,L_{Vap}^{HF}} + \underset{(8)}{C_{VL}\,M_{HFL}^i\,(T_{HFBPT} - T_{HF}^i)}\end{aligned}$$

where

N_{HF1}, H_{HF2}, N_{HF6} = no. of moles of monomer, dimer, hexamer respectively.

$\Delta U_{1\to 2}$, $\Delta U_{1\to 6}$ = internal energy change per mole of product for formation of dimer, hexamer, respectively, from monomer.

C_1, C_2, C_6 = molar heat capacities at constant volume of the respective oligomers.

C_{VL} = specific heat capacity of liquid HF.

L_{Vap}^{HF} = constant volume energy of vaporization of HF.

W_{HF1} = molecular weight of HF monomer.

$$\begin{aligned}\Delta U_{H_2O} = {} & \underset{(1)}{C_{WV}\,M_{WV}^i\,(T_{HFBPT} - T_{Air}^i)/W_{H_2O}} + \underset{(3)}{C_{WV}\,M_{WV}^f\,(T^f - T_{HFBPT})/W_{H_2O}} \\ & - \underset{(4)}{M_{WL}^f\,L_{Vap}^{H_2O}}\end{aligned}$$

(nb: assume $M_{WL}^i = 0$)

where

C_{WV} = molar heat capacity of water vapour at constant volume

$L_{Vap}^{H_2O}$ = constant volume energy of vaporization of H_2O

W_{H_2O} = molecular weight of H_2O

$$\Delta U_{mix} = \underset{(6)}{M_{mix}^f\,C_{V,mix}\,(T^f - T_{HFBPT})} + \underset{(5,7)}{U_M}$$

where

M_{mix}^f = $M_{WL}^f + M_{HFL}^f$

$C_{V,mix}$ = specific heat capacity of the mixture, appropriate to the composition

and U_M is the energy of mixing of liquid phase HF and H_2O at the reference temperature T_{HFBPT}. This is obtained from the algorithms describing the phase diagram behaviour as explained in Reference 1.

4.4 Approach to establishing equilibrium

To determine the parameters required to evaluate the enthalpy changes, such as liquid mole or mass fractions, partial pressures etc. it is necessary to determine whether a liquid phase is present. In WETAHF, two different but related approaches are used according to whether a liquid phase is or is not present. The criterion for the existence of a condensed phase is that the combined partial pressure of HF and H_2O shall be greater than the combined saturated vapour pressures, i.e. $P_{HF}^{sat} + P_W^{sat}$. As WETAHF uses iterative approaches to solution it is essential to have a convenient and economical phase test that is continuous in temperature and liquid phase composition. As a trial partial pressure of HF is needed before any phase test can be performed, for the very first iteration of the enthalpy determination it is assumed that no liquid phase is present and P_{HF} evaluated accordingly.

If a liquid phase is present saturation conditions are assumed and super-saturation is not allowed. The phase test may thus be performed by taking the trial P_{HF} evaluated, regarding it as a saturation pressure and using the phase testing routine to investigate what saturation water partial pressure it would correspond to at the given temperature. If the evaluated water partial pressure equals or exceeds the value obtained from the phase testing subroutine, then the combined partial pressures must indeed have equalled or exceeded the saturation value, and the presence of two phases is thus identified. If the evaluated water partial pressure is less than the value from the phase testing routine then only a vapour phase is present. The convenience of the phase test sub-routine allows repeated phase tests to be performed, as the iteration approach to solution is made with reasonable economy of computer time.

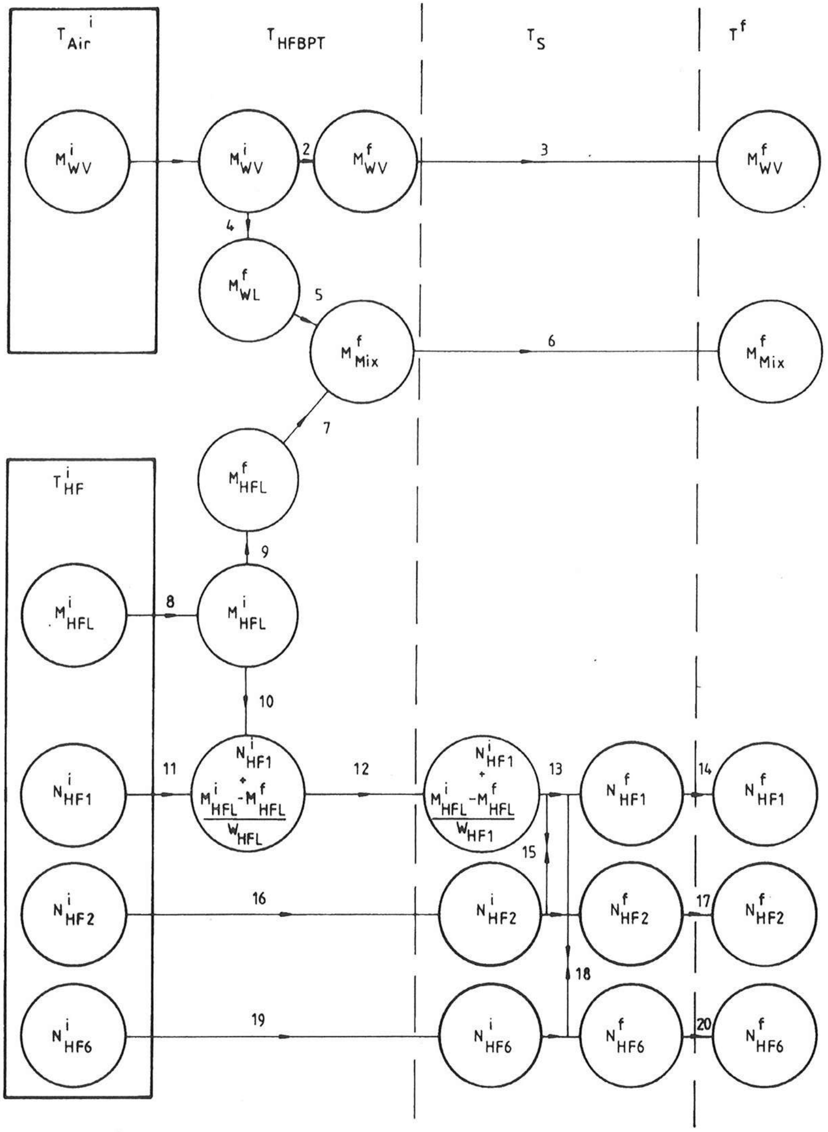

FIG. A1.1 CALCULATIONAL ROUTE FOR HF AND H_2O CONTRIBUTIONS TO ΔH (T^f)

5. APPENDIX 2

Chemical model of HF oligomerisation; the 126 model

The model used to describe the vapour phase association of hydrogen fluoride is based on the assumption that HF exists as an equilibrium mixture of monomer, dimer and hexamer (126), each of which may be treated as an ideal gas. The evidence for this approach and the derivation of equilibrium constants is discussed in this appendix.

The self-association of hydrogen fluoride due to hydrogen bonding has been known since the latter part of the 19th century(4,5) and the literature on the subject up to about 1950 has been reviewed by Rushmere.(6) There exists, even in the most recent literature, conflicting evidence concerning the nature of this vapour phase association. Infrared spectroscopic measurements(7) favour the predominance of monomer and hexamer with traces of dimer and tetramer. However, the values of the heat capacity have been interpreted(8,9) in terms of a stable hexamer and a large sequence of other oligomers. In contrast to this, pressure-volume-temperature measurements have been used(10) to support the view that a large number of species are present but that the formation of hexamer is not particularly favoured. The properties of the saturated vapour have been investigated,(11) and theoretical expressions for the density of the vapour and the curvature of the saturated vapour pressure line have been derived on the basis of a single equilibrium between monomer and hexamer. Good agreement between the results of this theoretical approach and the available experimental data is claimed. Extensive analysis(12,13,14,15) of experimental PVT measurements(16) has been carried out in an attempt to identify which combination of oligomers in mobile equilibrium would best fit the data. It was concluded that there was definite evidence for the existence of monomer, dimer and hexamer, but it was conceded that intermediate and higher oligomers might also be formed. More recently, Beckerdite et al have re-examined some of the earlier experimental data and suggest that a 136 model, with the trimer replacing the dimer assumed in this work, may fit the data a little better.(17)

For the present work, the vapour phase association of hydrogen fluoride is thus based on a model assuming that macroscopic or observable HF is an equilibrium mixture of monomer, dimer and hexamer, each of which may be treated as an ideal gas.

This approach has been adopted in accord with Maclean et al(15) who have reviewed the various models put forward in the light of their ability to fit the experimental data of Strohmeier and Briegleb.(16) Maclean et al conclude that although an extended series model,(10) including oligomers up to $(HF)_9$, gives a good description of the data over the whole pressure range, the precision of the data does not warrant analysis in terms of nine independent parameters. Moreover, this extended treatment gives no particular evidence for the formation of trimer, tetramer and pentamer since a good fit can also be obtained by omitting these species from the model.

Maclean et al point out that the extended model fits the data better than a simple monomer, dimer, hexamer model at low temperatures and high pressures but comment that this cannot be taken as evidence supporting the existence of oligomers higher than the hexamer, as this is the region of pressures and temperatures in which deviations from ideality would be most marked, and in any case, the partial pressures encountered in a dispersing cloud will normally be sub-atmospheric.

The following two equilibria have been considered:-

$$2HF = (HF)_2 \qquad \ldots (5.1)$$

$$6HF = (HF)_6 \qquad \ldots (5.2)$$

The equilibrium constants for dimerisation and hexamerisation have been related to the changes in enthalpy and entropy associated with these processes, using the Van't Hoff isotherm and the Gibbs-Helmholtz equation:

$$\Delta G^\circ = -RT \ln Kp \qquad \ldots (5.3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \ldots (5.4)$$

Thus

$$Kp = \exp\left\{(\Delta S^\circ - \Delta H^\circ/T)/R\right\} \qquad \ldots (5.5)$$

where Kp may be expressed in terms of partial pressures as follows:

$$K_2 = P_2/P_1^2 \qquad \ldots (5.6)$$

$$K_6 = P_6/P_1^6 \qquad \ldots (5.7)$$

where P_1, P_2 and P_6 are the partial pressures of monomer, dimer and hexamer respectively.

If the different species are treated as ideal gases then the total pressue of the system P may be regarded as being equal to the sum of the partial pressures

$$P = P_1 + P_2 + P_6 \qquad \ldots (5.8)$$

Combining Equations (5.6), (5.7) and (5.8) gives

$$P = P_1 + K_2 P_1^2 + K_6 P_1^6 \qquad \ldots (5.9)$$

If the mole fraction of monomer in the vapuor phase is X_1 then

$$P_1 = X_1 P \qquad \ldots (5.10)$$

Substituting in Equation (5.9) gives

$$P = X_1 P + K_2 (X_1 P)^2 + K_6 (X_1 P)^6 \qquad \ldots (5.11)$$

Hence

$$1 = X_1 + K_2 P X_1^2 + K_6 P^5 X_1^6 \qquad \ldots (5.12)$$

At a given temperature the values of K_2 and K_6 may be generated using the values of ΔH and ΔS, mentioned previously, in Equations (5.5). Inserting the values of K_2 and K_6 in Equations (5.12) together with the system pressure, which in the case of a gas mixture is the partial pressure of HF, this reduces to a polynomial in X_1.

The mole fractions of dimer (X_2) and hexamer (X_6) are then given by:

$$X_2 = K_2 P X_1^2 \qquad \ldots (5.13)$$

$$X_6 = K_6 P^5 X_1^6 \qquad \ldots (5.14)$$

The mean molecular weight is then given by:

$$W = X_1 W_1 + X_2 W_2 + X_6 W_6 \qquad \ldots (5.15)$$

(W_1, W_2 and W_6 are the molecular weights of the monomer, dimer and hexamer respectively.)

From this the association factor may be obtained:

$$F = W/W_1$$

It can be seen that from these equations, if the temperature and combined partial pressure of HF are given, then it is possible to evaluate the equilibrium mole fractions of the chemical species and the mean molecular weight.

Values for the change of enthalpy and entropy on dimerisation and hexamerisation are available from several sources,(9.10.15) however, care must be exercised over units when using these data. The units of the equilibrium constants quoted in these sources are not specified and the values do not correspond numerically with those quoted by Vanderzee and Rodenburg,(18) which are specified in atm^{-1} and atm^{-5} respectively. It is apparent that the equilibrium constants in references (8), (9) and (14) have been expressed in terms of mm of Hg. In general, a correction must be applied to the ΔS values used if values of Kp in the correct units of pressure are to be generated from Equation (5.5).

The values for the enthalpy and entropy changes associated with dimerisation and hexamerisation which have been used to calculate equilibrium constants as a function of temperature are as follows:-

$$\Delta H_2 = -\,3 \cdot 3076 \times 10^4 \text{ J Mole}^{-1} \ (40\text{ g}) \qquad \Delta S_2 = -\,2 \cdot 24 \times 10^2 \text{ J Mole}^{-1}\text{ K}^{-1}$$

$$\Delta H_6 = -\,1 \cdot 6747 \times 10^5 \text{ J Mole}^{-1} \ (120\text{ g}) \qquad \Delta S_6 = -\,1 \cdot 023 \times 10^3 \text{ J Mole}^{-1}\text{ K}^{-1}$$

K will then be obtained in MKS units.

These values have been chosen to give reasonable agreement with published experimental results(16.18) and are similar to the values quoted by Maclean et al, which were also chosen to fit experimental data.

A comparison of the results calculated using these two sets of values with experimental data is shown in Tables A2.1 and A2.2.

TABLE A2.1

Predicted and experimental association factors
Vanderzee & Rosenberg(18)

T (°C)	P (Mn^{-2})	Fexp	Fcal
– 20	$2 \cdot 00 \times 10^4$	4·048	4·172
– 10	$3 \cdot 13 \times 10^4$	3·905	3·948
0	$4 \cdot 85 \times 10^4$	3·750	3·758
10	$7 \cdot 15 \times 10^4$	3·591	3·533
15	$8 \cdot 61 \times 10^4$	3·510	3·427
19·7	$1 \cdot 01 \times 10^5$	3·429	3·318

TABLE A2.2

Predicted and Experimental association factors
(Briegleb & Strohmeier(10))

T (°C)	P (Nm^{-2})	Fexp	Fcal
26	6·96 x 10^4	1·832	2·008
	5·62 x 10^4	1·431	1·630
	3·67 x 10^4	1·104	1·173
	2·30 x 10^4	1·034	1·042
	1·46 x 10^4	1·019	1·019
	0·89 x 10^4	1·011	1·010
32	8·64 x 10^4	1·743	1·915
	6·77 x 10^4	1·338	1·512
	4·00 x 10^4	1·065	1·096
	1·20 x 10^4	1·012	1·011
38	9·04 x 10^4	1·391	1·563
	1·37 x 10^4	1·011	1·010

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6. APPENDIX 3

Parameters required and selected values

In addition to the readily obtainable parameters, e.g. heat capacity of water, molecular weights of oligomers, etc. many parameters are required within the code WETAHF for which further explanation is required. Instances of data problems include inadequate experimental measurements published or the need for data that cannot be directly measured, such as properites of the individual monomers. Each of the parameters for which some elaboration is necessary are discussed in turn below. The remaining readily obtainable data were drawn from standard sources, notably the CRC handbook and Perry and Chilton.

Molecular weight of air. For convenience an apparent molecular weight of air is required. The value of 0·028966 kg was obtained from the CRC handbook.

Enthalpy of the change $(HF)_1 = (HF)_n$

where n is 2 or 6 respectively.

As discussed in Appendix 2,

$$\Delta H_2 = -3\cdot3076 \times 10^4 \text{ J mole}^{-1} \text{ (40 g)}$$

$$\Delta H_6 = -1\cdot6747 \times 10^{\overset{5}{4}} \text{ J mole}^{-1} \text{ (120 g)}$$

Entropies of the change $(HF)_1 = (HF)_n$

where n is 2 or 6.

From Appendix 2,

$$\Delta S_2 = -2\cdot24 \times 10^2 \text{ J mole}^{-1} \text{ K}^{-1} \text{ (40 g)}$$

$$\Delta S_6 = -1\cdot023 \times 10^{\overset{3}{\cancel{6}}} \text{ J mole}^{-1} \text{ K}^{-1} \text{ (120 g)}$$

Internal energy or constant volume heat for reaction for conversion of monomer to dimer or hexamer.

The values used were obtained from the enthalpy and entropy values using

$$\Delta H = \Delta U + \Delta nRT$$

$$\left.\begin{array}{l} \Delta U_2 = -3\cdot0815 \times 10^4 \text{ J mole}^{-1} \\ \Delta U_6 = -1\cdot5617 \times 10^{\overset{5}{4}} \text{ J mole}^{-1} \end{array}\right\} \text{at } 273.15 \text{ K}$$

Constant volume specific heat of HF liquid. Obtained from Reference (19)

$$= 3\cdot027 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$$

Internal energy of vaporisation for the process $(HF)_{liq} \rightarrow (HF)_1$, i.e. producing monomer only at the atmospheric pressure boiling point. Note that the internal energy, not the more customary enthalpy is required. The enthalpy or latent heat of vaporisation at the atmospheric pressure boiling point is stated to be 7·4894 x 10^3 J mole^{-1}.(20) In accordance with earlier work by Wheatley(21) the enthalpy is corrected to an internal energy producing monomer only using

$$U^{BPT}_{L\rightarrow 1} = \frac{H^{BPT}_{L\rightarrow v}}{W_1} - \frac{RT_{BPT}}{W^{BPT}_{HF}} - N^{BPT}_2\,\Delta U^{S}_{1\rightarrow 2} - N^{BPT}_6\,\Delta U^{S}_{1\rightarrow 6}$$

$$+ \left(C_{1,V}\,.\,N^{BPT}_1 + C_{2,V}\,N^{BPT}_2 + C_{6V}\,N^{BPT}_6\right)\left(T_S - T_{BPT}\right) + C_{1,V}\left(T_{BPT} - T_S\right)/\cancel{W_1}\ N_1$$

w constant

dimensions

?

where the phase changes are assumed to occur at the boiling point T_{BPT} and the oligomerisation/de-oligomerisation reactions at a reference temperature T_S. The specific heats $C_{n,V}$ are noted below and the numbers of moles, N_n are obtained from the chemical model. $U^{BPT}_{L\rightarrow 1}$ = HFLHVB = 1·436 x 10^6 J kg^{-1}.

Density of liquid HF. A single value of the density at 20°C (obtained from correlations in Reference 19) is chosen for use at all temperatures = 1·0015 x 10^3 kg m^{-3}.

Constant volume heat capacity of water vapour, at 20°C is chosen for use at all temperatures,(3.1) = 3·041 J mole^{-1} K^{-1}

Constant volume heat capacity of water liquid(19) = 4·1576 x 10^3 J kg^{-1} K^{-1}

Density of all compositions of mixed HF/HW liquid phase is assumed to be 10^3 kg m^{-3}.

Liquid phase constant volume specific heat of mixed HF/H_2O liquid phase is derived from a simple mass fractional combination of the values for each pure substance.

Density of dry air obtained using the molecular weight of air and the ideal gas equation.

Density of wet air. A correlation for the density of air of specified relative humidity and temperature from the CRC handbook, based on the ICAO standard atmosphere, was used.

SVP correlations. The correlations for the vapour pressures of pure HF and H_2O as a function of temperature were obtained from Reference (19). For both substances, $\log_{10} P = A + B/T + C \log_{10}T + DT + ET^2$ where T is the temperature, A, B, C, D, E are parameters.

For HF,

A = 66·244
B = − 2588·0
C = − 25·14
D = 28·493 x 10^{-3}
E = − 9·9602 x 10^{-6}

For H_2O,

A = 16·373
B = − 2818·6
C = − 1·6908
D = − 5·7546 x 10^{-3}
E = 4·0073 x 10^{-6}

The parameters lead to pressures in Torr and a correction factor (133·322) is applied for conversion to N m^{-2}.

Oligomer specific heats. In the models developed in WETAHF it is assumed that the observable behaviour of HF may be described by a mixture of oligomers (see Appendix 2) each of which behaves as an ideal gas. It is thus necessary to have available data on the properties of individual oligomers. A simple model based on the number of degrees of freedom of each oligomer structure was developed for earlier work(21) and is adopted here.

$C_{1,V}$ = 2·5 R J K^{-1} $mole^{-1}$

$C_{2,V}$ = 5·5 R J K^{-1} $mole^{-1}$

$C_{6,V}$ = 9 R J K^{-1} $mole^{-1}$

Phase diagram parameters. Four parameters, w_A, r_A, w_B, r_B are required to specify the phase diagram using the models and equations developed in Reference 1. Raw data or measurements of partial pressures above HF/H_2O mixtures at specified temperatures and pressures are available from four sources.(22.23.24.26) Each set of experimental data was used to derive expressions of the form P = Exp [− A/T + B], using a least squares fitting procedure. It was then necessary to attempt to fit values of the r and w parameters to these expressions. Plotting the data, though is made difficult by the choice of different temperatures by different authors. Figures A3.1-3 show that, with the exception of the Russian data the experimental measurements are reasonably consistent, where appropriate mole/mass fraction conversions have been made on the raw data. It was therefore decided to give equal weight to all the data, with the exception of the Russian data which was ignored, in evaluating the r and w parameters.

Two approaches to fitting the r and w parameters were used, simple least squares fitting and graphical, visual inspection. In view of the range of temperatures of potential interest it was decided to ensure optimum fitting in the range 10 - 30°C. For the purposes of this exercise the experimental data are unfortunately centred on rather high temperatures, and also with a bias to lower HF mole fraction solutions. The parameters chosen were:

$r_A = r_B = -0·705$

w_A = 1·0 x 10^4

w_B = 14·91

Figures A3.1-3 demonstrate that good fits were achieved using these correlation parameters.

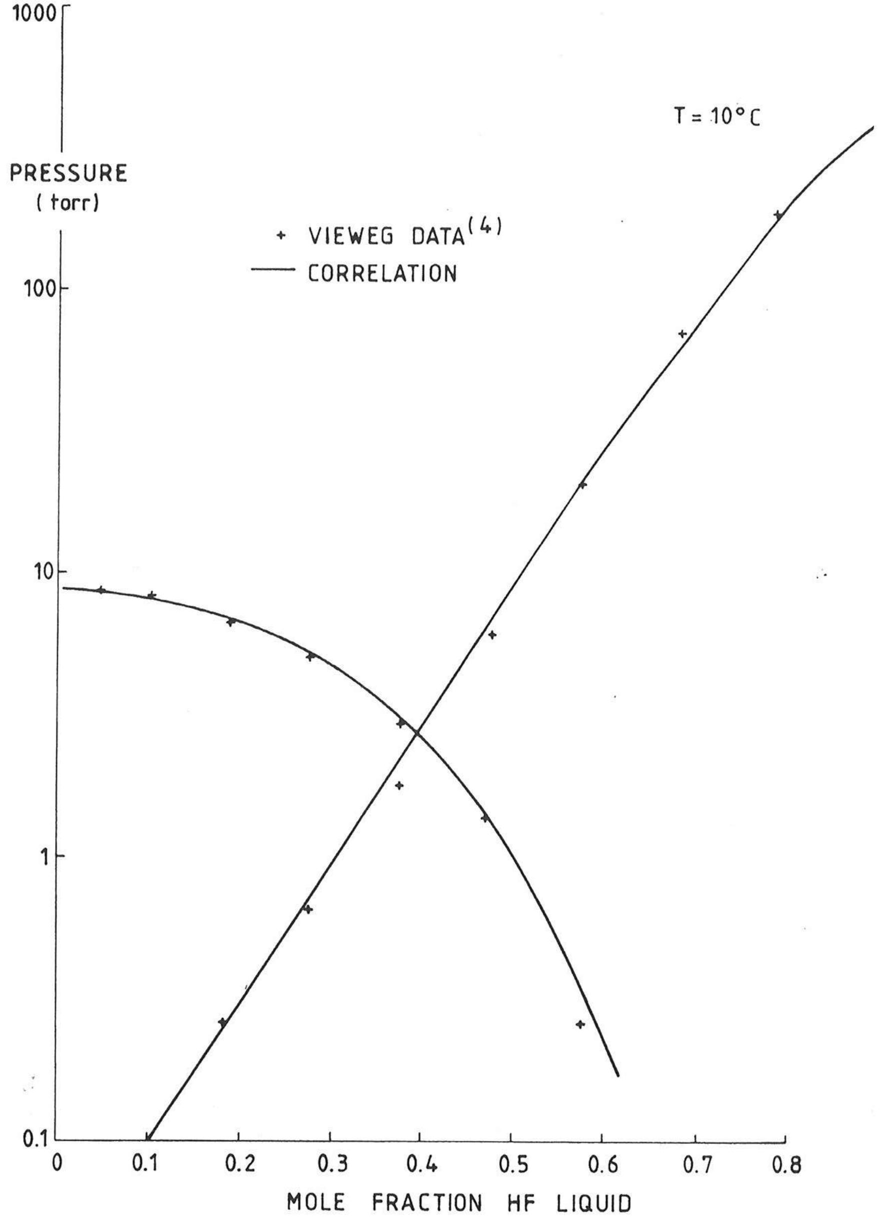

FIG. A3.1 COMPARISON OF CORRELATION WITH DATA FOR HF AND H_2O PARTIAL PRESSURES

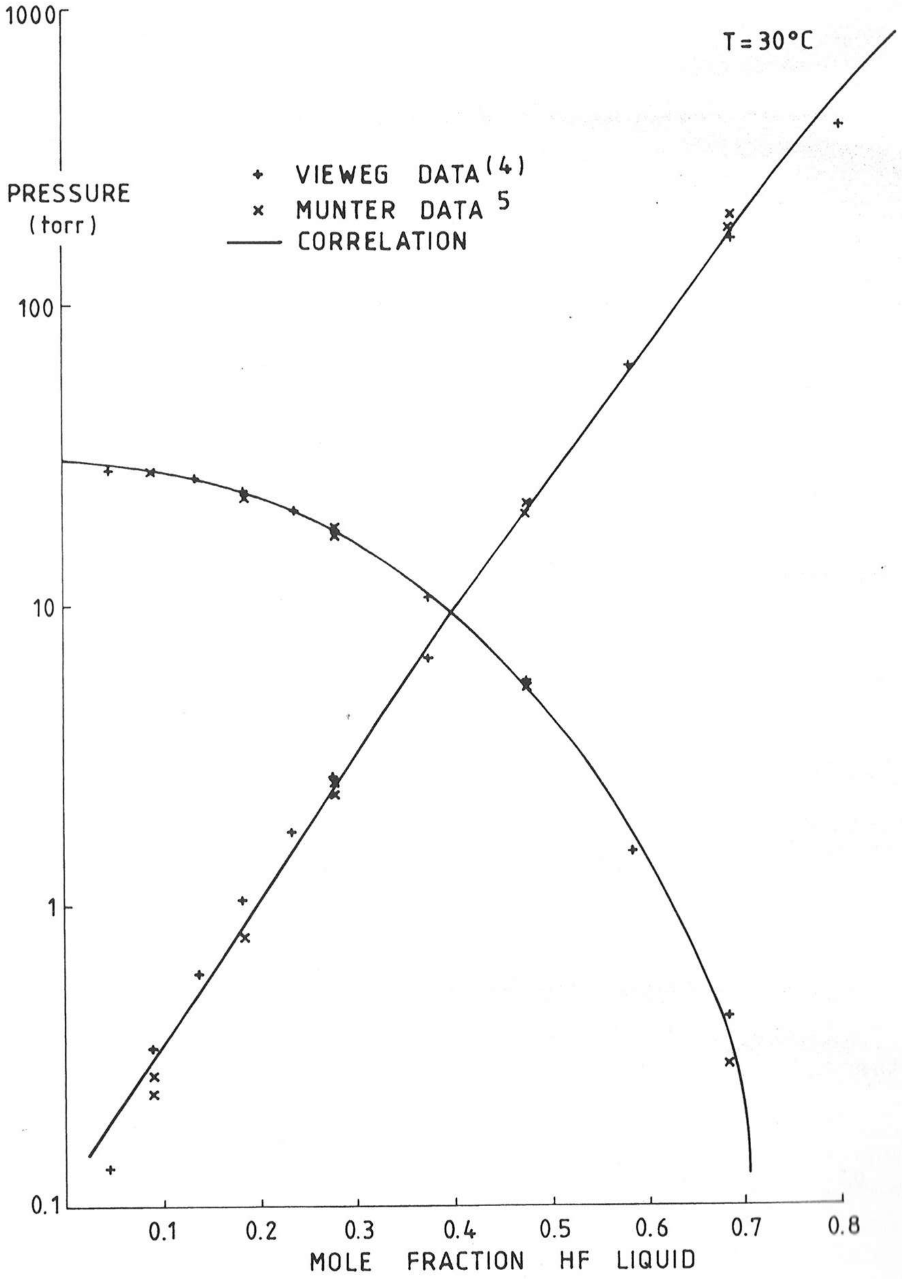

FIG. A3.2 COMPARISON OF CORRELATION WITH DATA FOR HF AND H_2O PARTIAL PRESSURES

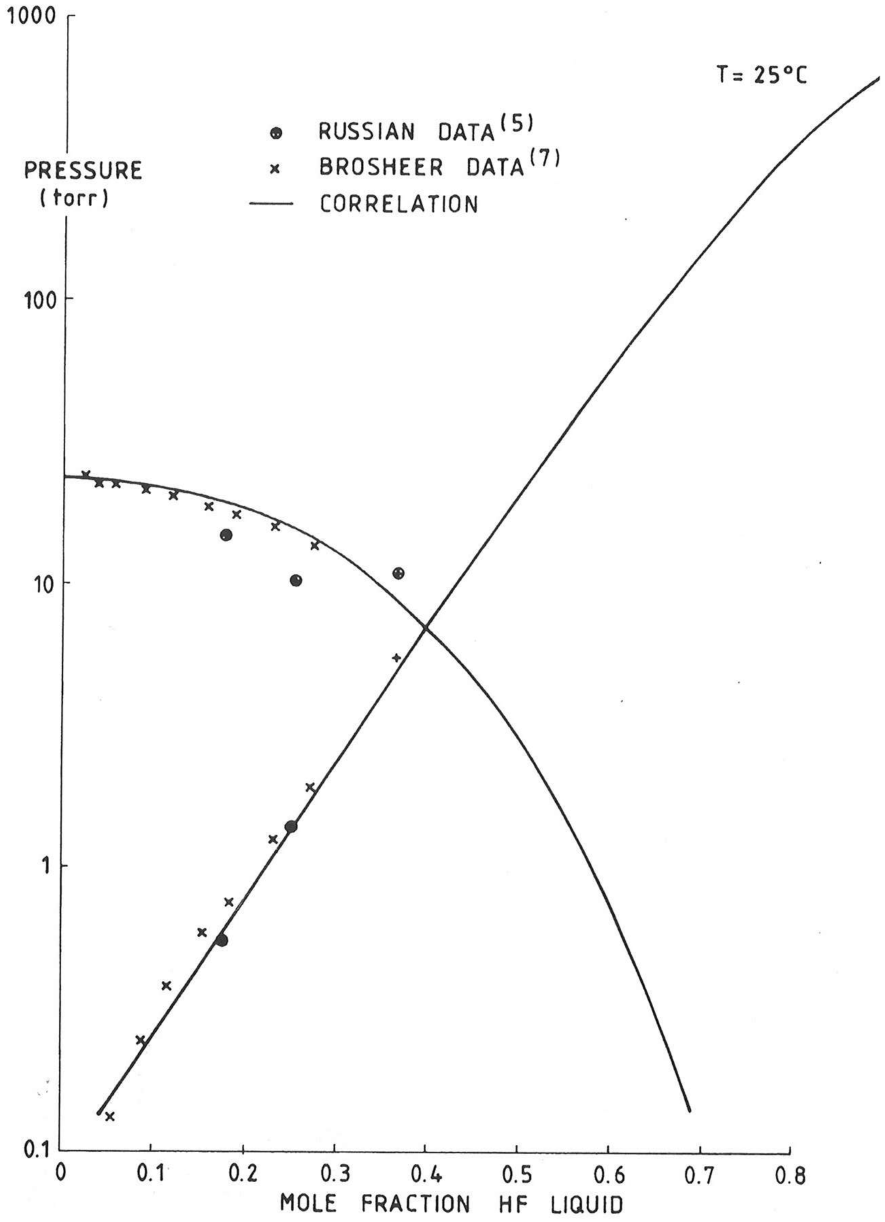

FIG. A3.3 COMPARISON OF CORRELATION WITH DATA FOR HF AND H_2O PARTIAL PRESSURES

7. REFERENCES

1. WHEATLEY, C. J. A theory of heterogeneous equilibrium between vapour and liquid phases of binary systems and formulae for the partial pressures of HF and H_2O vapour. SRD R357 (1985)
2. UNDERWOOD, B. Y., WALKER, B. C. and WILLIAMS, R. J. Development of interpolation formulae for rapid evaluation of the attenuation due to aerosol processes of radioactive release following hypothetical fast reactor accidents. Proc. of the CSNI Specialists Meeting on Nuclear Aerosols in Reactor Safety. NUREG/CR-1724 (1980)
3. PRUPPACHER, H. R. and KLETT, J. D. Microphysics of clouds and precipitation. D. Reidel Publishing Co., 1978
4. MALLET, J. W. On the molecular weight of hydrofluoric acid, American Chemical Journal, **3**, p.187 (1881)
5. THORPE, T. E. and HAMBLY, F. J. The vapour density of hydrogen fluoride. JCS **55**, p.163 (1889)
6. RUSHMERE, J. D. The molecular association of hydrogen fluoride. A short review of the published literature, SCS-TN-31, (1954)
7. SMITH, D. F. Hydrogen fluoride polymer spectrum, hexamer and tetramer. J. Chem. Phys., **28**, p.1040 (1958)
8. SPALTHOFF, W. and FRANCK, E. U. Hydrogen fluoride II. Association in the gas at high pressure. Z. Elektrochem, **61**, p.993 (1957)
9. FRANCK, E. U. AND MEYER, F. Hydrogen fluoride III. Specific heat and association in the gas phase at low pressure. Z. Elektrochem, **63**, p.571 (1959)
10. BRIEGLEB, G. and STROHMEIER, W. Association of hydrogen fluoride in the gas at high pressure. Z. Elektrochem, **57**, p.668 (1953)
11. ARMITAGE, J. W. et al. Thermodynamic properties of a saturated polymerising vapuor I. The liquid vapour equilibrium for hydrogen fluoride, J. Chem. Socl., p.1796 (1963)
12. ROSSOTTI, F. J. C. and ROSSOTTI, H. S. Graphical methods of determining self-association constants. I Systems containing few species. J. Phys. Chem., **65**, p.926 (1961)
13. ROSSOTTI, F. J. C. and ROSSOTTI, H. S. Graphical methods of determining self-association constants. II Systems containing many species. J. Phys. Chem., **65**, p.930 (1961)
14. ROSSOTTI, F. J. C. and ROSSOTTI, H. S. Graphical methods of determining self-association constants. III Refined treatment of molecular weight data. J. Phys. Chem., **65**, p.1376 (1961)
15. MACLEAN, J. N. et al. The self-association of hydrogen fluoride vapour. J. Inorg. Nucl. Chem., **24**, p.1549 (1962)
16. STROHMEIER, W. and BRIEGLEB, B. The state of associations of hydrofluoric acid in the gaseous state I. New experimental measurements Z. Elektrochem, **57**, p.662 (1953)
17. BECKERDITE, J. M. et al. Self-association of gases 2. The association of hydrogen fluoride. J. Chem. Eng. Data, **28**, pp.287-293 (1983)
18. VANDERZEE, C. E. and RODENBERG, W. W. Gas imperfections and thermodynamic excess properties of gaseous hydrogen fluoride. J. Chem. Thermodynam, **2**, (4), pp.461-478 (1970)
19. Series of publications presenting physical properties data published by the journal "Chemical Engineering": Parts 5, 22, 23, 24, 22 August 1974
20. American Institute of Physics Handbook. Pub. McGraw Hill
21. WHEATLEY, C. J. SRD Unpublished work 1986
22. VIEWEG, R. Betrachtung zum System Fluorwasserstoff-Wasser, Chem Tech **15**, no. 12, p.734 (December 1963)

23. Russian data reported in I. G. Ryss. The chemistry of fluorine and its inorganic compounds. AEC-tr-3927, Part 1 (1956)

24. MUNTER, P. A. Partial pressure measurements on the system hydrogen-fluoride/water. Ind. & Eng. Chem., **41**, no. 7 (1949)

25. BROSHEER, J. C. Vapor pressures of hydrofluoric acid solutions. Ind. Eng. Chem., **39**, no. 3 (1947).