Report

UNCLASSIFIED
AEAT/NOIL/27328006/002 (R) Issue 2

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Thermodynamic Modelling of Anhydrous HF / Moist Air / Immiscible Component Mixtures and Validation against Experimental Data

A Deliverable produced under Work Package 7 of the EC URAHFREP Project, Contract No. ENV4-CT97-0630

June 2001

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Title	Thermodynamic Modelling of Anhydrous HF / Moist Air / Immiscible Component Mixtures and Validation against Experimental Data
Customer	European Commission
Customer reference	ENV4-CT-97-0630
Confidentiality, copyright and reproduction	Unclassified
File reference	HF Thermodynamic Modelling Issue 1.doc
Report number	AEAT/NOIL/27328006/002 (R)
Report status	Issue 2

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Executive Summary

The occurrence and quantification of the mitigation of anhydrous hydrogen fluoride (AHF) clouds due to buoyancy generation is currently very uncertain. The EC URAHFREP research programme is aimed at reducing these uncertainties to enable more reliable estimates to be made of the hazards associated with accidental hydrogen fluoride releases.

Thermodynamic experiments on the mixing of AHF with moist air and isobutane have been conducted under the URAHFREP project. These extend the earlier fog chamber studies of Schotte which covered a smaller range of HF concentrations and did not include isobutane. Additionally releases of HF, some including isobutane, have been undertaken in the URAHFREP Field Trials. This report concerns the validation and extension of an existing HF thermodynamic equilibrium model against this new and existing data.

The model of Clough et al is extended to include an immiscible liquid phase. The main complication in extending the model is in evaluating the phase boundaries for the system. Phase tests for determining these boundaries are given. The extended thermodynamic model, incorporating isobutane as the immiscible component, has been coded. The resultant computer model is called HFMIXTURE. During the course of this work some errors in the thermodynamic model implementation in AEAT/HSE dispersion codes EJECT and DRIFT were found and corrected.

HFMIXTURE predictions for the pure HF-moist air system compare favourably with the original data of Schotte and also with the data from the new URAHFREP thermodynamic experiments. It is concluded that a simple "126 model", with only HF monomers, dimers, hexamers and no $HF.H_2O$ complex in the vapour phase, is sufficient for predicting the equilibrium temperature of HF-air mixtures over the range of conditions in the experiments.

Model predictions also compare favourably with the URAHFREP thermodynamic experiments for isobutane mixtures. The model indicates that for these experiments, under equilibrium conditions, no liquid isobutane is present. Isobutane is thus acting as an inert diluent with smaller temperature rise (and fall) attributable to the relatively large heat capacity of the isobutane vapour.

Comparisons with temperature measurements from the URAHFREP Field Trials indicate good agreement for the maximum temperature rise. For the releases involving isobutane, the thermodynamic model predicts no rise above ambient temperature, whereas some rise may have been observed in the trials. Possible reasons for these differences are discussed in the report.

The effect on temperature and density of including increased amounts of immiscible isobutane liquid with HF has been investigated using the thermodynamic model. The results indicate that the inclusion of liquid isobutane as an immiscible component significantly reduces the magnitude of the temperature rise and decreases the region of positive buoyancy.

Contents

1 Introduction

Anhydrous hydrogen fluoride (AHF) is commonly stored and used in bulk in the chemical and nuclear industries. Notably large amounts are used as an alkylating agent in the petrochemical industry [1]. The high toxicity of hydrogen fluoride [2] means that accidental releases may lead to significant hazards to both people and environment. Reliable estimation of the dispersion behaviour of anhydrous hydrogen fluoride is therefore of considerable importance, but is complicated by the complex thermodynamic behaviour of mixing AHF with moist air. HF thermodynamic models (e.g. refs. [3] and [4]) indicate that for ambient humidities frequently encountered in European climes, HF clouds which are initially heavier-than-air may become lighter-than-air as the cloud disperses (ref. [4]). The influence of such buoyancy generation may be to mitigate the hazard as compared with a non-buoyant release, due to enhanced dilution and possibly also buoyant lift-off of the cloud from the ground.

The occurrence and, in particular, the quantification of the mitigation of HF clouds due to buoyancy generation is currently very uncertain. Firstly, the generation of buoyancy is based on the predictions of theoretical thermodynamic models that make certain simplifying assumptions which need to be validated. Secondly, the current understanding of the dispersion behaviour of ground based buoyant releases is somewhat limited, even for buoyancy conserving plumes, let alone for plumes with changing buoyancy. Thirdly, there is the lack of field data for releases of AHF under humid conditions with which to validate models. The EC URAHFREP research programme, of which the work here is a part, is aimed at reducing these uncertainties to enable more reliable estimates to be made of the hazards associated with accidental AHF releases.

In this report we are concerned with modelling the thermodynamics of mixing AHF with moist air and the extension to including with HF an immiscible volatile compound such as isobutane. The inclusion of isobutane is of interest, since it is possible that the presence of such a volatile component in a release may negate the buoyancy effects due to the HF chemistry. Such HF/immiscible liquid releases may occur in, for example, accidental releases from separators in HF alkylation units.

2 Background

As already mentioned hydrogen fluoride exhibits complex thermodynamic behaviour when mixed with moist air. In the vapour phase, hydrogen fluoride (HF) associates due to hydrogen bonding to produce short polymers called oligomers $(HF)_n$ where n = 1,2,6,… and may also associate with water forming an $HF.H_2O$ complex. Oligomer formation is exothermic and oligomer dissociation is endothermic. Oligomerisation is somewhat like liquid condensation/vaporisation in that oligomer formation (absorbing heat) is most favoured by high HF concentrations and low temperatures, whereas mixing with other vapour leads to dissociation (releasing heat). In the liquid phase, hydrogen fluoride strongly interacts with liquid water, releasing significant amounts of heat on mixing. The reduction in vapour pressure above the highly non-ideal liquid mixture favours condensation of hydrogen fluoride vapour in a moist atmosphere to produce hydrofluoric acid mist. Liquid AHF thus initially cools when mixed with air (due to depolymerisation and vaporisation), the mixture subsequently heats up due to condensation of water and heat of solution of HF. Formation of liquid tends to increase the cloud density, whereas heating lowers the density. The cloud density and hence its buoyancy thus results from a number of competing influences.

HF thermodynamic models incorporating some or all of the above complex behaviour are increasingly being included in atmospheric dispersion models [5,6,7]. The adopted thermodynamic models are generally either based on either the work of Schotte [3], or the work of Clough et al [4]. Subsequent studies build on these models in various ways. For example, efficient numerical solution techniques for these two models (eg Webber and Wren [8], Mandellos et al [9]), extension to include the interaction with a chemical additive intended to enhance rainout (Muralhidar et al [10]), the comparison of dispersion models results with hydrogen fluoride release field trials conducted in the Nevada desert [11] and theoretical studies of the influence of high humidity [12]. All these studies rely strongly on the two aforementioned models. It is therefore pertinent that we consider in this report the validition of such models against new data.

Both the models of Schotte and Clough et al were published in 1987 and are apparently independent pieces of work, although it is believed that some correspondence between model developers occurred after publication. Schotte's [3] is the slightly more complex of the two models, in that it includes vapour phase association up to octomer (H_8F_8), $HF.H_2O$ complex and uses a Peng-Robinson equation of state. The model of Clough et al [4] is somewhat simpler, being based on an association model up to hexamer (H_6F_6), ignoring $HF.H_2O$ complex and uses an ideal equation of state for each oligomer species. The model of Clough et al [4] uses a parameterisation of activity coefficients for the liquid mixture due to Wheatley [13]. The Wheatley parameterisation explicitly relates the heat of mixing to the activity coefficients in a thermodynamically consistent way. Although the HF models of Schotte and Clough et al use different parameterisations, they are generally derived from the same experimental data and so one might suppose that they behave similarly.

Schotte [3] validated his model by conducting a series of fog chamber experiments. In these experiments vapour streams of hydrogen fluoride and moist air were mixed and the resultant mixture temperatures measured. Excellent agreement between model and experiment were

found. We are not aware of any similar comparisons being published for the model of Clough et al, although it is understood that Schotte performed some (unpublished) comparisons of the two models and found good agreement. In another study [14], Schotte validated his oligomerisation model for pure saturated HF.

As part of the URAHFREP programme, AEA Technology has performed some HF fog chamber experiments [15] with the aim of confirming and extending Schotte's [3] original experiments. These new experiments are reported elsewhere [15] and extend Schotte's [3] to higher HF concentrations and additionally include measurement on mixtures of hydrogen fluoride, isobutane, water and air.

In this report we shall concentrate mainly on the model of Clough et al, although it is expected that many of the findings might apply also to the model of Schotte. Section 3 gives an overview of the model and in Section 4 we show how this model may be extended to include an additional immiscible volatile liquid component. Model validation is discussed in Section 5. In particular, model results are compared with the URAHFREP fog chamber experiments [15] and with the temperature measurements from the URAHFREP Campaign 2 field trials at Porton [16]. In Section 7 we show the results of some theoretical studies indicating the possible effects on lift-off of introducing liquid isobutane to an AHF release.

3 HF Thermodynamic Model

In Section 3 we discuss the thermodynamic model for mixtures of HF and moist air. This model is extended in Section 4 to include an immiscible liquid component. The base thermodynamic model is essentially that of Clough et al [4], although to facilitate extension , some of the equations have been written in slightly different forms. The solution method adopted here also differs slightly from that of ref.[4].

The model equations are grouped according to:

- HF oligomerisation model for the vapour phase
- Liquid mixture model for vapour pressures and heat of mixing
- Phase equilibrium
- Material balance
- Enthalpy balance
- Phase tests

3.1 PRINCIPAL ASSUMPTIONS

Clough et al [4] state the principal assumptions of their model. These assumptions are crucial to the applicability of the model and are worth repeating here:

- The system is assumed to be well mixed and homogeneous. This is clearly not the case for dispersing clouds, which show inhomogeneity and spatially and temporally varying regions of higher and lower concentration. Consideration of such effects was outside the scope of Clough et al's study and is generally glossed over in application of thermodynamic models to simple dispersion models. Such considerations may be important, but we shall defer discussion to later, noting here only that they are not confined solely to HF clouds.
- As soon as saturation conditions are attained it is assumed that a liquid phase condenses. This can be viewed as a requirement for there to be sufficient nucleation sites for condensation to readily occur. In the atmosphere and for flashing liquid releases where the HF liquid drops act as nucleation sites for water condensation this is probably reasonable well satisfied, except possibly close to the release point.
- The behaviour of HF in the vapour phase is described by an equilibrium association model. The bulk vapour behaviour is described in terms of a mixture of oligomers, each of which is assumed to behave as an ideal gas. Non-ideality in the vapour phase is then assumed to be described solely in terms of changes between the oligomer states.
- Partial pressures of HF and H_2O above the liquid phase and their heat of mixing is parameterised using the methods described by Wheatley . These parameterisations are based on Margules type expansions for activity coefficients modifying the pure substance values.
- Kinetics of the HF oligomerisation and aerosol condensation are not modelled, rather the processes are assumed to be near instantaneous and equilibrium values are assumed.

3.2 HF OLIGOMERISATION MODEL

The oligomerisation model of Clough et al is based on vapour-phase equilibria between the monomer, dimer and hexamer:

$2HF \Leftrightarrow (HF)_2$
$6HF \Leftrightarrow (HF)_6$

Oligomer equilibrium is represented by the equation

$$y_{11} + a_2 y_{11}^2 + a_6 y_{11}^6 = y_1 \qquad (1)$$

where y_1 is the overall vapour fraction of HF (summed over oligomers), y_{11} is the HF monomer vapour fraction, a_2 and a_6 are dimensionless constants parameterised in terms of the enthalpies and entropies of oligomerisation:

$$a_i = \left(\frac{P}{P_{ref}} \right)^{i-1} \exp\left[\left(-\frac{\Delta S_i}{T} + \Delta H_i \right) \Big/ R \right] \qquad \text{i=1,2 and 6} \qquad (2)$$

Constant values adopted by the model are given in Table 1.

The dimer and hexamer vapour fractions are given by

$$y_{12} = a_2 y_{11}^2 \qquad (3)$$

and

$$y_{16} = a_6 y_{11}^6 \qquad (4)$$

respectively.

Constant	Value
ΔH_2 (J mol^{-1}) (40g)	-3.3076×10^4
ΔH_6 (J mol^{-1}) (120g)	-1.6747×10^5
ΔS_2 (J mol^{-1} K^{-1}) (40g)	-2.24×10^2
ΔS_6 (J mol^{-1} K^{-1}) (120g)	-1.023×10^3

Table 1 Enthalpy and entropy of formation for HF oligomers [4]. The 40g and 120g in brackets indicate the values are per oligomer mole. Note there is an error of the exponent of ΔH_6 in ref. [4], this has been corrected in the table here.

3.3 LIQUID MIXTURE MODEL

The binary mixture model adopted by Clough et al is that of Wheatley [13] who used an expansion of the Gibbs Free Energy fitted to experimental data for the vapour pressure over binary HF-H_2O mixtures.

Vapour pressures, P_i (i=1,2) of the binary mixture are modelled by:

$$P_i = x_i \gamma_i P_i^{sat} \tag{5}$$

where x_i are the mole fractions in the liquid mixture, γ_i are the activity coefficients and the P_i^{sat} are the pure component vapour pressures.

In this model, i=1 represents HF and i=2 represents H_2O. The activity coefficients, γ_i (i=1,2), and enthalpy of mixing, H_m are parametrised by:

$$\ln \gamma_i = -\frac{A_i}{T} + B_i \quad \text{i=1,2} \tag{6}$$

and

$$H_m = -R\sum_{i=1}^{2} A_i x_i \tag{7}$$

where the coefficients are given by the following expressions

$$\begin{aligned} A_1 &= w_A\{(1+r_A) - r_A x_1\}(1-x_1)^2 \\ B_1 &= w_B\{(1+r_B) - r_B x_1\}(1-x_1)^2 \\ A_2 &= w_A\{(1+3r_A/2) - r_A(1-x_2)\}x_2^{\,2} \\ B_2 &= w_B\{(1+3r_B/2) - r_B(1-x_2)\}x_2 \end{aligned} \tag{8}$$

The parameters r_A, r_B, w_A and w_B are determined from fitting to data from measurements of partial pressures over HF/H_2O mixtures. Ref.[4] recommended values, correcting the sign for r_A and r_B, are given in Table 2.

Constant	Value
r_A	-0.705
r_B	-0.705
w_A	10000 K
w_B	14.91

Table 2. Interaction parameters for HF-H_2O binary mixtures [13]. w_A has dimesnions of temperature and is given in units of Kelvin.

3.4 MATERIAL BALANCE

Material balance, i.e. species conservation, is made slightly complicated due to the oligomerisation of HF. Although the total number of HF molecules is conserved, these may be associated and hence the total number of actual moles present will be less than implied by simply counting HF molecules. For conservation equations, rather than using actual mole fractions, it is convenient to define mole fractions based on the number of HF (monomer) atoms.

If we denote the actual vapour mole fractions of HF oligomers by y_{1k} (k=1,2,6) and of the remaining vapour species by y_i (i=2,3….), then we define effective mole fractions, $\tilde{y}_i$ based the HF (monomer) moles as

$$\tilde{y}_1 = \frac{\sum_k k y_{1k}}{1 + \sum_k (k-1) y_{1k}} \qquad \text{for HF} \qquad (9)$$

and

$$\tilde{y}_i = \frac{y_i}{1 + \sum_k (k-1) y_{1k}} \qquad \text{for other vapour components} \qquad (10)$$

Material balance for each species may then be written as:

$$z_i = \tilde{y}_i \tilde{V} + x_i L \qquad (11)$$

where z_i is the overall mole fraction for the species i, x_i is the mole fraction for species i in the liquid phase, L is the overall mole fraction of liquid in the mixture and $\tilde{V}$ is the overall mole fraction in the vapour phase. All mole fractions in this material balance are with respect to total number of effective monomer moles.

When there is just one distinct liquid phase then

$$1 = \tilde{V} + L \qquad (12)$$

3.5 PHASE EQUILIBRIUM

Each species which coexists in vapour and liquid phases is required by the model to be in phase equilibrium.

For the HF this requires:

$$y_{11} + y_{12} + y_{16} = \frac{x_1 \gamma_1 P_1^{sat}}{P} \tag{13}$$

and for water

$$y_2 = \frac{x_2 \gamma_2 P_2^{sat}}{P} \tag{14}$$

In terms of the $\tilde{y}_i$ variables, these equilibrium relations may be written in the form:

$$\tilde{y}_i = \frac{x_i \gamma_1 P_i^{sat}}{\Phi_i} \tag{15}$$

where

$$\Phi_1 = \frac{(\sum_k y_{1k})(1 + \sum_k (k-1) y_{1k})}{\sum_k k y_{1k}} \tag{16}$$

and

$$\Phi_i = 1 + \sum_k (k-1) y_{1k} \qquad \text{for } i \neq 1. \tag{17}$$

3.6 ENTHALPY BALANCE

The enthalpy of the mixture may be written in terms of the constituents. Again it is convenient to use quantities based on the total number of (effective monomer) moles. The mixture enthalpy per effective monomer mole may be written as:

$$\tilde{h} = \tilde{V} \sum_i \tilde{y}_i \tilde{h}_{vi} + L \left[\sum_i x_i h_{Li} + H_m \right] \tag{18}$$

Individual terms in the above expression are determined as follows. The reference state is chosen to be the (monomer) component in the vapour phase at temperature T_{ref}. In accordance with ref.[4] we take T_{ref}=273K for oligomerisation changes.

(i) Enthalpy of HF vapour

The individual oligomer enthalpies (per oligomer mole) are approximated by:

$$
\begin{aligned}
h_{11} &= C_{p11}(T - T_{ref}) \\
h_{12} &= C_{p12}(T - T_{ref}) + \Delta H_2 \\
h_{16} &= C_{p16}(T - T_{ref}) + \Delta H_6
\end{aligned}
\qquad (19)
$$

where ΔH_2 and ΔH_6 are the enthalpy change (per oligomer mole) of forming the oligomer state from the monomer state. The specific heat capacities of the oligomers are determined based on assumed degrees freedom as in Clough et al [4].

The contribution per HF effective monomer mole in the vapour phase is then

$$\widetilde{h}_{v1} = \frac{y_{11}h_{11} + y_{12}h_{12} + y_{16}h_{16}}{y_{11} + 2y_{12} + 6y_{16}} \qquad (20)$$

(ii) Enthalpy of other vapour components

$$\widetilde{h}_{vi} = C_{pvi}(T - T_{ref}) \qquad (21)$$

(iii) Enthalpy of liquid components

$$h_{L,i} = C_{L,i}(T - T_{bi}) - \Delta H_{vap,i} + C_{pvi}(T_{bi} - T_{ref}) \qquad (22)$$

where $\Delta H_{vap,i}$ is the enthalpy of vaporisation of component *i* at the normal boiling temperature, T_{bi}.

(iv) Enthalpy of mixing per mole of the binary liquid mixture, H_m, is obtained from Wheatley's formula [13], our equation (7).

The enthalpy balance follows from equating the enthalpy per mole of the mixture to the initial enthalpy (per mole of the mixture) prior to mixing.

3.7 PHASE TESTS

It is important that the phase equilibrium equations are only applied if there is liquid present. This requires testing to see whether the given overall molar composition and temperature imply the presence of a liquid phase. To perform such tests, it is necessary to evaluate the saturation conditions corresponding to the given overall molar composition and temperature. The implied partial pressures may be compared with the overall mole fractions to see whether supersaturation of vapour would be implied.

The test for the presence of liquid may be deduced as follows.

Consider the material balance equations for HF (i=1) and H_2O (i=2):

$$z_1 = \tilde{y}_1 \tilde{V} + x_1 L \tag{23}$$

$$z_2 = \tilde{y}_2 \tilde{V} + x_2 L \tag{24}$$

We seek the condition for vanishing liquid. If liquid is present then phase equilibrium requires

$$\tilde{y}_i = \frac{x_i \gamma_i P_i^{sat}}{\Phi_i P} \equiv \chi_i \qquad \text{i=1,2} \tag{25}$$

which also serves as a definition for χ_i

Adding (23) and (24) and using (12) gives an expression for the liquid fraction

$$L = \frac{z_1 + z_2 - \chi_1 - \chi_2}{1 - \chi_1 - \chi_2} \tag{26}$$

So long as $1 - \chi_1 - \chi_2 > 0$, then $L > 0$ implies

$$z_1 + z_2 > \chi_1 + \chi_2 \tag{27}$$

The condition $1 - \chi_1 - \chi_2 > 0$ when liquid is present, is equivalent to the condition $1 - \tilde{y}_1 - \tilde{y}_2 > 0$, which is satisfied for a two-phase system with another vapour component. If no other vapour components are present, then the liquid fraction is not determined by equation (26). Subject to this restriction the inequality (27) must be satisfied if liquid is to be present.

At the point of vanishing L, the material balance equations imply

$$\frac{\chi_1}{\chi_2} \to \frac{z_1}{z_2} \quad \text{for } L \to 0 \tag{28}$$

Which means that the condition (27) is also equivalent to

$$z_1 > \chi_1 \tag{29}$$

or equivalently

$$z_2 > \chi_2 \tag{30}$$

confirming that presence of one component in the liquid phase, implies presence of the other (so long as that component is present).

Any of the inequalities (27), (29) or (30) may be used for testing for the presence of liquid.

To apply the above tests, the χ_i values must first be determined. For the HF-H_2O system these depend non-linearly on the fractions, x_i in the liquid phase, and also on the oligomerisation state at the equilibrium conditions. This problem may be reduced to one of solving a single implicit equation as follows:

Let the unknown we are solving for be a variable ε, defined such that

$$x_1 = \frac{1-\varepsilon}{2} \tag{31}$$

and

$$x_2 = \frac{1+\varepsilon}{2} \tag{32}$$

For a given value of ε we may determine the oligomerisation state by solving:

$$y_{11} + a_2 y_{11}^2 + a_6 y_{11}^6 = \frac{x_1 \gamma_1 P_1^{sat}}{P} \tag{33}$$

Hence we may determine the Φ_i from (17) and the χ_i from (25). Eliminating the L and $\widetilde{V}$ using (26) and (12) from the material balance equations (23) and (24) gives an implicit equation in ε of the form:

$$\begin{aligned}\varepsilon[z_1 + z_2 - \chi_1 - \chi_2] + (z_1 - z_2)[1 - \chi_1 - \chi_2] \\ + (1 - z_1 - z_2)[\chi_2 - \chi_1] = 0\end{aligned} \tag{34}$$

The above equations are solved for ε, which for a physical solution must lie in the range (-1,1). If a physical solution for ε exists, then we can determine the x_i and hence χ_i from (25). We can then perform the phase test (27). If there is no physical solution then there cannot be liquid phase present at the current temperature and molar composition and it is not necessary to check the inequality (27).

3.8 SOLUTION METHOD

The problem of determining the equilibrium conditions for the mixture is to solve the material balance, phase equilibrium and enthalpy balance equations for a given overall molar composition, with a known initial total enthalpy (per mole).

The method adopted here is to take the primary unknown as being the temperature, and to write the enthalpy balance as an implicit function of temperature which is solved numerically.

At a given temperature we determine whether liquid is present by employing the phase test. If liquid is present, the vapour fractions for the two-phase components are set according to the phase-equilibrium equations. In fact, if there is liquid present we have already solved for the x_i, χ_i and oligomerisation state in evaluating the phase test and, so long as the system is not pure HF and H_2O we use these values to determine the liquid fraction from equation (26). With the vapour and liquid compositions determined all the terms in the phase balance equation may be determined. If there is no liquid present then

$$\widetilde{y}_i = z_i \qquad (35)$$

and the oligomerisation state is obtained by solving equation (1).

4 Extension to include an immiscible volatile liquid phase

In this section the model of Section 3 is extended to include the possibility of an additional liquid-phase being present. For the modelling purposes it is supposed that the additional liquid-phase is completely immiscible with the first liquid (HF-H_2O) phase. This allows the model to be extended without requiring additional empirical input of activity coefficients between the HF and H_2O components.

For simplicity we shall consider the second phase may consist of just one compound (eg isobutane). In principle the extension to more than one compound in the second liquid phase is straightforward with the proviso that the compounds are all mutually miscible (not necessarily forming an ideal solution), and crucially that each is, at least approximately, immiscible with both HF and H_2O.

At the equation level, incorporation of another two-phase compound simply introduces another phase-equilibrium equation that must be satisfied. However, there are more phase boundaries to this system, since the immiscible liquids may be present independently. Consequently the phase testing required is more complicated.

As in the base model, all components in the vapour phase are assumed to behave ideally.

Now we may have two distinct liquid phases. We shall denote these with α for the HF-H_2O phase and β for the immiscible phase.

4.1 MATERIAL BALANCE

The material balance equations may be written

$$z_i = \tilde{y}_i \tilde{V} + x_i^{\alpha} L_{\alpha} \qquad i=1,2 \tag{36}$$

$$z_{\beta} = \tilde{y}_{\beta} \tilde{V} + L_{\beta} \tag{37}$$

The x_i^{α} are mole fractions in the liquid phase α only; L_{α} denotes the mole fraction of liquid phase α; L_{β} denotes the mole fraction of liquid phase β. The vapour fraction $\tilde{V}$ is related to these liquid fractions by

$$\tilde{V} + L_{\alpha} + L_{\beta} = 1 \tag{38}$$

4.2 PHASE EQUILIBRIUM

Phase equilibrium for the immiscible component is given by

$$\tilde{y}_\beta = \frac{P_\beta^{sat}}{\Phi_\beta P} \equiv \chi_\beta \tag{39}$$

where Φ_β is given by equation (17).

4.3 PHASE TESTS

As for the HF-H_2O system in Section 3.7, phase tests may be deduced from vanishing liquid limits of the material balance and phase equilibrium equations.

It is convenient to define the following two variables:

$$z_\alpha \equiv z_1 + z_2 \tag{40}$$

$$\chi_\alpha \equiv \chi_1 + \chi_2 \tag{41}$$

Taking the vanishing liquid limit of the phase equilibrium equations, the following conditions may be determined:

(i) no liquid:

$$\begin{aligned} z_\alpha &< \chi_\alpha \\ z_\beta &< \chi_\beta \end{aligned} \tag{42}$$

(ii) β liquid only:

$$\begin{aligned} z_\alpha &< \frac{(1-z_\beta)\chi_\alpha}{1-\chi_\beta} \\ z_\beta &> \chi_\beta \end{aligned} \tag{43}$$

(iii) α liquid only:

$$\begin{aligned} z_\alpha &> \chi_\alpha \\ z_\beta &< \frac{(1-z_\alpha)\chi_\beta}{1-\chi_\alpha} \end{aligned} \tag{44}$$

(iv) both liquid phases present

$$z_\alpha > \frac{(1-z_\beta)\chi_\alpha}{1-\chi_\beta}$$
$$z_\beta > \frac{(1-z_\alpha)\chi_\beta}{1-\chi_\alpha} \qquad (45)$$

Interestingly, the above conditions are precisely the same as for an immiscible binary liquid mixture of pure compounds having mole fractions $\{z_\alpha, z_\beta\}$ and normalised vapour pressures $\{\chi_\alpha, \chi_\beta\}$ (eg ref.[8]). The phase diagram for the {α,β} system is illustrated schematically in Figure 1.

As was the case in Section 3.7 for the HF-H_2O system, the $\{\chi_\alpha, \chi_\beta\}$ are not a priori known and must be obtained from solution of the material balance and phase equilibrium equations.

When determining the condition for the presence of liquid phase α in the absence of liquid phase β, then the χ_1 and χ_2 at saturation are obtained by the solution procedure given in Section 3.7.

When determining the condition for the presence of liquid phase β in the absence of liquid phase α, the state of oligomerisation is determined from solving

$$y_{11} + a_2 y_{11}^2 + a_6 y_{11}^6 = \frac{z_1\left[1 - P_\beta^{sat}/(\Phi_\beta P)\right]}{1-z_\beta} \qquad (46)$$

hence χ_β is obtained from equation (39).

When determining the condition for the presence of liquid phase β in the presence of liquid phase α, or vice versa, we must solve using the equilibrium conditions for both the α and β liquid phases. This may be done in a similar manner to the α equilibrium case considered in Section 3.7.

Let the unknown we are solving for be the variable ε, defined such that

$$x_1^\alpha = \frac{1-\varepsilon}{2} \qquad (47)$$

and

$$x_2^\alpha = \frac{1+\varepsilon}{2} \qquad (48)$$

We determine the oligomerisation state by solving:

$$y_{11} + a_2 y_{11}^2 + a_6 y_{11}^6 = \frac{x_1 \gamma_1 P_1^{sat}}{P} \quad (49)$$

Hence we may determine the Φ_i from (17) and the χ_i from (25) and (39). In this case the material balance and phase equilibrium equations give an implicit equation in ε of the form:

$$(z_\alpha + z_\beta - 1)\left[\chi_2^\alpha - \chi_1^\alpha - \varepsilon\chi_\alpha\right] + (\chi_\alpha + \chi_\beta - 1)\left[\varepsilon z_\alpha - (z_2 - z_1)\right] = 0 \quad (50)$$

The above equations are solved for ε, which for a physical solution must lie in the range (-1,1). If a physical solution for ε is found, then we can determine the x_i^α, hence χ_i (i=1,2) from (25) and χ_β from (39). If there is no physical solution then there cannot be liquid phase α present at the current temperature and molar composition.

$\tilde{V}$ in this case obtained from

$$\tilde{V} = \frac{1 - (z_\alpha + z_\beta)}{1 - (\chi_\alpha + \chi_\beta)} \quad (51)$$

and the fractions in each liquid phase are

$$L_\beta = z_\beta - \chi_\beta \tilde{V} \quad (52)$$

and

$$L_\alpha = z_\alpha - \chi_\alpha \tilde{V} \quad (53)$$

4.4 SOLUTION METHOD

The above equations have been coded in C++, compiled as a Windows 32 bit DLL, and called from Microsoft Excel 97. The resultant model has been named HFMIXTURE Version 1.10. HFMIXTURE solves for the equilibrium conditions for mixtures of HF, H_2O, isobutane and air. HFMIXTURE has been used to compare model predictions against experimental data and to perform theoretical studies.

5 Model Verification

As a check on the coding of HFMIXTURE, its predictions have been checked against an earlier implementation of the Clough et al model, called WETAHF. The HFMIXTURE and WETAHF (Version 3.00 April 1992) predictions are found to closely agree for the range of conditions in the Schotte experiments. This acts as a check of the model solution for HF-moist air system.

The AEAT/HSE dispersion models DRIFT Version 2.25 (and earlier versions) and EJECT Version 2.05 (and earlier versions) use a differential form of thermodynamic equilibrium model developed by Webber and Wren [8]. For HF, this differential model is based on the model of Clough et al [4], using the same empirical parameters, and should yield very similar predictions. This is apart from small differences that may result from DRIFT and EJECT allowing some substance properties such as specific and latent heats to vary with temperature, whereas they are approximated as being constant in HFMIXTURE and the original WETAHF code.

In fact, comparison of the different models showed significantly different temperature predictions in humid conditions. Further investigation highlighted some subtle differences between the model implementations (see Sections 13.1 and 13.2 for details) and some small errors (the HF vapour specific heat was incorrectly calculated as per HF oligomer mole, rather than the required per HF mole). Most crucially for the predictions in high humidity, the wrong sign was used for the heat of mixing of HF with water. This error is traceable back to the original differential equilibrium document, ref.[8] and also afflicts the ammonia-water heat of mixing calculation.

With the appropriate fixes made to DRIFT and EJECT, the different model implementations are found to be in excellent agreement for 0% to 100% air humidities. The resulting new code versions are denoted DRIFT 2.26 and EJECT 2.08.

As a check of the isobutane equilibrium solution in HFMIXTURE, the model has been run for a mixture of isobutane with moist air with no HF present. The results, including the dry out point, are found to agree with the predictions of DRIFT 2.26 for this case.

6 Model Validation

6.1 COMPARISON WITH SCHOTTE DATA

Schotte [3] conducted fog chamber experiments of mixing HF vapour with air at 0%, 50%, 60%, 80% and 100% relative humidity. The fog chamber was placed in a water bath, the temperature of which was varied to eliminate heat losses. Initial HF and air temperatures were 298-299K. Schotte presents measurements of the resulting temperature change when the streams are mixed. Schotte estimated the maximum error on the temperature change measurements to be 2.7K. Schotte compared his temperature measurements with the predictions of his equilibrium model and apart from mixing with dry air found excellent agreement over the range of compositions (0% to 20% mole HF). The large temperature drop associated with mixing with dry air led to problems in matching the water bath temperature in Schotte's work.

HFMIXTURE Version 1.10 has been run to model mixing HF and moist air both initially at 299K over the range of relative humidities in Schotte's experiments. Mixing of HF with dry air is shown in Figure 2. Agreement is very similar to Schotte's model compared with the measurements. Experimental data points here possibly suffer from the water bath problems mentioned above, which would give rise to higher temperatures than for a truly adiabatic system.

Mixing with humid air is shown in Figure 3. The model and data show good agreement over the range of HF concentrations and humidities in the experiments. We note however a slight tendency to underestimate the maximum observed temperature rise. Schotte's own model appears to be slightly better in this respect, however the differences of both models are small compared with estimated maximum errors in the experimental data.

These comparisons indicate that the model of Clough et al [4] adequately describes the observed temperature changes in the experiments. These predictions depend upon the oligomerisation model as well as the heat of mixing and vapour pressures over the mixture. The comparisons indicate that to get good temperature agreement over the experimental range it is not necessary to extend the model to include octomer or $HF.H_2O$ complex contributions that are present in Schotte's model.

6.2 COMPARISON WITH URAHFREP MIXING CHAMBER DATA

Under the URAHFREP programme, AEA Technology has performed some HF fog chamber experiments [15] with the aim of confirming and extending Schotte's [3] original experiments. These new experiments are reported elsewhere [15] and extend Schotte's [3] to higher HF concentrations and additionally include measurement on mixtures of hydrogen fluoride, isobutane, water and air. In these experiments vapour streams initially at approximately 294K are mixed in an insulated chamber.

Comparisons of the HFMixture 1.10 model predictions with the URAHFREP thermodynamic data are reported below.

Figure 4 shows model predictions against experimental data for HF mixing with moist air. The data covers a wider range of HF mole fractions than Schotte. Although the experimental data shows some degree of scatter, the new measurements are broadly supportive of Schotte's and show reasonably good agreement with data across a wide range of HF concentrations. The scatter shown in the new data is somewhat more marked than in Schotte's measurements. It is not clear what causes this scatter, and in some cases there seem to be some systematic differences between the different measurement runs.

Figure 5 shows the results for mixing with dry air. The measured cooling compares favourably with the model prediction and show lower temperatures than Schotte. This is probably due to improvements in the new experiments over the heat bath arrangement used by Schotte. For mixing with humid air, the model compares favourably with the data. Exceptions are

(i) the warming phase for 60% humidity, where the measurements look anomalous compared with the trend implied by the neighbouring (50% and 80%) humidity results
(ii) at 100% relative humidity the model shows slightly more warming than measured, although there is considerable scatter in the experimental data near the peak temperature

Figure 5 also shows comparisons for the mixing of HF with dry air and dry isobutane streams. The isobutane percentage is the fraction of isobutane mole fraction of the feed streams (air and isobutane). Smaller temperature drops are obtained than for the dry air case. The HFMIXTURE model predicts that isobutane does not condense in these releases, despite the large temperature drops involved. The smaller temperature change when isobutane is present is understandable in terms of the larger heat capacity of isobutane vapour compared with dry air.

Figure 6 shows the same series of graphs, but his time when the air and isobutane feed mixture is moist with a relative humidity of 50%. The graphs are again similar to the moist air cases. The presence of isobutane gives slightly smaller temperature drops and rise than for the moist air system. Some warming above initial temperature is still evident for this humidity. The model also shows this effect and predicts that no isobutane condenses, despite the condensation of HF and H_2O to form a hydrofluoric acid fog. This again would imply that this quenching effect on temperature is due to the large heat capacity of isobutane compared with air.

Figure 7 shows a similar situation for air and isobutane feeds with a relative humidity of 100%. Again the model predicts no condensation of isobutane under these conditions.

In summary, the URAHFREP fog chamber thermodynamic studies are supportive of Schotte's earlier findings for HF mixing with moist air. Extension to large HF fractions have allowed model predictions to be compared with measurements over a wider range than previously possible. Good agreement with the model predictions is generally obtained over this extended range. Introduction of moist isobutane leads to slightly less cooling and slightly less warming when compared with mixing with moist air alone. This behaviour is also

observed in the model predictions which generally compare favourably with the measurements. That isobutane is acting mainly as a diluent is not too surprising if the model is correct in predicting that the isobutane does not condense. In this respect the fog chamber experiments differ substantially from accidental releases of liquid HF and liquid isobutane where vaporisation of the liquid isobutane will extract its heat of vaporisation from the cloud mixture. Section 7 discusses HFMIXTURE predictions for mixtures involving liquid isobutane.

6.3 COMPARISON WITH URAHFREP FIELD TRIALS DATA

The URAHFREP field trials involved the release and dispersion of HF and HF/isobutane mixtures in humid atmospheric conditions. All the releases were of HF liquid below its normal boiling temperature. The releases involving isobutane, mixed a flashing superheated isobutane jet with the HF jet near to the release point. Temperature measurements are available from the HSL thermocouple arrays in the near field of the URAHFREP field trials [16]. Measurement problems mean that only temperature differences from the ambient values are viewed as being reliable. It is interesting to compare the thermodynamic model predictions with these temperature measurements.

HSL have analysed the results by dividing the thermocouples into groups based on the measurement height and distance from source. Peak temperatures in each group are then averaged over the duration of each release. We have extracted the largest of these average peak values from each of the trials and compare these values with the maximum temperature rise above ambient predicted by the HFMIXTURE model using as input the trial release and ambient conditions [16,17]. The results are given in Table 3. There are no data available from HF003, and at the time of writing no ambient temperature data for trials HF001 and HF002.

Table 3. Maximum and minimum temperature predictions for URAHFREP Field Trials and observed peak values averaged over release durations

Trial	Predicted		Observed
	maximum temperature rise (K)	maximum temperature fall (K)	maximum temperature rise (K)
HF004	6.9	-42	6.35
HF005	5.5	-43	5.62
HF006	4.7	-43	4.88
HF007	1	-45	1.73
HF008	4.6	-43	3.96
HF009	0	-68	0.53
HF010	5.2	-41	4.57
HF011	0	-67	2.85
HF012	5.9	-40	3.94

Table 3 shows that there is generally a good correlation between the temperature rises predicted by the thermodynamic model and the average maximum rises observed in the field trials. In fact, due to concentration fluctuations, we expect the average maxima determined

from the field trials to be less than the maximum predicted by the model. Generally the values are found to be quite similar. In trials HF009 and HF011 liquid isobutane was mixed with the HF jet. In these cases the thermodynamic model predicts no rise above ambient temperature, whereas for trial HF009 the observed average peak rises are 0.53 and 2.85 above ambient. Such differences might be explained by errors resulting from any changes in ambient temperature during release, or possibly a less than complete mixing of HF and isobutane liquid jets.

The maximum falls in temperature predicted by the model are also given in Table 3. These temperature falls appear to be significantly larger than those observed by the thermocouple arrays, the nearest array being at 5m distance from release. It is possible that the cloud is already too dilute by 5m to show such large temperature drops. This cannot be answered by the thermodynamic model alone, but requires the modelling of the dilution as a function of distance. This aspect is covered by the modelling studies reported in ref.[18].

7 Predictions for Mixtures with Isobutane Liquid

Apart from the two URAHFREP Field Trials releases HF009 and HF011, the above validation studies don't cover the situation where there is liquid isobutane mixed with the HF. This situation is of practical interest to accidental releases which may occur from a separator in an HF alkylation unit. In the absence of experimental data it is instructive to consider the (theoretical) predictions of the HF-immiscible-moist air model applied to this case.

As an example, let us consider HF and isobutane liquid stored under pressure at a temperature of 288K. HFMIXTURE predictions for a release from these conditions mixing with the moist air at a temperature of 280K and relative humidity of 90% are considered below. The initial flash process is treated as being isenthalpic in the calculations.

Figure 8 shows the influence of isobutane/HF mass ratio on temperature over the whole dilution range. Introducing more isobutane leads to much lower temperatures on cooling. The additional cooling is by virtue of the isobutane's heat of vaporisation. The temperature minimum corresponds generally to the point where liquid isobutane dries out, although HF and water are still present when this occurs.

Now let us concentrate in more detail on the region of generation of positive buoyancy since it is this region which may lead to lift-off of a cloud.

Figure 9 shows the density difference relative to air as a function of HF concentration for different mass ratios of HF and isobutane. Not surprisingly, increasing the isobutane content decreases the region over which the mixture is positively buoyant. For the conditions in this example, the mixture is no longer buoyant for isobutane/HF mass ratios greater than about 4. In the context of a dispersing cloud, depending upon an appropriate bulk Richardson number, the relative density difference may have ceased to be dynamically important at lower isobutane/HF mass ratios.

Figure 10 shows the temperature difference relative to air. It is interesting to compare Figure 9 and Figure 10. The temperature difference remains positive (cloud warmer than air) at small HF concentration, even where the density difference is positive (cloud denser than air). Thus we cannot rely on the temperature difference alone to infer the buoyancy of the cloud, there is still liquid present at this stage (the cloud can only go buoyant while there is still liquid present) and also the density difference is sufficiently small that oligomerisation still has an influence.

8 Conclusions

The model of Clough et al [4] for the pure HF-moist air system compares favourably with the data of Schotte and also with the data from the new URAHFREP thermodynamic experiments. It therefore appears that a model with only HF monomers, dimers and hexamers is sufficient for predicting the equilibrium temperature of HF-air mixtures over the range of conditions studied. In a separate study [19] it was concluded the partial pressure of the $HF.H_2O$ complex is small enough such that neglecting this reaction leads to negligible errors.

During the course of this work some errors in the thermodynamic model implementation in AEAT/HSE dispersion codes EJECT and DRIFT were found and corrected. These errors resulted mainly in an underestimation of the heating of the cloud under humid conditions. The corrected versions are now in agreement with the earlier thermodynamic model WETAHF, and with the new thermodynamic model, HFMIXTURE, developed for this study.

The model of Clough et al [4] has been extended to include an extra immiscible liquid phase. For simplicity this immiscible phase is assumed to consist of a single component. The main complication in considering such an extra immiscible phase, is the determination of the boundaries of the phase regions to enable the conditions for the onset of condensation or dry out to be determined. By considering the vanishing liquid limit of the vapour-liquid equilibrium equations, the vaporisation/condensation conditions are (reassuringly) found to be in direct correspondence with those for immiscible binary liquid systems. Further extension of the model to a mixture of components in the immiscible liquid is expected to be straightforward, so long as the extra components are mutually miscible, but are immiscible with HF and water.

Comparison with the URAHFREP thermodynamic experiments which incorporated isobutane show quite good agreement. Both model and experiments indicate the isobutane acting as an inert diluent with smaller temperature rise (and fall) attributable to the relatively large heat capacity of the isobutane vapour. For the conditions in the experiments the model indicates that no liquid isobutane is present in the equilibrium mixture. It is therefore not surprising that isobutane is acting in the observed way.

Comparisons with temperatures measured in the URAHFREP Field Trials indicate that the model predictions for the maximum rise above ambient temperature appear to be well correlated with measurements. For the releases involving isobutane, no rise above ambient temperature is predicted by the models, whereas small rises above ambient may have been observed. These differences may be due to changing conditions in the field, e.g. due to changing ambient temperature, due to an incomplete mixing of the HF and isobutane jets, or a deficiency in the thermodynamic model. The minimum temperatures predicted are not observed in the analysed experimental data, but this does not rule out such temperatures closer to the source than the nearest thermocouple array.

The effect on temperature and density of including increased amounts of immiscible isobutane liquid with HF has been investigated using the thermodynamic model. The results indicate that the inclusion of liquid isobutane as an immiscible component significantly

reduces the magnitude of the temperature rise and decreases the region of positive buoyancy for the HF mixture with moist air.

9 Acknowledgements

This work is funded as part the European Commission's URAHFREP research project, investigating the behaviour and effects of accidental releases of anhydrous hydrogen fluoride, under contract No. ENV4-CT97-0630. This work is co-funded by the UK Health and Safety Executive as part of their research programme into Major Hazards under Contract: RSU 3773/Z 75.029. All funding is gratefully acknowledged.

10 Nomenclature

a_i	dimensionless coefficients in HF oligomer equilibrium
A_i,B_i	parameters in activity coefficient formula
C_{pvi}	constant pressure molar specific heat capacity of vapour component i
C_{pli}	constant pressure molar specific heat capacity of HF i-mer (i=1,2,6)
$\widetilde{h}$	molar enthalpy of mixture (moles based on treating HF as entirely monomer)
H_m	heat of mixing per mole of liquid mixture
L	mole fraction in liquid phase (moles based on treating HF as entirely monomer)
P	system pressure (generally taken to be 1 atmosphere)
P_i^{sat}	saturated vapour pressure for pure component i
P_{ref}	reference pressure 1 N/m^2
R	universal molar gas constant
r_A, r_B	constants in parameterisation of activity coefficients
T	absolute temperature of the mixture
T_{ref}	reference temperature for enthalpy
T_{bi}	normal boiling temperature of component i
$\widetilde{V}$	mole fraction in vapour phase (moles based on treating HF as entirely monomer)
w_A,w_B	constants in parameterisation of activity coefficients
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapour phase (moles based on HF oligomerisation state)
y_{1k}	mole fraction of HF k-mer (k=1,2,6) in the vapour phase (moles based on HF oligomerisation state)
$\widetilde{y}_i$	effective mole fraction of component i in the vapour phase (moles based on treating HF as entirely monomer)

z_i overall mole fraction of component *i* in all phases (moles based on treating HF as entirely monomer)

α denotes the liquid phase consisting of HF-water mixture

β denotes the liquid phase which is immiscible with liquid phase α

γ_i activity coefficient for component *i*

ΔH_2 enthalpy of HF dimerisation per dimer mole

ΔH_6 enthalpy of HF hexamerisation per hexamer mole

ΔS_2 entropy of HF dimerisation per dimer mole

ΔS_6 entropy of HF hexamerisation per hexamer mole

χ_i relates to partial pressures above mixtures $i = \alpha, \beta$

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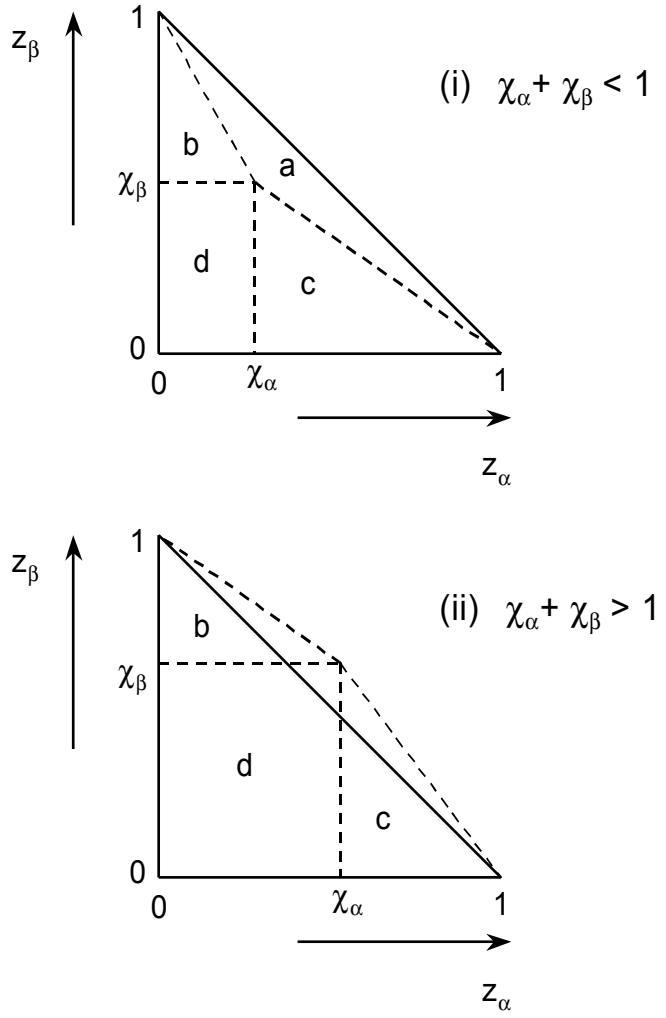
12 Figures



(a) Both Liquid Phases α and β
(b) Liquid β only
(c) Liquid α only
(d) No liquid

Figure 1. Phase Regions for Immiscible Liquid Phases α and β.

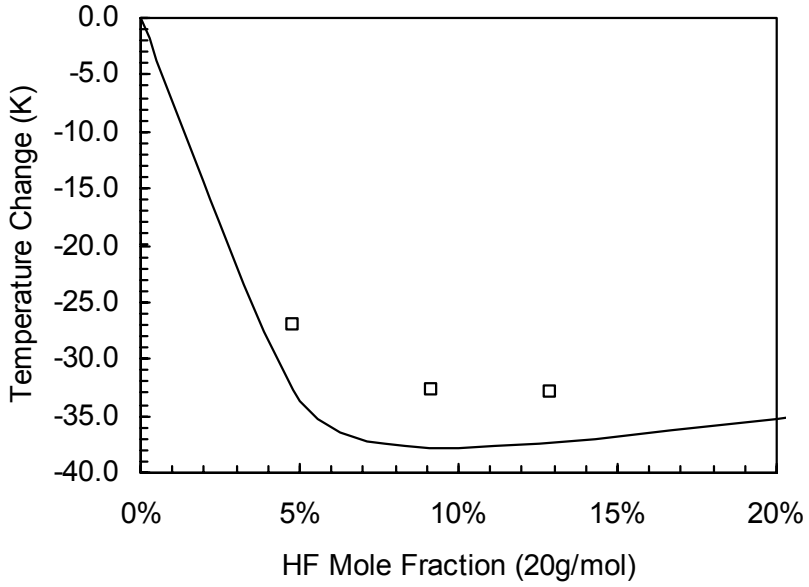


Figure 2. Temperature change during mixing of HF and dry air at 299K. HFMIXTURE predictions compared with Schotte data [4].

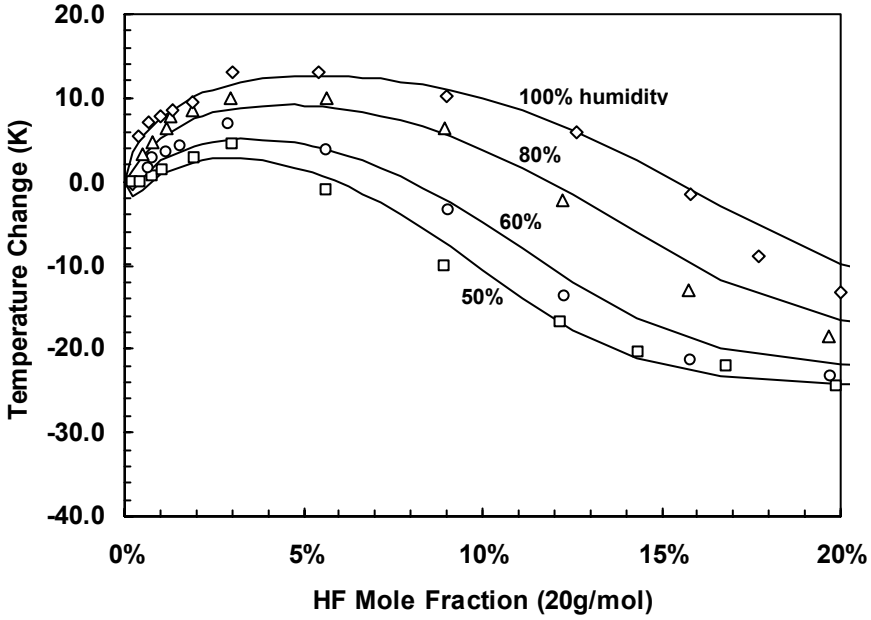


Figure 3. Temperature change during mixing of HF and moist air at 299K. HFMIXTURE predictions compared with Schotte data [4].

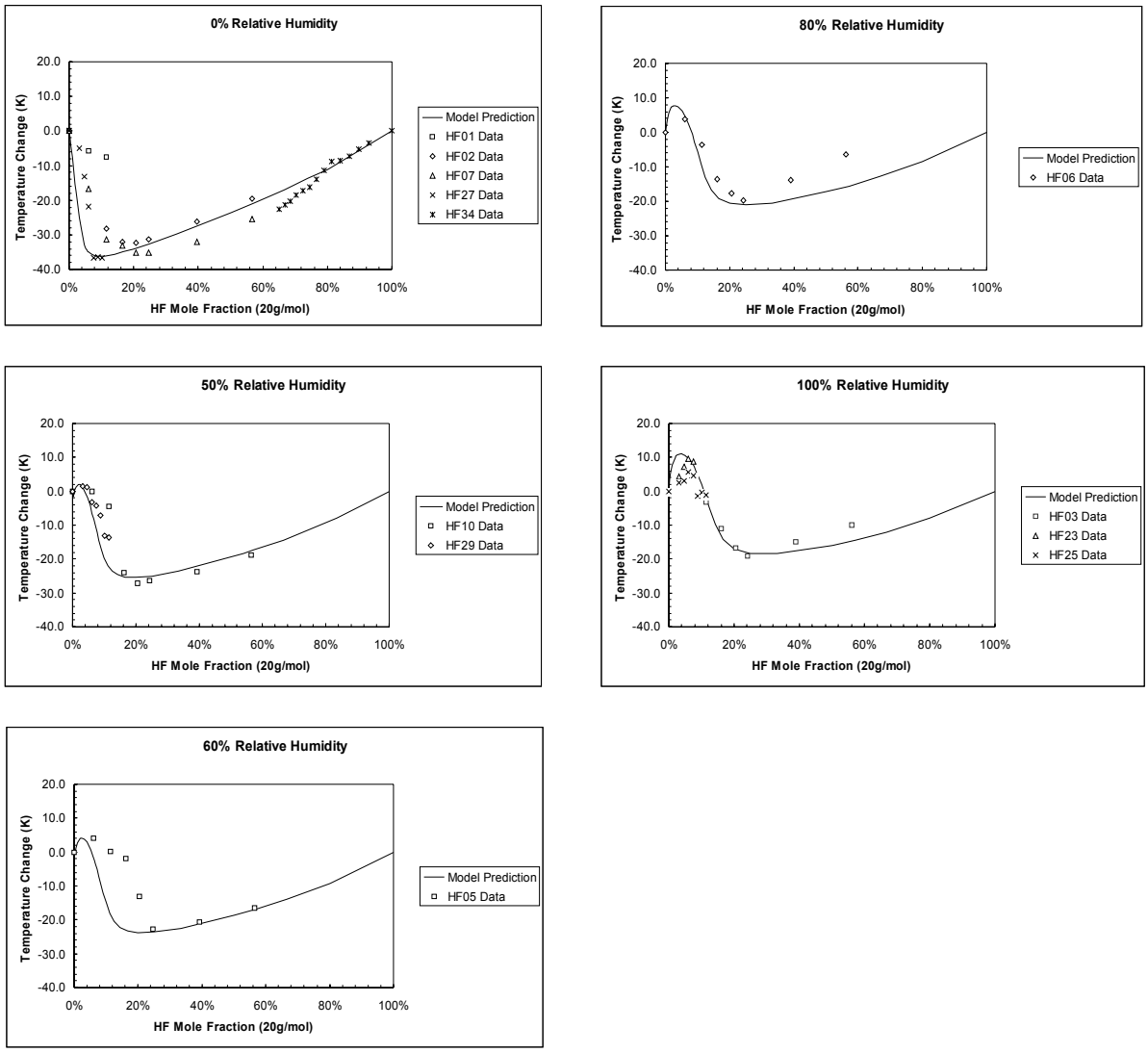


Figure 4. Temperature change during mixing of HF with moist air. HFMIXTURE predictions compared with data of Kemp and Newland [15].

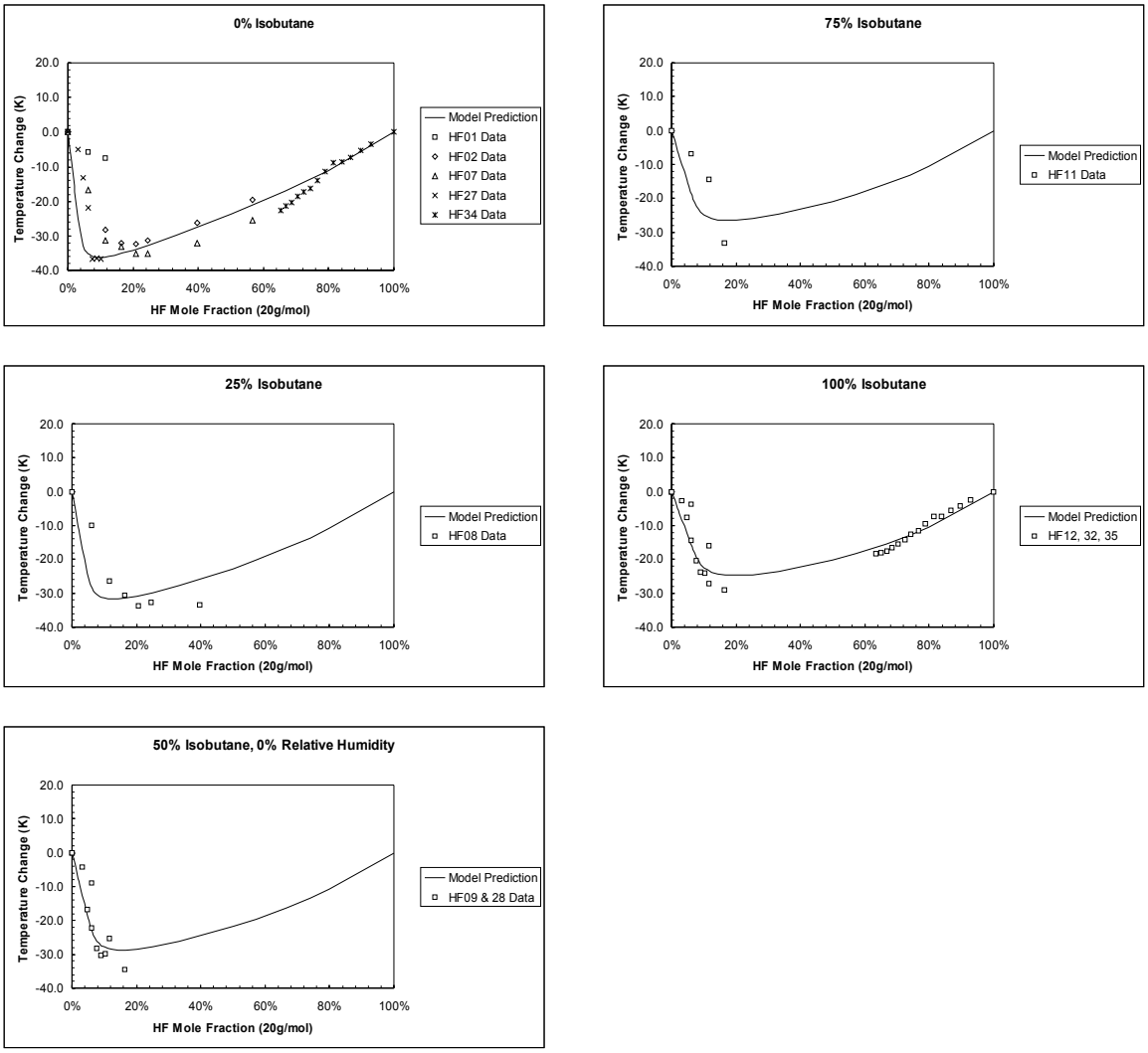


Figure 5. Temperature change during mixing of HF with mixtures of dry air and dry isobutane. HFMIXTURE predictions compared with data of Kemp and Newland [15].

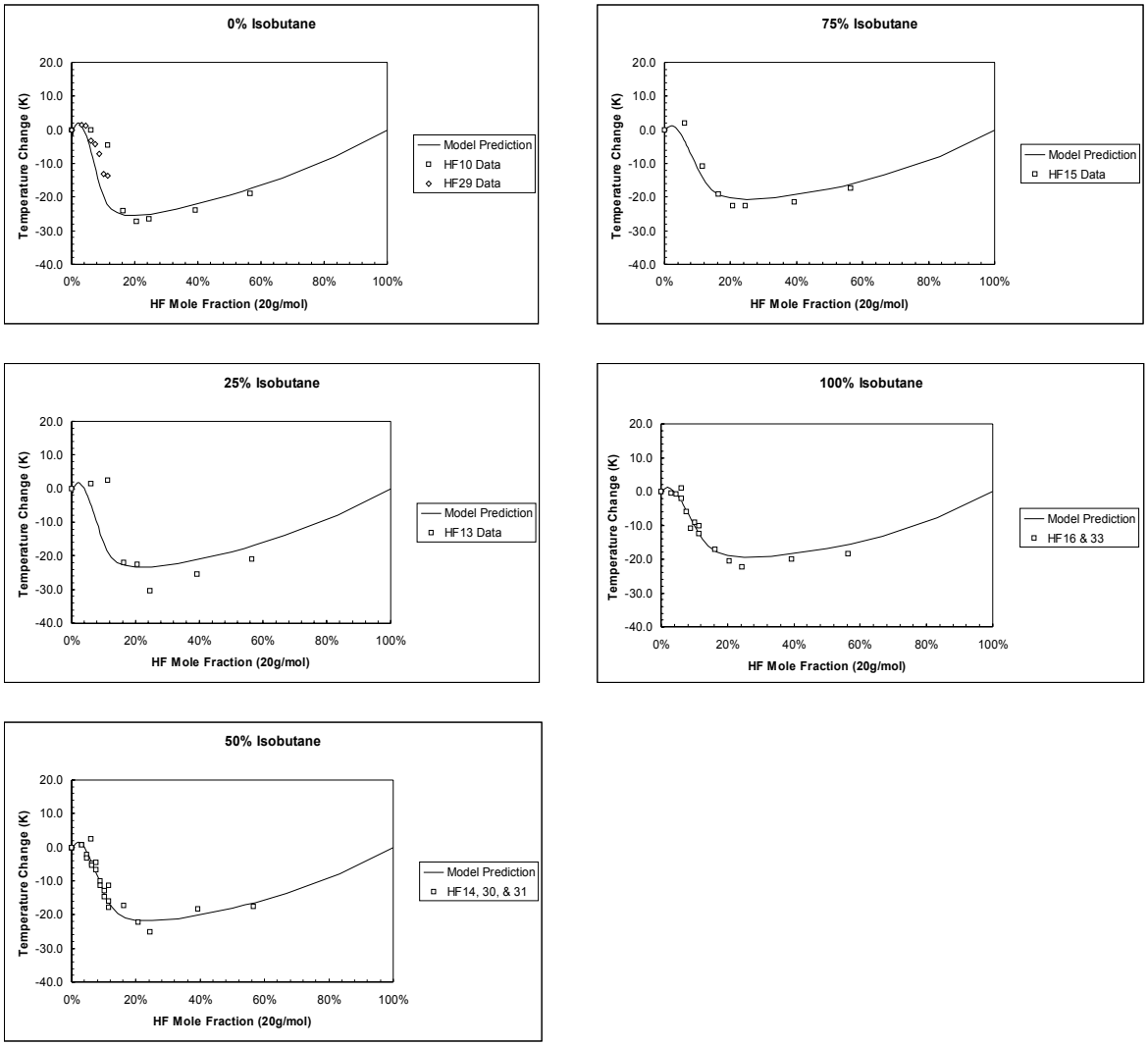


Figure 6. Temperature change during mixing of HF with mixtures of 50% relative humidity moist air and isobutane. HFMIXTURE predictions compared with data of Kemp and Newland [15].

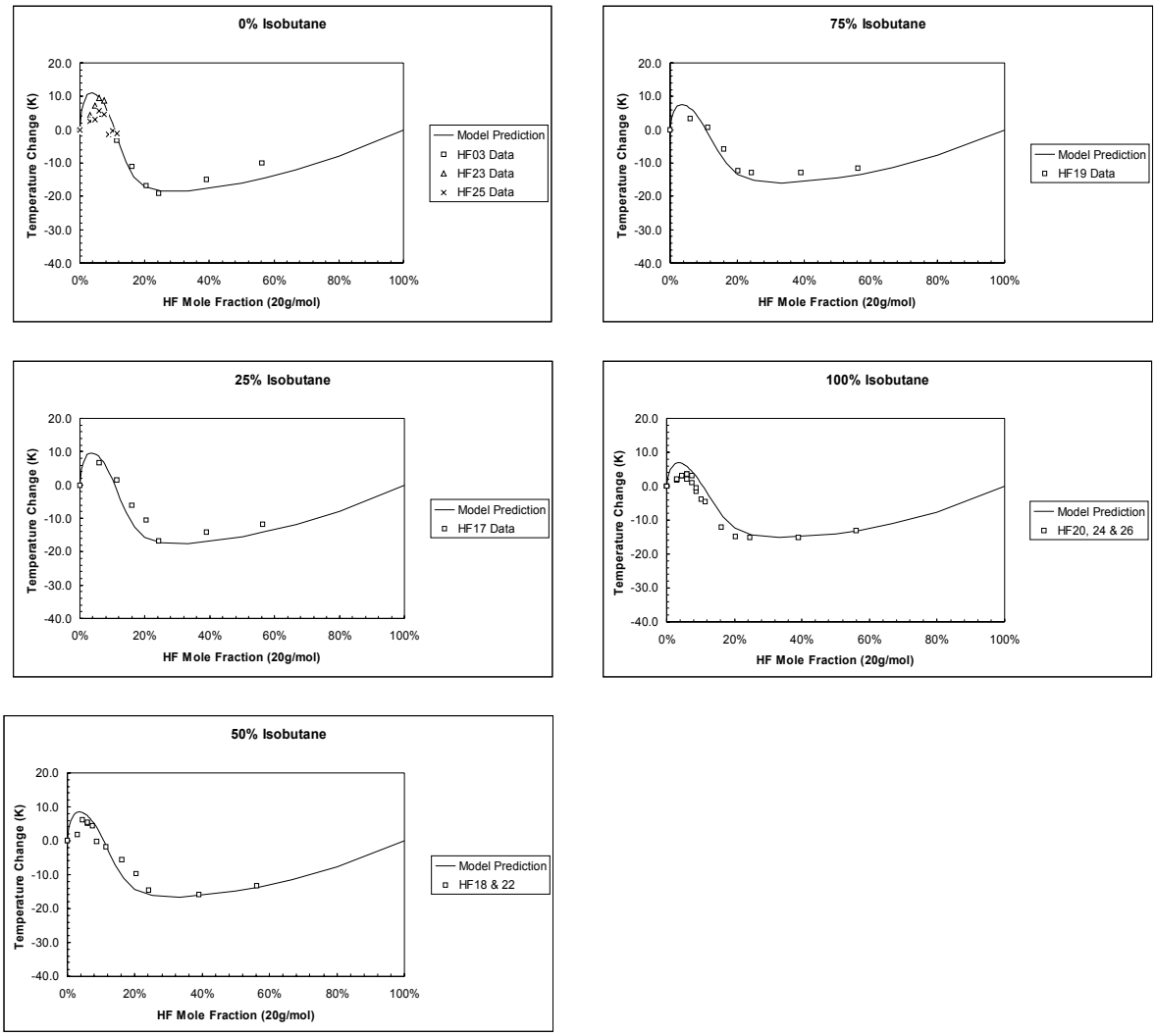


Figure 7. Temperature change during mixing of HF with mixtures of 100% relative humidity moist air and isobutane. HFMIXTURE predictions compared with data of Kemp and Newland [15].

Figure 8. The effect of different isobutane/HF mass ratios, r, on the temperature as a function of HF mole fraction. Moist air at 280K and relative humidity of 90% .

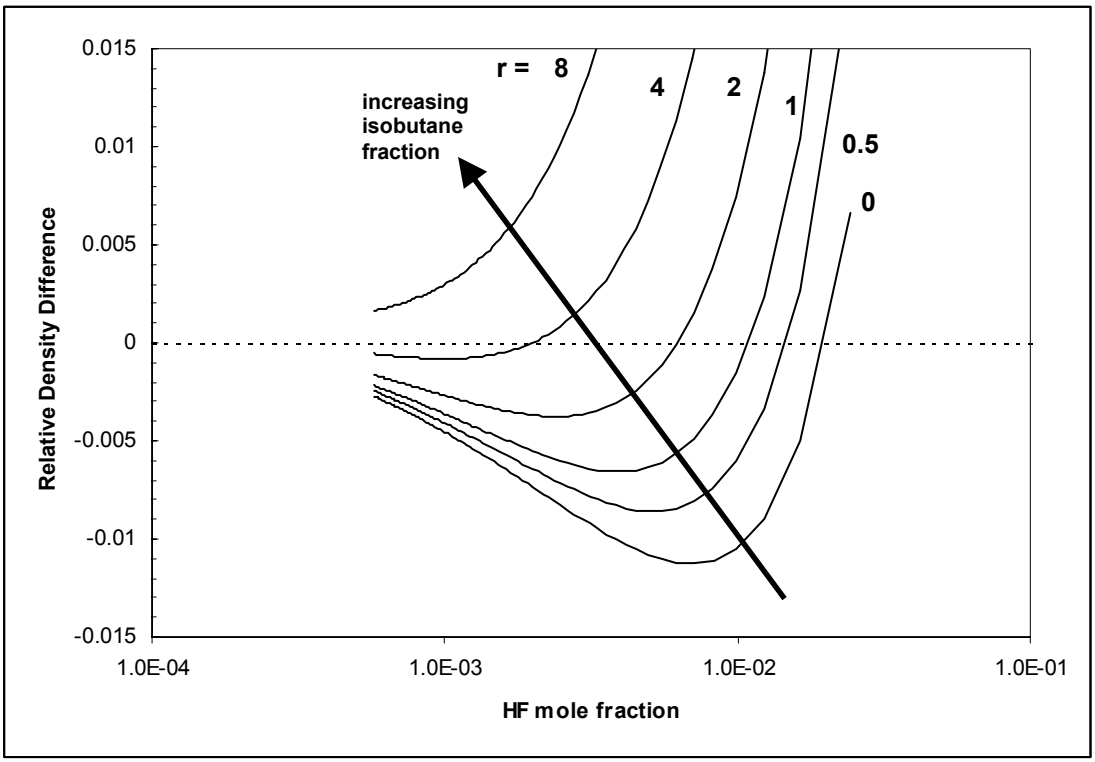


Figure 9. Influence of increasing isobutane fraction on the density difference relative to air. Negative value = less dense than air. r = isobutane/HF mass ratio.

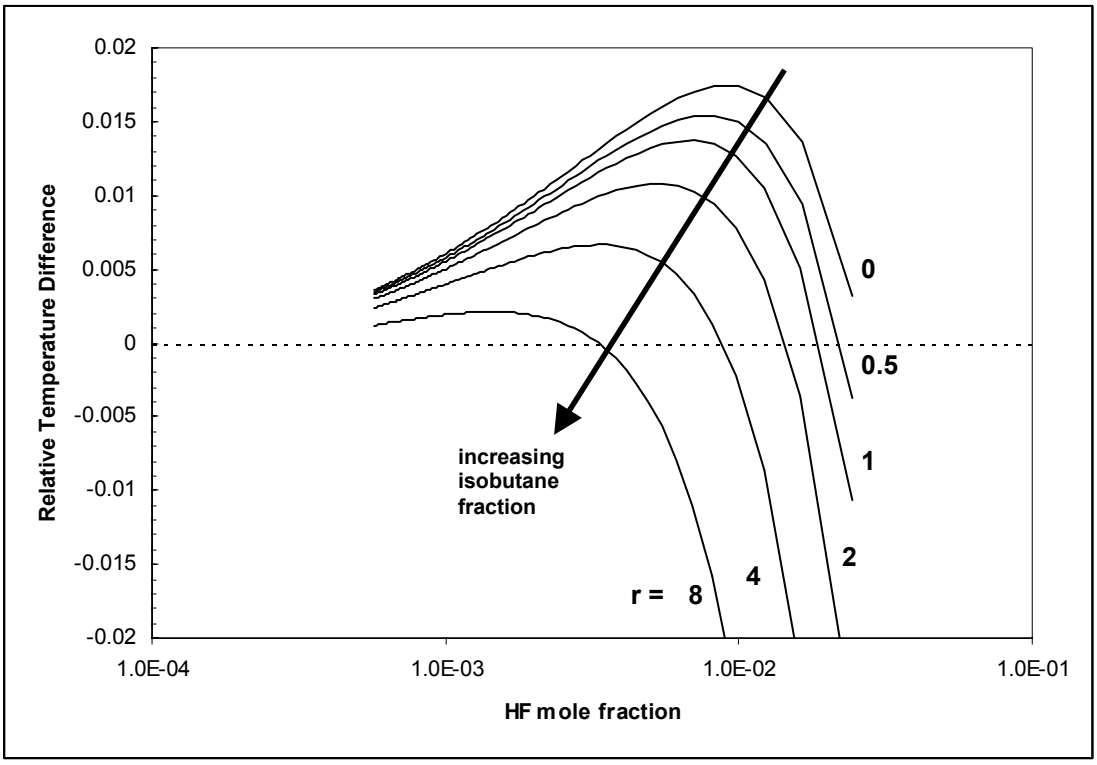


Figure 10. Influence of increasing isobutane fraction on the temperature difference relative to air. Negative = colder than air. r = isobutane/HF mass ratio.

13 Appendices

13.1 HEATS OF HF OLIGOMERISATION AS USED IN DRIFT AND EJECT

DRIFT and EJECT thermodynamic models are based upon the differential equilibrium model of Webber and Wren [8]. This model incorporates terms for the heats of oligomerisation in going from monomer to dimer and from monomer to hexamer. The implementations in the codes EJECT and DRIFT use *constant* values:

$$\Delta H_2 = -3.3076 \times 10^4 \text{ J/(dimer mol)}$$
$$\Delta H_6 = -1.6747 \times 10^5 \text{ J/(hexamer mol)}$$

as given in Clough, Grist and Wheatley [4]. However, in the model in the ref. [4], implemented as WETAHF, there is implicit temperature dependence of the heat of oligomerisation by virtue of the chosen thermodynamic path for calculating enthalpy changes. The thermodynamic path is:

1. Starting from monomer moles at temperature T
2. The monomer moles are taken isobarically to T_{ref}
3. The appropropriate number of oligomers (determined by partitioning at temperature T) are formed from monomer moles at T_{ref}, with a constant heats of oligomerisation (ΔH_2 or ΔH_6 as appropriate)
4. These oligomers are then taken (isobarically) to temperature T.

The effect of the above thermodynamic path is that the effective heats of oligomerisation, L_n (per oligomer mole) have the following temperature dependence:

$$L_n = \Delta H_n + n \cdot C_1 \cdot (T - T_{ref}) + C_n \cdot (T_{ref} - T) \qquad \text{with } n = 2, 6$$

where C_n are the specific heat capacities of the oligomers at constant pressure, with 1 denoting the monomer. Based on degrees of freedom considerations and the assumption that the oligomers behave as ideal gases these specific heat capacities are assumed to have values:

$$C_1 = 7R/2$$
$$C_2 = 13R/2$$
$$C_6 = 10R$$

where R is the universal molar gas constant.

This gives:

$$L_2 = \Delta H_2 + \frac{1}{2} \cdot R \cdot (T - T_{ref})$$
$$L_6 = \Delta H_6 + 11 \cdot R \cdot (T - T_{ref})$$

Clough, Grist and Wheatley [4] take T_{ref}=273K.

Minimum temperatures are obtained when mixing HF with dry air. For HF initially at 290K, minimum temperatures of approximately 260K may be obtained. At these temperatures the temperature dependence leads to slightly more negative heats of oligomerisation: a 0.1% change for dimerisation; 0.7% change for hexamerisation.

Maximum temperatures are obtained by mixing HF with moist air. For HF initially at 290K, maximum temperatures of around 300K may be obtained. This leads to slightly less negative heats of oligomerisation: a 0.3% change for dimerisation; a 1.4% change for hexamerisation.

The above changes in heats of oligomerisation are considered to be insignificant and the current DRIFT and EJECT values are considered equally appropriate.

13.2 ENTHALPY OF VAPORISATION FOR HF IN DRIFT AND EJECT

DRIFT and EJECT thermodynamic models are based upon the differential equilibrium model of Webber and Wren [8]. This model incorporates a term for the effective latent heat of vaporisation per HF mole. This effective heat of vaporisation, denoted $L(T)$, is defined by

$$L(T) \equiv \sum_k \left[c_k h'_k(T)\right] - h_{gL}(T)$$

where the index k= 1, 2, 6 represents the oligomer states, the coefficients, c_k are related to the mole fractions, x_k, of oligomers in the vapour phase

$$c_k \equiv \frac{kx_k}{\sum_k kx_k}$$

and $h'_k(T)$ are the oligomer enthalpies (per HF mole) and $h_{gL}(T)$ is the liquid enthalpy (per HF mole).

The term $L(T)$ is referred to as an effective molar heat of vaporisation since it corresponds to the change in enthalpy when one mole of HF liquid vaporises at temperature T. As well as being useful in thermodynamic modelling, it seems likely that $L(T)$, for a pure HF system at saturation, is also what is most naturally measured and quoted for HF latent heat of vaporisation.

Probably, with the above in mind, the implementations in DRIFT 2.25 and EJECT 2.05 use for $L(T)$ the SRD DATABANK [20] correlation for HF's latent heat of vaporisation. Unfortunately, this approach is no longer applicable once the system is dilute, i.e. includes vapour other than HF. The introduction of other vapour lowers the oligomer mole fractions, altering the c_k from those of the pure system and hence altering $L(T)$.

Solution Method A

Denoting the pure HF system values with superscript 0 we may write:

$$L(T) = L^0(T) + \sum_k \left(c_k - c_k^0(T)\right) h'_k(T)$$

where $L^0(T)$ may be represented by the correlation to measurements on the pure system.

The $h'_k(T)$ may be estimated from constant pressure specific heat capacities, C_k derived from the values given in Clough, Grist and Wheatley [4]. Taking the reference state to be monomer at a reference temperature T_{ref}, the oligomer enthalpies per HF mole are given by:

$$h'_k(T) = \left[C_k \cdot (T - T_{ref}) + \Delta H_k\right] / k$$

where ΔH_k is the enthalpy of oligomerisation at temperature T_{ref}.

The c_k are available from solution of the oligomer (phase) balance equations in equilibrium model. The $c_k^0(T)$ may be determined by solving for the oligomer composition of the pure HF system at temperature T and pressure, presumably the saturated vapour pressure, at which the correlation for $L^0(T)$ applies.

For a pure HF cloud the $c_k = c_k^0(T)$, hence $L(T) = L^0(T)$, as required. For a cloud sufficiently dilute such that HF is (almost) totally dissociated, the $c_k \approx 1$ and at T=298K the correction on the DATABANK [20] value of $L^0(T)$ = 7074 J/(mol HF) is calculated to be +23485 J/(mol HF), giving a value of $L(T)$ = 30559 J/(mol HF). This value compares favourably with of 30275 J/(mol HF) of Vanderzee and Rodenburg as reported in Schotte [3].

Solution Method B

The problem in applying the above correction method to the DATABANK correlation [20] is that it requires solving for oligomer equilibrium for both the dilute system at ambient pressure, and for the pure system at the saturated vapour pressure. This involves some slight extra computational expense, but more importantly using pressures significantly different from ambient pressure introduces additional uncertainty in the oligomer equilibrium coefficients. Therefore as an alternative to Solution Method A we implement the approach based on that used in ref.[4] which is described below.

A fixed value for the heat of vaporisation, L_{1b} (taken at the normal boiling point, T_b of HF) is used to calculate the latent heat of vaporisation as follows:

The enthalpy (per HF mole) of hydrogen fluoride vapour at temperature T, relative to HF monomer at temperature T_{ref} is given by

$$h_{vap} = \frac{y_{11}C_{p11}(T - T_{ref}) + y_{16}C_{p11}(T - T_{ref}) + \Delta H_2 + y_{16}C_{p11}(T - T_{ref}) + \Delta H_6}{y_{11} + 2y_{12} + 6y_{16}}$$

The enthalpy (per HF mole) of hydrogen fluoride liquid at temperature T, again relative to HF monomer vapour at temperature T_{ref} is given by

$$h_{liq} = C_{LHF}(T - T_b) - L_{1b} - C_{p11}(T_b - T_{ref})$$

The latent heat of vaporisation is then given by

$$L = h_{vap} - h_{liq}$$