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# METERED ATOMISATION FOR RESPIRATORY DRUG DELIVERY

by

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**A Doctoral Thesis** 

## Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University of Technology

1991

<sup>©</sup> by Andrew Reginald Clark

This thesis is dedicated to my wife and family, for without their support it would not have been possible.

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### **Statement of Originality**

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Except where otherwise indicated and acknowledged, the author is responsible for the practical and theoretical developments recorded in this thesis, and for any original contribution therein.

#### **SUMMARY**

An investigation into the factors affecting the metered atomisation of superheated liquids has been carried out. The investigation was aimed primarily at developing an understanding of the factors which affect the performance of respiratory drug delivery systems (Suspension Pressurised Metered Dose Inhalers).

Initial investigations used a semi-empirical sizing technique, representing the human airways, to identify the major variables (formulation and geometric) which affect the performance of the MDI system.

Computer models were developed to describe both continuous and metered discharge from a superheated-liquid aerosol generator. These models were based on the concept of thermal and dynamic equilibrium, but they were improved and extended, to describe metered discharge, by including empirical corrections obtained from continuous discharge experiments. Experimental investigations using 'instrumented inhalers' were used to confirm the validity of the computer model. The experimental investigations encompassed the use of conventional CFC's and the new non-chlorinated propellants 134A and 227.

The atomisation process was investigated by measuring the residual droplet diameters resulting from the atomisation of propellants containing nonvolatile solutes. A correlation relating the calculated initial median droplet diameter to atomiser conditions was developed.

$$d_i = \frac{C_5}{q_e^m \left\{ \frac{P_e - P_A}{P_A} \right\}^n}$$
 5.41

The form of this correlation strongly suggests that the droplet formation mechanism is aerodynamic shear between the vapour and liquid phases rather than rapid bubble growth or 'flashing' as has hitherto been postulated.

The computer models and droplet correlation function developed during these investigations represent powerful tools for use in the design of both current and future HFC/HFA powered metered dose inhaler delivery systems.

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### **UPPER CASE**

Α	Orifice area [m <sup>2</sup> ]
С	Bubble growth rate [ms <sup>-1</sup> ]
Cg	Specific heat capacity of vapour [Jkg <sup>-1</sup> ]
C <sub>l</sub>	Specific heat capacity of liquid [Jkg <sup>-1</sup> ]
Cq	Orifice discharge coefficient
C <sub>p</sub>	Specific heat capacity at constant pressure [Jkg <sup>-1</sup> K <sup>-1</sup> ]
Cu	Cunnigham slip correction factor
С	Constant used in exit momentum velocity equation
C <sub>1</sub>	Clapeyron constant
<b>C</b> <sub>2</sub>	Clapeyron constant
<b>C</b> <sub>3</sub>	Constant relating pressure to droplet size
<b>C</b> <sub>4</sub>	Constant relating quality of flow to droplet size (Lefebvre, 1980)
C <sub>5</sub>	Constant relating pressure and quality to droplet size
C <sub>6</sub>	Velocity constant
<b>C</b> <sub>7</sub>	Deposition constant
D	Orifice diameter [m]
D <sub>e</sub>	Expansion chamber diameter (valve stem) [m]
D <sub>w</sub>	Impinger jet diameter [m]
Ε	Specific enthalpy [Jkg <sup>-1</sup> ]
E <sub>1cm,1%</sub>	UV absorbance constant relating absorbance to solution concentration
H	Enthalpy [J]
J	Exit momentum from spray orifice [kgms <sup>-1</sup> ]
L	Latent Heat of vaporisation [Jkg <sup>-1</sup> ]
L <sub>B</sub>	Jet break-up length [m]
Μ	Mass of propellant [kg]
N <sub>e</sub>	Euler number
No	Ohnesorge number
N <sub>re</sub>	Reynolds number
N <sub>st</sub>	Stokes number
Nw	Weber number
Р	Pressure [Pa]
P <sub>c</sub>	Pressure downstream of a discharge orifice [Pa]
P <sub>s</sub>	Initial saturation pressure upstream of an orifice [Pa]
Q	Heat flow [Js <sup>-1</sup> ]
R	Universal gas constant
R <sub>b</sub>	Bubble radius [m]
n -	[]
KS	Radius of expanding spray plume [m]

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#### UPPER CASE continued

Т	Temperature [K]
T <sub>B</sub>	Propellant boiling point at NTP
Tr	Thrust at radius r from spray axis [Nm <sup>-2</sup> ]
Ts	Shatter temperature [K]
V	Jet velocity [ms <sup>-1</sup> ]
Vol	Volume of chamber [m <sup>3</sup> ]
W	Orifice Length [m]

### LOWER CASE

d	Droplet, or particle, diameter [m]
d <sub>50</sub>	50% cut off diameter for inertial impactor [m]
k	Thermal conductivity [Js <sup>-1</sup> m <sup>-2</sup> K <sup>-1</sup> ]
m	Mass discharge rate [kgs <sup>-1</sup> ]
q	Mass fraction in vapour phase
q´	Pseudo propellant vapour mass fraction
r	Radial distance from axis of expanding spray plume [m]
r <sub>c</sub>	Critical pressure ratio
t	Time [s]
t <sub>di</sub>	Idle, or dwell, time for bubble nucleation [s]
t <sub>d2</sub>	Bubble growth time [s]
v	Volume of vapour phase
w	Fraction by weight of surfactant in propellant formulation

x Distance from spray orifice [m]

#### **SUBSCRIPTS**

air	Air
c	Chamber or can
cr	Critical or choked conditions
e	Expansion chamber
i	Initial conditions
1	Liquid
g	Vapour
m	Metering chamber
р	Peak conditions during a metered discharge

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### SUBSCRIPTS continued

- r Residual conditions
- s Spray orifice
- ss Choked or sonic velocity
- T Temperature
- v Valve orifice
- x Distance from spray orifice

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### SUPERSCRIPTS

m	Constant relating quality of flow to droplet size
n	Constant relating pressure to droplet size
-	Mean or average value
	First derivative with respect to time

/ Including the partial pressure of air

### GREEK

α	Void fraction
α <sub>k</sub>	Thermal diffusivity [m <sup>2</sup> s <sup>-1</sup> ]
α <sub>me</sub>	Empirical metastability correction constant (pressure)
β <sub>me</sub>	Empirical metastability correction constant (pressure)
γ	Ratio of specific heats of vapour phase
Υ <sub>me</sub>	Empirical metastability correction constant (temperature)
δ <sub>me</sub>	Empirical metastability correction constant (temperature)
θ	Half angle of expanding spray plume
κ	x.tan θ
<b>ک</b>	Evaporation rate, rate constant
ν	Kinematic Viscosity [m <sup>2</sup> s <sup>-1</sup> ]
ρ	Density [kgm <sup>-3</sup> ]
ρ´	Pseudo propellant vapour density [kgm <sup>-3</sup> ]
σ	Surface tension [Nm <sup>-2</sup> ]
x	Average molecular weight [kg]
φ	Factor relating initial to final droplet diameter
ψ	Inertial impaction parameter
ω	Bubble growth rate depression ratio

#### **PROPELLANT NUMBERS**

The propellant numbering system used throughout this thesis follows the currently accepted standard and is based on the molecular structure of the compound. The rules for determining a propellant number from its molecular structure, or vice versa, are as follows:-

1. The first number is the number of carbon atoms minus 1 (zero not shown).

- 2. The second number is the number of hydrogens plus 1.
- 3. The third number is the number of fluorines.
- 4. The forth number makes up to valency with chlorine.
- 5. Suffixes are used for asymmetry.
- 6. Cyclocompounds are prefixed with C.

#### FIGURE 2.1

Figure 2.1 is an extract from an article by Lefebvre (1980). Because of the complex nature of the abstract the notation has not been changed from that of the original article. In most cases the meaning of the symbols is self evident, however where doubt exists the original article should be consulted.

#### **APPENDIX I to VII**

The notation used in the appendices may differ slightly from the main text. However, any notation used is defined in each specific Appendix.

#### **COMPOUND NUMBERS**

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The numbers used throughout this thesis to donate pharmaceutical chemicals are the same as those to found in Chemical Abstracts. The prefix FPL donates Fisons Pharmaceuticals. The 5 digit number is unique, and refers to a specific chemical compound.

### **1. INTRODUCTION**

Superheated liquids, sometimes referred to as liquefied gases, have been used as a power source for domestic and medical aerosol sprays for over 4 decades. The products they have been used in range from insecticides and household air fresheners, to cosmetics and inhalation aerosol sprays. However, all of these systems have their roots in the work of Helbing and Pertch (1899) who in 1899 described the first aerosol generator to be driven by the vapour pressure of a propellant liquid. They used methyl or ethyl chloride as the propellant liquid and the heat of the hand caused enough pressure to develop to atomize the liquid via a small orifice. Some 2 years later Gebauer (1901) discovered that partial vaporization of the propellant liquid before final atomisation at the spray nozzle produced a finer spray and, in a US patent in 1901, he described the use of the first twin orifice 'expansion' chamber. In the early 1930's Rotheim (1931 & 1933) described the use of dimethyl ether and a twin nozzle expansion chamber to produce fine sprays of soaps, resins and lacquers. It was however, not until the refrigerant chlorofluorocarbon liquids such as propellants 12, 114, 11 and 22, were discovered in the 1930's and 40's that aerosol generation using 'liquefied gases' became a real and practical proposition. The first liquefied gas aerosols were developed during the second world war for spraying insecticides. These early, rather crude 'aerosols', were then developed during the late 1940's and finally lead to household insecticide sprays and the great boom in household aerosol products.

In the late 1950's pharmaceutical molecules were combined with chlorofluorocarbon aerosol technology to produce a metered aerosol system for facilitating topical application to the lung (Meshberg, 1956). The pressurized metered dose inhaler, as it is now known, delivers a metered volume of an aerosol propellant suspension, or solution, with each metered 'dose' containing a pre-determined quantity of active drug substance.

Because of their ease of use, simplicity of operation and undoubted efficacy, pressurized metered dose inhalers have now become <u>the</u> most popular form of respiratory therapy.

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However, in 1974 Molina & Rowland (1974) pointed out the danger chlorofluorocarbons presented to the earths protective ozone layer and, since that time, growing environmental pressure has resulted in the phased withdrawal of chlorofluorocarbon manufacture (Montreal Protocol, 1979).

Since it was realized that damage to the ozone layer was actually occurring (Lockerby, 1989) the development of a number of alternative non-chlorinated propellant liquids was accelerated. These liquids, mainly hydrofluorocarbons (HFC) or hydrofluoroalkanes (HFA) such as propellant 134A and propellant 227, are now under assessment for use in pressurized metered dose inhalers and may represent the only way that this valued and useful medicinal product may continue to be used.

The pressurised metered dose inhaler consists of three major components; a suspension reservoir, containing raw drug suspended in liquefied propellant gas; a metering valve, which when depressed dispenses a known quantity of the reservoir suspension; and a spray actuator which when combined with the stem of the metering valve comprises and expansion chamber and spray nozzle. **Figure 1.1** illustrates the major components of a typical inhaler and presents schematic diagrams of various metering valve designs.

In the rest position the metering chamber of the valve is connected directly to the suspension reservoir. On depression of the valve stem this connection is closed and the metered discharge process begins. The metered dose is ejected from the metering chamber under the pressure of the flashing liquid propellant.

The two phase (solution system), or three phase (suspension system), mixture then passes through the valve stem orifice into the actuator/valve stem expansion chamber. Inside the valve stem the mixture then undergoes 'expansion' before final discharge through the downstream spray orifice.

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It is still unclear whether the emergent spray then experiences break-up due to flash evaporation or whether it breaks-up a in manner similar to conventional airblast atomisation. (The term 'flash evaporation' refers to a process where rapid growth of vapour bubbles, or boiling, disrupts the spray. The term 'airblast' refers to the aerodynamic break-up of spray ligaments). In either case the emergent spray then entrains air and, as momentum transfer takes place, deceleration occurs. During this deceleration phase droplet evaporation also takes place.

Despite what appears to be a detailed description of the metering and atomisation process, and 20 years of use, the non-equilibrium thermodynamics and the atomisation process, or processes, involved in the final spray formation are still not understood on a quantitative basis. Indeed, conflicting views still exist as to the importance of flash atomisation downstream of the final spray orifice. For example Fletcher (1975) states that 'flashing' does not occur, whereas Sher and Elata (1977), used a theoretical model based upon the flashing process to predict droplet size distributions. Also, to date no work has been reported on the thermodynamics of the metered discharge process.

Thus, despite many years of use, and development, very little quantitative fundamental scientific data detailing the factors affecting the performance of metered dose inhalers has been reported. In recent years the growing understanding of the dynamics of lung deposition together with and understanding of the sites of action of drugs within the lung, has lead to a requirement for better design of inhalation dosage forms. With the added incentive of the necessary introduction of new propellants, it is opportune to investigate and elucidate the important factors and mechanisms involved in 'Metered Atomisation for Respiratory Drug Delivery'. The main aim of the work was to put metered dose inhaler design on sound scientific footing and thus, hopefully, to improve drug delivery from this form of 'inhaler'.

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In order to carry out this investigation it was apparent that the important factors affecting the performance of metered dose inhalers needed to be identified early in the work program, and that the quasi-equilibrium continuous spray process needed to be understood on a more quantitative basis before the metering process could be studied. This thesis therefore contains three major phases of work.

The first phase, section 4, identifies the major variables affecting the performance of metered dose inhaler systems and quantifies the magnitude of their effect using an empirically designed impaction apparatus. The effects of formulation variables and hardware design are both discussed in detail.

The second phase, section 5, uses more fundamental techniques, including the measurement of thermodynamic variables, to assess the importance of thermodynamic and geometric variables on the continuous discharge and atomisation process. A computer model describing the continuous discharge process is presented and the mechanisms by which this type of aerosol generator operate are discussed. A correlation relating the droplet size generated by the atomiser to the quality of flow and differential pressure across the spray orifice is also presented.

The final phase of the work, section 6, then goes on to extend the computer model to describe the metered discharge process and to confirm that the atomisation mechanisms are the same as those for continuous flow.

Section 7 presents a discussion of the results. A proposed droplet correlation function and the computer model's predictions are used to explain the effects noted in section 4 and to develop a quantitative measure of metered dose inhaler performance that should be relevant to the clinical use of this type of aerosol generator.

In prelude to the work reported in sections 4 to 7, section 2 presents a detailed literature survey and section 3 a project justification.

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### 2. **LITERATURE SURVEY**

### 2.1 **INTRODUCTION**

### 2.2 **ATOMISATION**

- 2.2.1 ATOMISATION OF SUPERHEATED LIQUIDS
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### 2. <u>LITERATURE SURVEY</u>

### 2.1 INTRODUCTION

It is clear, from the broad description of the metering process presented in section 1, that the understanding of metered spray discharge requires a multi-disciplinary approach. As a consequence the literature survey must cover a number of subject areas. The two main areas of direct relevance are liquid atomisation and two-phase gas/liquid flow.

Considering the atomisation literature first, the obvious area of direct relevance is that of superheated liquid atomisation in both single orifice (monofilament), and twin-orifice form. Also, since rapid bubble growth, usually referred to as 'flashing', is believed to be one of the major mechanisms involved in the formation of sprays from superheated liquids, the literature on bubble growth in superheated fluids must be considered. The 'airblast' atomisation literature must also be considered since gas/liquid atomisation bears an important physical resemblance to the conditions prevailing in the spray nozzle of a metered atomiser. Finally, the papers detailing with the many empirical studies involving aspects of aerosol formulation will also be considered.

Because of its importance to nuclear engineering, and safety assessment in the nuclear industry, the amount of literature available on two-phase gas/liquid flow is extensive. The literature discussed below will therefore be restricted to those areas of direct relevance to the present study. That is, two-phase gas/liquid flow and two-phase superheated liquid flow through nozzles and orifices.

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### 2.2 **ATOMISATION**

#### 2.2.1 ATOMISATION OF SUPERHEATED LIQUIDS

The atomisation of superheated liquids may conveniently be divided into two areas studies, usually empirical in nature, of capillary or two-orifice nozzle assemblies, and studies of monofilament (single orifice) systems. Figure 2.1 illustrates the important features of each type of atomiser. The latter category, monofilament atomisation, is easier to study both experimentally and theoretically and will be considered first.

#### 2.2.1.1 Monofilament Superheated Sprays

The first group to carry out detailed studies upon monofilament superheated sprays was lead by Professor York at Michigan University and resulted in 3 PhD dissertations and a published paper.

Brown and York (1962) studied the atomisation of water and, separately, propellant 11. Each fluid was held in superheated state and from double flash photographs of the emergent spray they concluded that atomisation was caused by cavitation and bubble growth within the superheated jet. They also concluded that atomisation was influenced by aerodynamic forces acting upon the jet. A correlation was obtained for water which related the number median diameter  $(d_n)$  of the spray to Weber number  $(N_w)$ .

$$d_n = \frac{1597 - 10.9T}{N_W}$$
 2.1

Lack of data prevented a similar correlation being developed for propellant 11.



Single Orifice or Monofilament







Figure 2.1 The Major Types of Liquefied Gas Atomiser

Short (1963) continued the work of Brown and studied the atomisation of water, propellant 11 and propellant 113. Final nozzle diameters of 0.38 to 1.65 millimetres were investigated. The break-up of the superheated jets was characterized by a 'shatter temperature' which was defined as "the minimum degree of superheat required in order to ensure disintegration at the nozzle exit".

A general shatter temperature correlation was developed which adequately fitted the data for all the fluids tested and related a dimensionless shatter temperature group to the Weber number, the Ohnesorge number  $(N_0)$ and the liquid/vapour density ratio  $(\rho_l/\rho_g)$ . (The Ohnesorge number is defined as the quotient of the fluid viscosity and the square root of the product of the density, the surface tension and the jet diameter).

$$\frac{T_{s}k}{v.L} = 0.344 N_W^{-0.23} N_O^{-0.27} \left(\frac{\rho_l}{\rho_g}\right)^{0.139} 2.2$$

Where  $T_s$  is the shatter temperature, k is the thermal conductivity, v is the liquid viscosity and L is the latent heat of vaporisation.

Short also studied the evaporation kinetics of the droplets within the resulting spray plume.

Ostrowiski (1966) completed the investigations at Michigan and continued the work of his predecessor by studying the evaporation and induced airflow in sprays formed from superheated water jets. He also investigated the effects of nozzle surface roughness upon the break-up mechanism. He concluded that shatter temperature decreased as nozzle roughness increased. A new correlation involving Euler number  $(N_e)$ , Weber number and Ohnesorge number was developed.

$$\frac{T_{S} - T_{B}}{T_{S}} \left(\frac{1}{N_{e}}\right) = 4.6 \times 10^{4} N_{O}^{2} N_{W} - 0.15$$
 2.3

Where  $T_s$  is the shatter temperature,  $T_B$  is the fluid's normal boiling point and the Euler number is the ratio of the pressure forces within the jet to the inertial forces acting upon the jet. Lienhard and Day (1970) studied the break-up length ( $L_B$ ), and hence the delay time between emergence from the nozzle and spray disintegration, of ambient and superheated water jets using short pulse flash photography. At high Reynolds numbers (aerodynamic region) break-up lengths for ambient jets were shown to be related to both Weber number and Reynolds number ( $N_{Re}$ ).

$$L_B = 2.75 \times 10^{10} D \sqrt{\frac{N_W}{N_{Re}^2}}$$
 2.4

Where D is the jet diameter. At values of  $N_{Re}$  below 48,000 (capillary region), jet break-up length was shown to be related to  $N_{Re}$  only.

For superheated sprays break-up time (break-up length divided by jet velocity) was shown to be the sum of the idle time  $(t_{d1})$  for bubble nucleation and the growth time  $(t_{d2})$  needed for the bubble to grow large enough (usually defined as twice the diameter of the jet) to disrupt the jet.  $t_{d2}$  is defined as the bubble growth rate constant (see section 2.2.1.3) and  $t_{d1}$  is shown to be a stochastic variable of the form:-

$$t_{dI} = \frac{1}{4(t_{d\bar{l}})} \cdot \frac{27}{2} \left(\frac{t_{dl}}{t_{d\bar{l}}}\right)^2 \cdot \exp\left(\frac{-3 t_{d\bar{l}}}{t_{d\bar{l}}}\right)$$
 2.5

Where  $t_{\overline{dT}}$  is the mean idle time.

Lienhard also developed an expression for the maximum break-up length. If heat conduction from the jet is rapid enough to eliminate the superheat in a time shorter than  $t_{d1} + t_{d2}$  then bubble growth cannot disrupt the jet. This maximum break-up length is given by:-

$$L_{\max} = 0.0205 \cdot \frac{VD^2}{\alpha_k}$$
 2.6

Where  $\alpha_k$  is the thermal diffusivity of the fluid and V is the jet velocity.

Suzuki *et al* (1978) also carried out photographic studies of the atomisation of superheated water and developed a similar expression for break-up length to that of Lienhard. However, the bubble growth rate constant used to define  $t_{d2}$  was shown to underestimate bubble growth times. Their

experimental values for bubble growth rate were shown to be proportional to the square of the theoretical growth rate constant. (Bubble growth rates will be discussed in more detail below).

Sher and Elata (1977) studied sprays formed from pressure cans and thus strictly speaking their work was not carried out on monofilament jets. However, because they ignored pre-flashing within the aerosol valve (they mistakenly considered it to be unimportant) and used a bubble growth model to predict the aerosol size distribution, it will be discussed here.

A rather complex expression for the median diameter of an aerosol produced by the flashing process was developed with the aid of the bubble growth rate constant, an empirical efficiency factor and a number representing the number of bubble nuclei per unit volume of liquid. They carried out droplet size measurements using a 'shuttered spray sampling system' designed to ensure the capture of an optimum number of droplets upon a slide coated in magnesium oxide. Their results showed that mass median droplet size was dependant upon propellant temperature and pressure but was independent of spray orifice diameter.

Initially they showed their theoretical expression for the median diameter to be inadequate but, by applying a correction to the bubble growth rate constant in line with that of Suzuki *et al* (1978) and Hooper and Abdelmessih (1966) they were able to show reasonable agreement with the theoretically predicted values.

Not surprisingly bubble growth rate features heavily in all the experimental and theoretical work associated with the flash atomisation of superheated sprays. Published work in this area will be discussed below (section 2.2.1.3).

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#### 2.2.1.2 Capillary Tube and Twin-Orifice Sprays

Fulton *et al* (1950) studied the atomisation of a mixture of 43% propellant 11, 43% propellant 12 and 14% insecticide through both capillary tubes and twin-orifice nozzles. Size analysis of the residual aerosol was used to investigate the performance of capillary tubes of different diameters. A range of capillary diameters from 0.34 mm to 0.74 mm was found to produce the minimum MMD of approximately 16  $\mu$ m. For twin-orifice systems an expansion chamber volume of 0.13 cm<sup>3</sup> and upstream and downstream orifice diameters of 0.38 mm and 0.53 mm respectively, were found to produce the optimum spray. The killing rate of the house fly (*Musca domestica*) was the method used to define the optimum spray production.

York (1956) reviewed the literature on liquefied gas aerosol generators and divided the atomisation process into four stages:-

- 1. Primary atomisation due to flashing.
- 2. Secondary atomisation of droplets from stage 1 due to aerodynamic forces during impact with the atmosphere.
- 3. Evaporation of the propellant droplets.
- 4. Entrainment and deceleration of the spray.

It was concluded that existing literature covered stages 2 to 4 but that no experimental work of a fundamental nature had been reported on stage 1. This was the driving force for the investigations at Michigan University reported above.

Lefebvre and Tregan (1964) investigated some of the factors affecting the size distribution of kerosene propellant mixtures. Aerosols generated from mixtures of propellants 11 and 12 were sized using a sedimentation chamber and glass slides coated in magnesium oxide. Flash photography was used to aid the qualitative study of the atomisation process. The investigations were of an observational nature and no attempt was made to relate aerosol properties to fundamental parameters. Four variables were studied:-

- 1. Temperature of the kerosene mixture (15°C to 35°C).
- 2. Propellant/kerosene ratio (60% to 80%).
- 3. Percentage of propellant 12 in the propellant mixture (30% to 70%).
- 4. Different nozzles (four).

Figure 2.2 presents their results. It can be seen that the spray becomes finer as propellant temperature is increased, as the percentage of propellant is increased and as the fraction of propellant 12 in the propellant mixture is increased. An increase in all these variables brings about an increase in the vapour pressure of the atomized solution and hence provides additional energy for the atomisation process. No attempt was made to analyze the data in terms of vapour pressures or available energies. Nozzle design was also shown to dramatically affect the size distribution of the aerosol.

Teslin (1969) measured the size distribution of kerosene and oil aerosols generated by continuous sprays. A sedimentation chamber was used to collect the residual droplets on glass slides coated with dimethylchloride and MMD's were determined by optical microscopy. It was found that increasing solution vapour pressure by increasing the percentage of propellant, or increasing solution temperature, produced a finer cloud. These observations are in line with those of Lefebvre and Tregan. Teslin used calculations based upon ideal gases to relate spray properties to 'Specific work of expansion'. He concluded that "specific work of vapour expansion was a quantitative characteristic that causes dispersion by a superheated liquid to be different from that of other spray processes."

Fletcher (1975) studied continuous atomisation from a twin-orifice system. Atomisation of a mixture of 39.6% propellant 11, 59.4% propellant 12 and 1% surfactant (sorbitan trioleate) was investigated using a double flash photographic technique.

Droplet size and velocity at the exit of the twin-orifice system were assessed by measurements made upon enlarged photographic plates. Upstream and downstream nozzle diameters ranging from 0.25 mm to 0.7 mm were

# The influence of propellant composition upon droplet size.

The influence of temperature upon droplet size.





The influence of propellant concentration upon droplet size.



Figure 2.2. The Influence of Propellant, Composition, Concentration and Temperature upon the Droplet Size Produced from Aerosols containing Kerosene and Freon Propellants (Lefebvre & Tregan, 1964)
investigated. Expansion chamber volume (see fig 2.1) and formulation variables were not studied. Fletcher concluded that the mass flowrate, or delivery rate, in such a system was proportional to the product of the upstream and downstream orifice diameters and that the quality of the propellant (mass fraction evaporated in the expansion chamber) could be predicted from geometric and thermodynamic variables. An empirical expression was also developed showing that the MMD of the residual surfactant aerosol generated from a twin-orifice assembly, where the upstream and downstream orifice were of nominally similar diameter, was proportional to the spray orifice diameter. It was argued that these relationships, although developed for continuous sprays, were generally applicable to metered systems.

Atomisation was described in terms of the break-up of propellant ligaments, formed as the vapour liquid mixture generated in the expansion chamber, accelerated through the spray (downstream) orifice. It was claimed that "flashing" did not take place outside the final spray orifice. However, this view is difficult to reconcile with the fact that a pressure term representing metastability (non-thermal equilibrium) was needed in the formulation of the mass flow equations for the expansion chamber. (Metastability is a measure of the variance between the superheated and measured vapour pressure and, as such it represents available energy within the propellant which is not utilized in the expansion chamber). However, metastability notwithstanding, the process as described by Fletcher bears more resemblance to airblast, or aerated, atomisation than to monofilament superheated sprays.

Oza (1984) used short pulse flash photography to study the mechanisms of flash atomisation in subcooled fuels. His investigations were mainly qualitative in nature and covered the atomisation of propane, methanol and indolene under different injection/ambient pressure ratios. Two atomisation regimes were identified. The first, was believed to be associated with bubble growth, or expansion, within the injector nozzle. The second, at higher pressure ratios, was associated with external expansion. It is believed that this external expansion was due to 'flashing', or flash boiling, of the atomizing fluid. If Oza's interpretation is correct 'flash atomisation' would, in this case, play an important role in the atomisation process.

However, it is interesting to note here that Fletcher also observed a rapid external expansion of the two-phase jet during his studies of twin nozzle systems. Fletcher attributed this rapid expansion to choking flow within the final spray nozzle. Indeed, he took its very existence to be confirmation of the choking phenomena. Of course either explanation may be correct. That is, Oza may have been observing a choking phenomena or, Fletcher may have been observing 'flash atomisation' downstream of the final spray orifice.

Soloman *et al* (1982) studied the performance of flashing fuel injectors utilizing either liquids containing dissolved gases (jet A/air) or, superheated propellants (propellant 11). Photography was used to qualitatively study both spray formation and spray angles as well as combustion properties.

A Malvern laser diffraction size analyzer was used to measure the droplet size of the generated sprays. Both local homogeneous and separated flow models provided good predictions for mass flowrates. Using the separated flow model to calculate atomizer exit conditions, conventional airblast atomisation correlation functions, relating droplet sizes to atomizer conditions, were shown to successfully describe droplet data for aerated jet A fuel delivered with a pre-flashing atomizer. Similar data for propellant 11 was not reported.

The successful use of conventional correlations to describe the droplet sizes produced from per-flash atomisation of jet A/air mixtures is perhaps not too surprising since the air/liquid mixture ejected from the final orifice is identical to a similar mixture produced by a conventional airblast atomizer, with the exception that the fuel may still contain some dissolved gas. However, bubble growth rate constants are usually low for dissolved gas and consequently spray disruption is unlikely to be due to processes other than those associated with airblast atomisation.

#### 2.2.1.3 Bubble Growth in Superheated Fluids

Section 2.2.1.1 described the break-up of monofilament superheated jets in terms of bubble formation and growth within the jet filament. Many authors used models based on bubble growth rates to calculate break-up lengths and droplet size. Literature on bubble growth in superheated fluids will now be discussed.

Rayleigh (1879) was the first to formalize the problem of bubble growth (or collapse) within a fluid. He considered the growth of a bubble in an inviscid, incompressible fluid and developed a differential equation describing the change in radius ( $\mathbf{R}_{b}$ ) as a function of time.

$$R_{b}\frac{d^{2}R_{b}}{dt^{2}} + \frac{3}{2}\left(\frac{dR_{b}}{dt}\right)^{2} = \frac{\left[P_{(R_{b})} - P_{o}\right]}{\rho_{l}}$$
 2.7

Where  $\rho_1$  is the liquid density,  $\mathbf{P}_o$  is the external pressure in the liquid or pressure at infinity and  $\mathbf{P}_{(Rb)}$  is the pressure in the liquid at the bubble boundary.

Poritsky (1952) extended Rayleigh's model to cover bubble growth in a viscous, incompressible fluid. However, Poritsky's equation was not tractable by analytical techniques and numerical and graphical solutions had to be used.

Plesset and Zwick (1954) obtained a general solution to Rayleigh's equation for bubble growth in superheated liquids. They replaced  $P_{(R)}$  by taking into account the surface tension ( $\sigma$ ) forces and equilibrium vapour pressure at the bubble boundary.

$$P_{(R_b)} = P_{V_{(T)}} - \frac{2\sigma}{R_b}$$
 2.8

They then assumed that the rate of bubble growth was limited by the need for energy transport to the bubble surface, to supply the latent heat of vaporisation needed to ensure vapour was available to fill the expanding bubble cavity. The rate of heat transport to the bubble surface  $(\mathbf{Q})$  is given by :-

$$\dot{Q} = 4\pi R_b^2 k \left(\frac{\partial T}{\partial r}\right)_{R_b}$$
 2.9

Where  $\mathbf{k}$  is the thermal conductivity of the liquid.

They considered two regions of bubble growth. The first was the initial growth, when the bubble radius had not departed markedly from its initial value. The second was when the bubble radius was much larger than the initial value. They concluded that a small bubble would remain at rest, in an unstable state, until acted upon by a perturbing force. Once the bubble began to grow its initial growth would be exponential in nature until the bubble surface cooled sufficiently for heat conduction to the surface to became the controlling factor. Under these conditions (bubble radius much larger than the initial radius) they developed an asymptotic solution which showed that bubble growth was proportional to the square root of the growth time. The constant of proportionality was defined as the bubble growth rate constant.

$$C = 2\sqrt{\frac{3}{\pi}} \alpha_k \frac{\rho_l}{\rho_g} \frac{C_P}{L} \Delta T \qquad 2.10$$

Where  $\alpha_k$  is the thermal diffusivity, L is the latent heat of vaporisation, C<sub>P</sub> is the specific heat capacity of the vapour at constant pressure and  $\rho_1$  and  $\rho_g$ are the liquid and vapour densities respectively.

The limitation of Plesset and Zwick's analysis is that they assumed a small degree of superheat and hence used a linear function to relate vapour pressure to temperature. At high levels of superheat this assumption is obviously invalid.

Foster and Zuber (1954) also developed a variant of Rayleigh's equation for a superheated fluid where bubble growth was limited by thermal conduction through the fluid. In this case the Clausius-Clapeyron equation was used to relate vapour pressure to bubble temperature. Their model also predicted that bubble growth was proportional to the square root of growth time and an inequality defining a lower limit for this growth region was obtained.

$$t > \left(\frac{R_{bi}}{C}\right)^2$$
 2.11

Where  $\mathbf{R}_{bi}$  is the "initial" growth radius.

Hooper and Abdelmessih (1966) constructed an apparatus which allowed the bubble growth rate within superheated water to be investigated. Their apparatus consisted of a compression chamber, which could be decompressed rapidly, and a high speed camera attached to a microscope objective. The Fastax camera was operated at 15,000 frames per second and bubble growth rates were determined by linear measurements made on the resultant films. Superheats from a few degrees to 55°C were investigated. The equations of Plesset and Zwick, and Foster and Zuber predict that bubble growth rate is linearly related to superheat. Hooper and Abdelmessih's data showed that this linear relationship only held when the degree of superheat was small. As superheat was increased bubble growth became progressively slower than the predicted value. This reduction in growth rate with increasing superheat was tentatively attributed "to the bubble vapour pressure equilibrium assumption" implicit in the analytical models.

Hooper and Abdelmessih also identified a "small, but always present" delay between pressure release and initial bubble growth. This delay period is now known as the idle time.

Abdelmessih (1969) reformulated the equations of Plesset and Zwick to include an empirical constant,  $\omega$ , the depression ratio, which was in itself a function of superheat. The depression ratio is defined as the ratio of the measured growth rate to the theoretical growth rate.

$$R_b = \omega 2 \sqrt{\alpha_k} \frac{\rho_l}{\rho_g} \frac{C_P}{L} t^{1/2} \Delta T \qquad 2.12$$

Using previously published data, Abdelmessih developed a correlation between the degree of superheat and the depression ratio. He showed that a polynomial of the second degree adequately fitted the experimental data.

When studying the atomisation of superheated monofilament sprays Suzuki *et al* (1978) confirmed the relationship of Abdelmessih (1969) for sprays emerging into normal atmospheric pressure. However, they challenged the validity of the expression for sprays emerging into a vacuum, showing that a plot of depression ratio versus theoretical growth constant produced a better correlation than that originally proposed. An extract from their paper is shown in **figure 2.3**. The depression ratio as measured by Abdelmessih and Hooper, for water, Sher and Elata, for freon 22, and Suzuki, for water emerging into atmospheric pressure and a vacuum, are shown plotted against superheat, **figure 2.3a**, and theoretical growth coefficient, **figure 2.3b**.

#### 2.2.2 Air Blast Atomisation

Because of its importance to combustion science, airblast atomisation has been studied extensively over the past few decades. The first major study of Nukiyawa and Tanasawa (1939) was conducted over 50 years ago and since then numerous experimental investigations have been reported. These studies initially concerned plain-jet atomisers and later covered the so called prefilming atomisers. Plain-jet atomisation consists of ejecting a gas and liquid phase mixture from a spray nozzle, or throat. As such, it bears an important resemblance to the final stage in the atomisation of superheated sprays through a twin-orifice system, where the gas is essentially propellant vapour and the liquid is the drug suspension. In a prefilming atomiser, the liquid is spread into a thin sheet before exposure to the high velocity gas stream. Prefilming atomisation bears little or no resemblance to the atomisation of superheated sprays through twin-orifice system and will not be discussed here. Lefebvre (1980) has presented an excellent review covering all aspects of airblast atomisation.





Nukiyawa and Tanasawa (1939) investigated the drop size produced from atomisation of gasoline, water, oil and solutions of glycerine and alcohol. Drop size was measured by capture upon oil-coated glass slides. An empirical correlation relating the Sauter mean diameter  $(d_{3,2})$  to fluid parameters and atomiser conditions was developed. Primary variables were found to be the relative velocity between the air and liquid, solution viscosity, surface tension and density and the ratio of air to liquid mass flowrate. Higher mass fractions of air produced finer droplets.

Nukiyawa and Tanasawa also investigated the influence of nozzle size and shape upon droplet size and concluded that these factors have virtually no effect on mean drop size. It is also interesting to note that their correlation was dimensionally correct and did not contain a term involving the density of gas phase (air).

Lewis *et al* (1948) studied nozzles with throat diameters ranging from 0.27 cm to 8.48 cm and investigated the influence of air/liquid mass ratio upon mean droplet size. By using helium, nitrogen and ethylene they were also able to study the influence of gas density. They concluded that when the gas density was reduced by one-seventh the mean droplet size of diesel-oil sprays increased by a factor of two. However, because of the poor counting statistics in their experiments, (typically they counted only 300 droplets) their conclusions must be a little suspect.

Anson (1953) and Golitzine *et al* (1961) atomised water with air and observed an inverse relationship between air/liquid mass ratio and mean drop size. Anson covered mass ratios ranging from 20 to 30, Golitzine investigated the range 1.5 to 10.

Radcliffe and Clare (1953) used molten wax, heated to different temperatures, to study the effect of liquid viscosity. They also studied the influence of air/liquid mass ratio and the effects of orifice diameter. They concluded that orifice diameter had little effect upon atomiser performance and that the main determinant of droplet size was air/liquid mass ratio. An inverse relationship between air/liquid mass ratio and droplet size was observed. Weiss and Worsham (1959) investigated both cross current and co-stream atomisation covering a range of orifice diameters, injector velocities and air densities. Based upon the assumption that the drop size distribution was related to "excitable wavelengths" upon the liquid surface they developed a correlation relating the Sauter median diameter to liquid velocity, gas density, relative air/liquid velocity and liquid viscosity. Their correlation again showed an inverse relationship between air/liquid mass ratio and droplet size and confirmed, over a limited range, that reducing the gas phase density increased droplet size. Their experimental data broadly agreed with the theoretical correlation, but predicted slightly different indices for the fluid properties.

Gretzinger and Marshall (1961) investigated the drop size distribution generated from a 'converging' nozzle of the type used by Nukiyama and Tanasawa and an 'impingement' nozzle. The latter nozzle consisted of a central air jet surrounded by an annular liquid jet. Separate correlations were developed for each type of nozzle.

The results of this investigation generally confirm previous findings, showing that air/liquid mass ratio, air velocity and air density are important factors determining the efficiency of the atomisation process.

Kim and Marshall (1971) used a novel and versatile nozzle design to study both plain-jet atomisation and a form of prefilming atomisation. Drop size measurements were carried out upon molten wax over a wide range of viscosities, relative air velocities and air/liquid mass ratio. As with the work of Gretzinger and Marshall, separate correlations were developed for each nozzle system.

It was concluded from the investigations that the important variables in airblast atomisation are the air/liquid mass ratio and the dynamic force  $(V_R^2 \cdot \rho_g)$ . Increasing either of these increases atomisation efficiency.

Many other studies on airblast atomisation have been carried out. **Table 2.1** is an extract from an excellent review conducted by Lefebvre (1980) and summarises the droplet correlation equations developed in a number of important studies, together with the range of variables studied. These equations all confirm the importance of factors identified above.

Recently, Lefebvre and Wang (1988) studied the atomisation of aerated sprays. Air and water were mixed in a small chamber prior to atomisation through a spray nozzle. The influence of gas/liquid mass ratio (0.01 to 0.24), nozzle dimensions (0.8 mm to 2.4 mm) and driving pressure (100 kPa to 690 kPa) were investigated. Drop sizes were measured by a Malvern laser diffraction size analyser. These investigations confirm previous observations with 'true' airblast systems. That is, drop size was independent of nozzle dimensions, but depended inversely on gas/liquid mass ratio and nozzle pressure. Figure 2.4 illustrates the observed relationships. Also shown in the figure is an empirical relationship, developed by the present author, to correlate drop size with quality of flow. This will be discussed further in section 5.

In true homogeneous mixtures, where there is no slip between the phases, there is no relative velocity between the gas and liquid ligaments and it is not possible to use the conventional 'airblast' correlations where droplet size is shown to be inversely related to the Weber number. Thus, no attempt was made by Lefebvre to correlate mean drop size data with atomiser or fluid parameters, but a qualitative understanding was developed using a simple relationship relating gas/liquid ratio, average gas bubble diameter and the gas/liquid density ratio, to liquid film thickness within the atomiser nozzle. This investigation, and the quality dependence illustrated in **figure 2.4b**, is of great importance because the atomisation process bears a close resemblance to the atomisation of superheated liquids through twin-orifice systems as described by Fletcher (1973). That is, atomisation of a true gas/liquid <u>mixture</u> through a spray nozzle.

											T															
								 	METHOD of MEASUREMEN	Coated slide	Microscope counting	High speed photography	Microscope counting and sifting	Micromerograph and sifting	Light scattering technique	=										
	dimensions	ed int of dependent	nizing	uids t of Do			ed wide		SMD×I0 <sup>6</sup>	15 - <del>9</del> 0	5 - 30	25 - 80	10 - 160	001 - 11	20-130	35-120										
REMARKS	fect of nozzle r air density	meter of wette iphery size independe viscosity but viscosity	w area of aton stream t W/W < 3 5 at W,/W, >3	w viscosity liq s independent jet diameter.	=	ross current up	iments cover of variables		AIR/LIQUID MASS RATIO	-  4	1 - 16	5 - 100	0.06 - 40	4 - 25	1 - 16	2-8	irblast									
	No eft o	Dag Dag Dag Dag Dag Dag Dag Dag Dag Dag	A=flo aii m = 1 c m = 0	For lo SMD initial		For cr break	Exper	ES	⊐*	60-340	up to sonic	30-210	75 - 393	60 - 300	60 - 180	70 - 135	for 'A									
		$= 2.6 \times 10^{3} \left( \frac{\mu_{A}}{R_{UL}} \right)^{0.4} (W_{V}W_{A})^{0.4}$ $= 5.36 \times 10^{3} \left[ \frac{\sigma_{C}^{0.41}}{(\rho_{A}U_{A}^{2})^{0.57} R^{0.56} \rho_{P}H_{B}} \right] + 3.44 \times 10^{3} \left( \frac{\mu_{c}^{2}}{\sigma_{c}} \right)^{0.1} \left( \frac{W_{W}}{W_{V}} \right)^{0.1} I/U_{R}^{0.5}$ $= 0.95 \left[ \frac{(\sigma_{c}-W_{V})^{0.33}}{\rho_{0.57}^{0.50} O_{L}H_{B}} (1+W_{V}W_{A})^{1.70} + 0.13 \left( \frac{\mu_{c}^{2}}{\sigma_{c}} \frac{D_{0}}{A} \right)^{0.5} (1+W_{V}W_{A})^{7.70}$ $= 0.19 \left( \frac{\sigma_{c}}{\rho_{c}} \right)^{0.3} (1/U_{A}) (1+W_{V}W_{A})^{0.23} + 0.127 \left( \frac{\mu_{c}^{2}}{\sigma_{c}} \frac{D_{0}}{A} \right)^{0.5} (1+W_{V}W_{A})^{1.70}$	4)04	×)04	×)04							( <u>wa</u> ) <sup>m</sup> 1/ J <sup>0</sup> 5	w_/w_)' <sup>70</sup>	۱۰۳٫/۳)			ROPERTI	۲×	295	295	298	298	298	295	295	ations
	$\left( \int_{a}^{b^{2}} + 53 \left( \frac{\mu^{2}}{q} \right)^{0.223} \left( \int_{a}^{0} \left( \int_{a}^{0} \right)^{1.5} \right)^{1.5}$												$10^3 \left( \frac{\mu_L^2}{\sigma_L^2} \right)^{-1}$	( <u> 년</u> 만) <sup>0.5</sup> (1.1	$27\left(\frac{\mu_{1}^{2}\Omega_{0}}{q}\right)^{3}$			AIF	P <sub>A</sub> ×10 <sup>3</sup>	0.1	l.6 - 4	04 - 1.64	076-2.0	1.0 - 5.0	01	0.1
UATION						.32 pp. 15 pp. 1344	210+ <sub>021</sub>	W) <sup>0.25</sup> +0.12			TIES	µ_×ا0 <sup>3</sup>	10 - 50	10	0.45 - 193	13-50	32-11.3	10 - 76	10 - 53.4	relatio						
EQ			<sup>4</sup> A 0.4 (W / V	<sup>4</sup> A 0.4 (W/L) UAL) (W/L) σ <sub>A</sub> U <sup>2</sup> 37 A03 W 102337 A033	α <sup>0.41</sup> μ α <sup>0.41</sup> μ α <sup>10</sup> μ α <sup>10</sup> μ (1+ w	W) <sup>033</sup> [1+W	عدر ۱۰۰۷, ۱۰۳ <sub>۲</sub>	20.25 ()	16 / 0.34	UID PROPER	βr	700 - 1200	•		800 - 960	806 - 828	794 - 2180	784 - 1000	of Cor							
	:0.585( <u>A</u> U		3.9 ( <u>0, 4, D</u>	a [00		σ <sub>L</sub> × 10 <sup>3</sup>	19 - 73	50	IE - 7I	30 - 50	I8 - 22	26 - 76	27 - 74	mary (												
ATORS	asawa <sup>27</sup> SMD =	MMD	hall <sup>3</sup> MMD	febvre <sup>is</sup> SMD=	5MD =	oster <sup>40</sup> VMD=	rsham <sup>35</sup> SMD		LIQUIDS	water, gasoline, alcohol, heavy fuel oil	aqueous solutions	water, iso-octane, benzene, JP5 fuet	wax melts	wax melts	water,kerosine special solutions	residual fuel oils	2.1 Sum									
INVESTIG	Nukiyama B Tan	Gretzinger B Mo	Kim & Mars	Lorenzetto B.	n devi	Ingebo & F	Weiss & Wor		PE of ATOMIZER	Plain-jet	=	=	=	=	=	=	Table									
				,					INVESTIGATORS TY	Nukiyama Banasawa	Gretzinger B Marshall	Ingebo B Foster 40	Kim B Marshall <sup>3</sup>	Weiss & Worsham <sup>35</sup>	Lorenzeito B. Lefebvre	Jasuja <sup>46</sup>										

Atomisers (extract from Lefebvre, 1980)

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It is interesting to compare the data of Lefebvre and Wang with those reported in section 3, using an impinger device to investigate spray quality, and those of Fletcher discussed above. Section 3 presents data showing that 'dispersion' (quantity of fine particles within the aerosol cloud delivered from a metered dose inhaler) is inversely proportional to spray orifice diameter. Fletcher presented data which shows that the volume median diameter of the residual surfactant aerosol, from a system with nominally similar upstream and downstream orifice diameters, is inversely proportional to spray orifice diameter. The independence of droplet diameter and nozzle diameter reported by Lefebvre and Wang is thus, at first sight, quite surprising. However, it should be remembered that the final spray orifice diameter, in a twin-nozzle system, controls both the mass fraction of propellant evaporated in the expansion chamber, and hence the gas/liquid mass ratio, and the pressure drop across the final spray orifice diameter in the above study.

### 2.2.3. AEROSOL FORMULATIONS

In addition to the atomisation literature discussed above, where the atomisation process itself was under investigation, a number of studies have been performed upon actual propellant based aerosol devices and formulations. These studies were primarily designed to produce empirical data to allow formulation scientists to develop specific products. The studies have involved both metered sprays of pharmaceutical compounds and domestic sprays such as hair sprays and polish. Attempts have also been made to visualize these sprays and measure velocity profiles and plume lengths. Since formulation variables have marked influence on the mechanism of spray production this literature will now be considered.

Polli *et al* (1969) were the first to consider factors which affect the performance of suspension metered dose inhalers. Their study was designed to investigate the effects of a number of formulation variables upon the particle size distribution of the generated aerosol cloud. A Delron cascade impactor equipped with a glass adaptor (a chamber of approximately 500 ml internal volume which was designed to capture the cloud emitted from the inhaler) was used to size the aerosol clouds. The results of their investigations are summarised in **Table 2.2**.

It can be seen from **Table 2.2** that the size distribution and concentration of the suspended drug particles have a marked effect upon the size distribution of the aerosol cloud generated by the inhaler. Increasing either the solids concentration or the median diameter of the suspended material increased the 'size' of the generated cloud. Decreasing the spray orifice diameter was found to reduce the size of the generated spray. The effects of vapour pressure upon aerosol size was studied by varying both ambient temperatures and formulation constituents. In general, the effects of vapour pressure and temperature were found to be similar to those reported by Lefebvre and Tregan (1964). Polli also found that pressures of about 520 kPa seemed to produce an aerosol with a similar size distribution to the original drug particles. However, it should be stressed that all of Polli's conclusions were based on a small number of observations.

TABLE 2.2 A Summary of the Effects of Formulation Variables upon the Performance of Metered dose Inhalers

(Polli et al, 1969)

### A. Suspended solids

Concentration of	MMAD <sup>1</sup> of		
Solid Phase	Aerosol		
mg/ml	μm		
0.126	3.2		
1.02	3.2		
2.05	18.0		

VMD <sup>2</sup> of	MMAD <sup>1</sup> of		
Suspended	Aerosol		
Solids µm	μm		
5.6	9.0		
4.3	6.0		
1.4	3.2		

### **B.** Propellant formulation

Vapour	MMAD <sup>1</sup>		
Pressure	of		
kPa	Aerosol		
	$\mu \mathrm{m}$		
109.2	11.0		
213.0	3.2		
529.0	1.3		

Sorbitan	MMAD <sup>1</sup> of		
Trioleate	Aerosol		
Conc W/W %	μm		
0.0	3.2		
0.2	4.6		

# C. Spray Orifice diameter

Spray Or	MMAD <sup>1</sup> of			
Diameter mm	Area mm <sup>2</sup>	μm		
0.76	1.81	11.0		
0.60	1.13	11.0		
0.46	0.66	3.2		

1. Mass Median Aerodynamic Diameter 2. Volume Median Diameter

Sciarra *et al* (1971) also used a cascade impactor and glass 'sampling chamber' to investigate the effects of formulation variables upon the performance of hair sprays. Using formulations containing 70% propellant (made up of 50:50 propellant 12/11), they demonstrated that a reduction in the final spray orifice diameter, whilst maintaining a constant valve orifice diameter, increased the quantity of fine particles within the spray. They also showed that increasing the fraction of propellant in the formulation also increased the fine particle content of the cloud.

Murayama *et al* (1970a, 1970b, 1970c, 1970d, 1970e) reported a number of studies investigating factors affecting the performance of aerosols using vapour tap valves. A vapour tap valve contains 3 orifices. Two orifices are in the valve stem, one connected to the fluid reservoir (valve stem orifice) and one, usually of much smaller diameter, connected to the vapour head space above the fluid reservoir (vapour tap orifice). The third orifice is contained in the spray button and acts as the spray nozzle.

They showed, perhaps not surprisingly, that a large number of interactions can occur between the various valve orifice ratios. By collecting residual spray droplets upon microscope slides they showed that increasing the vapour tap orifice reduced droplet size, but also reduced the mass discharge rate. This was attributed to a higher quantity of vapour being present in the valve stem, helping the atomisation process, but reducing the density of the discharged fluid. Decreasing the spray orifice diameter reduced droplet size. A linear inverse relationship was observed between the vapour tap/spray nozzle ratio, and the vapour tap/valve orifice ratio, and droplet size. This again is probably not too surprising since increasing either of these ratios increases the vapour/liquid ratio at the final spray nozzle which presumably enhances the efficiency of atomisation. It was also shown that increasing the vapour pressure of the propellant system decreased droplet size.

Vos and Thompson (1974) used a Royco model 220 particle counter to carry out particle size determinations upon "Eight Commercial Pressurized Products". No attempt was made to correlate formulation variables with aerosol size but 4 out of the 8 sprays tested did conform to a log normal size distribution.

Rance (1974) investigated the size distribution and plume dynamics (1972) of hair sprays. An image splitting technique was used to measure the size distribution of residual resin balls left after evaporation of the spray solvents. A range of formulation pressures were investigated and results similar to those of Polli et al and Lefebvre and Tregan were obtained. At pressures below 200 kPa aerosol size was found to be heavily dependant upon vapour pressure. At pressures greater than 200 kPa, aerosol size still decreased with increasing pressure but at a much reduced rate. In his second study Rance (1972) used a pitot tube to investigate the velocity profile within the spray plume of formulations with vapour pressure in the range 152 kPa to 359 kPa. An array of monofilament fibres were then used to measure the potential of the aerosol to penetrate into hair. Initial spray velocities were shown to be dependant upon vapour pressure and ranged from 25 to 60 metres per second. Axial spray velocity was found to decay in a manner inversely proportional to distance. Velocities perpendicular to the spray axis were shown to follow a Gaussian distribution.

Hiller *et al* (1978) investigated the aerodynamic size distribution of the aerosols generated from 9 commercial bronchodilator metered dose inhalers. A Single Particle Aerodynamic Relaxation Time analyser (SPART) was used to measure the size distribution of the residual aerosol particles.

The SPART uses a laser doppler technique to measure the vibrational frequency of particles subjected to an oscillating pressure field. The pressure field is produced by an acoustic transducer and the aerodynamic size distribution is determined by measuring the 'phase lag' between the pressure pulse and the vibrational amplitude of the particle. Mass median diameters covering the range 2.8 to 4.3  $\mu$ m were found. No attempt was made to relate particle distributions to formulation variables.

Meakin *et al* (1983) used a single stage impinger, Method A in the 1988 edition of the British Pharmacopoeia (1988), to assess the performance of 9 commercially available metered dose inhaler formulations. The impinger device is a hybrid between a single inertial impactor stage, designed to separate the aerosol into two size fractions ( < and > 6  $\mu$ m ), and a throat tube designed to simulate the mouth and oropharynx of a patient. Meakin's results are presented

in Figure 2.5. The percentage of the aerosol cloud that is less than 6  $\mu$ m aerodynamic diameter is plotted against the nominal dose delivered by the formulation. It can be seen that a very definite correlation between nominal dose and the quality of the delivered aerosol exists. As nominal dose, equivalent to powder loading and solids concentration, increases, the quality of the generated aerosol falls. This finding is in line with the reports of Polli *et al* and Lefebvre and Tregan.

Dalby and Byron (1988) reported the results of a comparison between aerosols containing suspended solids and aerosols where the drug had been solubilised in a co-solvent. They used a Delron DCI-6 cascade impactor coupled to a glass sampling chamber, similar to that of Polli *et al*, to measure the aerodynamic size distribution of a number of formulations. Using formulations containing disodium fluorescein suspension, or salicylic acid solution, they found that in general the solution aerosol produced a finer aerosol cloud. The volume median diameter of the suspended sodium fluorescein was 4.9  $\mu$ m.

Recently, Tsuda et al (1989) have reported further work on vapour tap valve systems utilizing a kerosene/butane formulation. As with Murayama they studied the effects of the various valve orifice ratios. They used a Malvern diffraction analyser to measure the droplet size distribution 30 cm from the spray nozzle exit. In general their findings are in agreement with Murayama. With the vapour tap orifice absent Tsuda showed that spray droplet size was a function of the valve/spray orifice ratio. Because of the relevance of this data to the twin-orifice work reported in this thesis, particularly in section 4, this data is presented in figure 2.6. It can be seen that a minimum droplet size exists at a particular valve/spray orifice ratio. However, the position of the minimum depends upon the physical diameter of the valve stem orifice. Tsuda believed that this minimum marked a change in the dominant mechanism of atomisation. He argued that with large valve stem orifices the fluid issuing from the spray nozzle contains very little vapour and the spray resembles monofilament atomisation of liquids, whereas with small valve stem orifices the fluid contains a large proportion of vapour and hence the spray resembles the more efficient 'airblast' process. However, no attempt was made to measure the vapour/liquid ratio either within the valve stem or at the spray nozzle exit.



A number of studies have used video and high speed filming to visualise the metered dose sprays.

Misuk *et al* (1980) used a high speed video technique, with dark ground illumination, to film orthogonal views of the sprays delivered by metered dose inhalers. Their data was mainly of a qualitative nature, but a comparison of the quantity of drug retained upon the adaptor with the visual plume appeared to show that the visual spray plume could be used as an indicator of poorly performing adaptors.

Hallworth and Kedgley (1986) used a single flash photographic technique to capture the plume patterns generated by a number of formulations containing various proportion of propellants 12, 114 and 11. The still photographs were used to assess plume lengths at 25 ms, 50 ms and 100 ms after actuation. The data showed that aerosols containing large proportions of non-volatile excipients, or aerosols containing large quantities of low vapour pressure propellants, had longer and more persistent plumes. Hallworth interpreted this to indicate that these formulations produced aerosols with larger and longer lived droplets.

Dhand *et al* (1983) used a high speed video technique (200 frames per second) to measure the velocity of expansion of the cloud, and the duration of the sprays, generated from 4 commercial metered dose inhaler preparations. Initial cloud velocities were shown to be of the order of 15 m s<sup>-1</sup> and spray durations were found to be of the order of 65 ms to 95 ms. Although not stated the metering volume of all the aerosols tested was  $0.05 \text{ cm}^3$ . These estimates are in broad agreement with those of Fletcher who measured both spray duration and cloud velocities during his preliminary investigations of twin nozzle systems.

#### 2.2.4 DISCUSSION AND CONCLUSIONS

Monofilament, or single orifice, atomisation has been successfully studied by a number of groups. The major jet break-up mechanism, and the droplet size produced by such a spray, has been shown to be related to the degree of superheat. At high superheats break-up is caused by rapid bubble growth within the jet causing 'explosive' disruption. At low superheats, where thermal dissipation can eliminate superheat before bubbles can form and grow large enough to disrupt the jet, break-up is caused by aerodynamic forces acting on the jet ligament. The minimum superheat depends upon jet velocity and jet diameter as well as the thermal properties of the liquid.

Twin orifice atomisation of superheated liquids has also been investigated by a number of groups. However, the dominant mechanism of atomisation is less clear. Some authors claim 'flash' atomisation is important; others describe the atomisation process in terms of the aerodynamic break-up of a two phase gas/liquid fluid, similar in nature to classical 'airblast' atomisation. The vast majority of reports are semi-empirical in nature and none has yet successfully attempted to correlate the droplet size produced by such a system to the geometric and thermodynamic variables involved. However, as with monofilament systems, it is likely that the degree of superheat may be important and indeed a situation similar to that for monofilament jets may exist. That is, at high superheats 'flashing' may be the dominant mechanism and at low superheats two-phase 'airblast' atomisation may be important. It should be remembered however, as will be shown in section 5, that the degree of superheat in a twin orifice system is inversely related to evaporation in the expansion chamber and hence inversely related to mass quality of flow. Mass quality is an important variable in 'airblast' systems.

Because of its importance to combustion science the atomisation of non-superheated two phase gas/liquid mixtures, or 'airblast' atomisation as it is known, has been studied extensively. In general, the factors affecting the droplet size produced by gas/liquid discharge through single nozzles, or orifices, are well understood. Droplet size decreases with increasing nozzle pressure and increasing gas/liquid mass ratio. Decreasing surface tension decreases droplet size and most droplet correlation functions indicate that increasing the density of

the gas, or vapour phase, or reducing the density of the liquid phase, also decreases droplet size. Droplet size has only a weak dependence upon the fluid phase viscosity and in most correlation functions its effect is restricted to what is usually a small additive term.

It will be shown in section 5 that vapour in a twin orifice system can be considered to be generated adiabatically. Thus, the amount of vapour generated, and hence the vapour/liquid mass ratio, is in direct proportion to the temperature fall of the fluid as it passes through the expansion chamber. The vapour/liquid mass ratio therefore increases as the fluid temperature falls and the degree of superheat decreases. The literature therefore indicates that, in a twin orifice superheated system, the efficiency of atomisation of the 'flashing' and 'airblast' processes may show an opposite dependence upon vapour/liquid mass ratio.

Increasing droplet size should be seen as vapour/liquid mass ratio increases if 'flashing' is the dominant mechanism; whereas decreasing droplet size should be seen if 'airblast' processes are dominant. This argument is obviously over-simplified since changes in pressure etc. also occur in the expansion chamber as evaporation takes place. These relationships and the atomisation mechanism itself will discussed in more detail in section 5.3 below.

A number of studies have investigated the effects of formulation variables upon the performance of both metered dose inhalers and conventional domestic aerosol sprays. In the current context the work of Polli *et al* (1969) and Meakin & Stroud (1983) is probably the most important. Polli showed that increasing either the solids concentration of the suspended drug particles, or the surfactant concentration, increased the particle size of the residual aerosol. Conversely, decreasing the particle size of the residual aerosol. Meakin's work inadvertently confirmed the first of these trends by examining the aerosols generated by a variety of commercial products. However, as with the other formulation work reported to date, both Polli's and Meakin's work was very limited in extent and can only be taken to indicate trends and not the magnitude of the various effects. All the work reported to date has only been of a qualitative nature and no attempts appear to have been made to investigate the fundamental mechanisms involved in the metered atomisation process.

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# 2.3 MASS DISCHARGE THROUGH ORIFICES AND SHORT TUBES

The rate at which superheated fluid leaves the spray nozzle of a liquefied gas aerosol generator not only controls the pulse width of a metered discharge, or the delivery rate of a continuous spray, it also has an overall effect on the efficiency of atomisation. Thus it is an important parameter in the understanding of superheated sprays.

As stated earlier, because of its importance to the nuclear engineering and reactor safety groups, two-phase single component flow has been studied extensively over the past 3 decades. Gouse (1966) in a comprehensive survey of the two-phase single-component flow literature up to 1966 lists over 5253 references. Many further papers have been published since this date. It is therefore not the purpose of this section to review the two-phase flow literature in its entirety, rather it is to review the key papers which have a direct bearing upon the theoretical development and understanding of the metered atomisation of a superheated liquid. In general, metastability notwithstanding, the flow through both the valve orifice and the spray orifice during metered discharge will be two-phase.

Because it was felt that continuous atomisation should be studied before attempts were made to develop theoretical models to describe the metered process, a number of papers relating to liquid-only metastable flow of a superheated fluid through single orifices will be considered. The term metastable usually refers to the situation were superheated liquid is not in thermal or dynamic equilibrium with its vapour. In general, metastable flow occurs when there is insufficient time for vapour bubbles to nucleate and grow. Liquid-only metastable flow is important in the context of continuous discharge of propellant liquids because during the propellants passage through the valve orifice it is likely to experience total metastable conditions, ie. to remain in the liquid state.

## 2.3.1 METASTABLE FLOW OF SUPERHEATED LIQUIDS THROUGH ORIFICES

Initial attempts to develop theoretical descriptions of the passage of a superheated liquid through an orifice or short tube (Stuart & Yarnell, 1936) assumed that the phase changes associated with the pressure reduction during flow through the nozzle were instantaneous. That is, as the pressure of the liquid fell during passage through the nozzle 'boiling' and vapour generation were assumed to be instantaneous. The theoretical consequences of this assumption were that the fluid had to be assumed to be two-phase and that the resulting mass discharge had to be analyzed as such. In subsequent experimental studies (Stuart & Yarnell, 1944), the use of these assumptions was found to grossly underestimate the actual mass discharge. In fact, a standard single component incompressible discharge equation was found to fit the experimental data far more accurately. This was attributed to the metastable flow of the superheated liquid.

It has since been demonstrated by a number of authors (Fauske, 1964, Isbin, 1964, Min, 1966) perhaps not surprisingly, that passage of a superheated liquid through an orifice of zero length results in total metastable flow. As the orifice length is increased vapour formation becomes progressively more likely and a vapour/liquid annulus is formed around the circumference of the orifice. Under these conditions it has been shown that a modified discharge coefficient is all that is needed in order to be able to use the standard incompressible orifice discharge equation (Bailey, 1951). This modified coefficient is a function of the fluid properties, the discharge rate and the orifice dimension (Fauske, 1964).

Pasque (1953) investigated the metastable flow of propellant 12 through short tubes. He developed an empirical expression defining a critical orifice-pressure-drop, below which metastable flow could be assumed and a standard incompressible orifice discharge equation could be used. This critical downstream pressure was defined as :-

$$P_c = 0.37 \left(\frac{W}{D}\right)^{0.2} P_s \qquad 2.13$$

Where  $P_c$  is the downstream pressure, W/D is the length to diameter ratio for the orifice and  $P_s$  is the initial saturation pressure. Pasque also developed an empirical contraction coefficient which, when combined with the standard discharge coefficient for an orifice, modified it such that the standard incompressible orifice discharge equation could be used. Although of great value this relationship will not be considered any further here because, in general, as will be described in **section 5**, the critical pressure drop is not reached in most practical valve systems.

Fauske & Min (1963) investigated the flow of propellant 11 through short tubes. Their results were in general agreement with Pasque. However, they described the critical pressure difference, below which complete metastable flow was ensured, in terms of an inequality based upon a modified 'cavitation number'.

$$\frac{2\left(P_{s}-P_{c}\right)}{\rho_{l}\dot{m}^{2}}A^{2}\left(\frac{W}{D}\right) \leq 10$$
2.14

Where A is the area of the orifice,  $\rho_1$  is the liquid density and m is the mass discharge rate. Again, it will be shown in section 5 that this inequality holds for all practical continuous valve systems.

Bryers (1966), in a report for the United States Department of the Interior, presents an excellent review of the literature on two-phase metastable flow up to 1966 and summarizes the theoretical and practical implications of the existence of metastable flow through short tubes and orifices.

Fletcher (1984) investigated the flow and atomisation of superheated propellant 11 through short tubes and nozzles. He confirmed that at low superheats the flow of propellant 11 could be described using the standard incompressible liquid discharge equation. For orifices of W/D < 3.8 this required a discharge coefficient of 0.57. His observations resulting from high speed filming at the nozzle exit also agreed with previous work on the atomisation of monofilament sprays. In line with the work of Lienhard and Day (1970) and Suzuki *et al* (1978), Fletcher demonstrated that for low superheats cavitation and bubble growth occurs several millimetres downstream of the spray nozzle. However, for high superheats the spray can 'shatter' at the nozzle exit.

#### 2.3.2 TWO-PHASE FLOW THROUGH ORIFICES AND SHORT TUBES

The vast majority of the work on two-phase single component flow took place in the early 1960's. This 'explosion' of work was the result of the major concerns of the then embryonic nuclear industry over the possibility of leaking coolant circuits leading to the discharge of radioactive two-phase steam/water mixtures. As a result of this, the vast majority of the investigations into two-phase single component flow have utilized steam/water mixture as opposed to propellant vapour/liquid systems.

One of the earliest reports on two-phase flow through an orifice or short tube was that of Tangren et al (1949). During their investigation Tangren's group developed what is now known as the homogeneous model of two-phase flow. The homogeneous model assumes that the two-phase mixture can be represented by a single fluid whose properties are characterized by the average properties of the 2 individual components. Tangren investigated the flow of air/water mixtures with void ratios of between 0.19 and 2. He developed an equation of state for the two-phase mixture which was similar to the adiabatic equation of state for an ideal gas. Equations of motion were then developed which were similar in form to those used to describe compressible single component flow through an orifice. It therefore followed that two-phase gas liquid flow would exhibit the same choking, or mass limiting, flow phenomena exhibited by single phase compressible flow. Based on this model the critical pressure ratio at which the orifice velocity became choked, or sonic, was calculated and ranged from 0.43 to 0.6 as the void fraction changed from 0.19 to 2.0. The calculations showed reasonable agreement (within 13%) with experimental values. Tangren's work had thus established the importance of choking in two-phase flow.

In 1963, Smith (1963) conducted a comprehensive review of the literature on two-phase flow through nozzles and orifices and recommended that for low quality (low weight fraction of gas to liquid) the homogeneous metastable model of the type developed by Tangren was appropriate.

The mass limiting flow of air/water mixtures through a 6 mm converging/diverging nozzle was investigated by Muir and Eichhorn (1963). They investigated mass qualities in the range 8 to 33 percent. This covered a region which they described as the bubble flow regime. Using high speed filming techniques they measured the velocity of the gas and liquid phases as they passed through the nozzle. They discovered that the gas, or bubble velocities were only 80 to 90 percent of that of the liquid phase. However, despite this the homogeneous model was found to predict the mass discharge rates reasonably well.

Fauske (1965) investigated the flow of both air/water and steam/water mixtures through 7.5 mm and 11 mm channels with length to diameter ratios of 11 to 50. Mass qualities of between 0.06 and 8 percent were investigated. For these short tubes, Fauske found discrepancies with the prediction of the homogeneous model and proposed a 'non-equilibrium-slip' model as a better physical representation of two-phase steam/water flow. The model assumed thermal equilibrium but allowed the velocities of the vapour and liquid phase to be different (to 'slip'). He concluded that the claimed accuracy of the previously published models, based on homogeneous flow, was probably a fortuitous combination of high velocity ratios compensating for metastability effects. The 'non-equilibrium-slip' model is now known as the Fauske model.

Edmonds and Smith (1965) investigated the mass limiting and near mass limiting flow of propellant 11. They studied a short tube, a long nozzle and a short nozzle, or orifice. The internal diameter of the tube and nozzles was 8.5 mm. They studied mass qualities in the range 4 to 16 percent and investigated mass limiting flow by drawing the propellant from the nozzle into a receiver maintained at a reduced pressure. The mass discharge was investigated as the receiver pressure was progressively lowered. The critical pressure ratios (downstream to upstream pressure ratio at which the flow become mass limited) were found to be 0.56, 0.53 and 0.6 respectively. It was found that predictions

based on both the homogeneous and Fauske models agreed reasonably well with experimental values.

Moody (1965) developed a theoretical model based upon annular flow, uniform linear velocity of each phase and equilibrium between the liquid and vapour phase. The calculation of the maximum discharge rate from a nozzle was performed by equating the maximum exit velocity to the sonic velocity of the two-phase mixture. However, it was generally agreed that even though the sonic velocity in a two-phase mixture was readily predictable the pressure ratio at which choked flow first began was difficult to predict and may to a large extent depend upon nozzle or orifice geometry.

Henry *et al* (1968) investigated the propagation velocity of pressure waves through air/water mixtures. They investigated what have now become the 3 classical flow regimes - bubble flow, stratified flow and slug flow. They demonstrated that in the bubble flow regime the homogeneous theory predicted the sonic velocity reasonably accurately. The velocity versus void fraction curve showed a marked minimum value at 0.5. This minimum sonic velocity of the two-phase mixture was well below the sonic velocity in either of the individual phases. Using a model based on no-slip between the phases a theoretical expression for the velocity of sound in a two-phase bubbly mixture was developed.

$$V = V_g \left[ \alpha^2 + \alpha (1 - \alpha) \left( \frac{\rho_l}{\rho_g} \right) \right]^{-\frac{1}{2}}$$
 2.15

Where V is the sonic velocity in the two-phase mixture,  $V_g$  is the velocity of sound in the gas phase and  $\alpha$  is the void fraction.

In a comprehensive text on one dimensional two-phase flow by Wallis (1969), a further model based upon the no-slip approximation was used to develop a theoretical expression for the sonic velocity in a truly homogeneous two-phase mixture. Wallis's exact expression for the sonic velocity was :-

$$V^{2} = \left[ (\alpha \rho_{g} + (1 - \alpha) \rho_{l}) \left( \frac{1 - \alpha}{V_{l}^{2} \rho_{l}} + \frac{\alpha}{V_{g}^{2} \rho_{g}} \right) \right]^{-1} \qquad 2.16$$

Where  $V_1$  is the velocity of sound in the liquid phase. In the situation where the density of the liquid phase is much greater than the vapour phase and where the sonic velocity in the liquid is also much greater than that in the vapour phase the above expression reduces to :-

$$V = V_g \left[ \alpha (1 - \alpha) \left( \frac{\rho_I}{\rho_g} \right) \right]^{-\frac{1}{2}}$$
 2.17

which is in general agreement with the expression developed by Henry *et al.* since, for low quality flows, where  $\alpha$  is small, the term  $\alpha^2$  may be neglected. Wallis's equation also predicts a minimum velocity at a void fraction of 0.5.

As an example of the variation of sonic velocity, or the critical discharge velocity in a choked nozzle, with void fraction, Wallis's expression is shown in **Figure 2.7**. Also plotted in this figure are the data and theoretical curves from the paper by Muir and Eichhorn for air/water mixtures. The theoretical curve used by Muir & Eichhorn was derived from that of Tangren *et al.* It can be seen that for low void fractions, low quality, the discharge velocity is steeply dependent upon void fraction.



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Figure 2.7 A Comparison of Theoretical Expressions For the Sonic Velocity in Air/Water with the Experimental Data of Muir & Eichhorn (1963)

#### 2.3.3 CONCLUSIONS

The flow of superheated liquids through orifices and nozzles, in both metastable and two-phase form, has been studied extensively by a large number of authors. It is undoubtedly very complex and a great number of theoretical models exist, each with their own simplifying assumption attached.

The conditions under which the discharge of a superheated liquid through a short tube or orifice will remain in a complete metastable state (liquid only) seem well understood and a number of empirical inequalities have been developed. In practical terms with reference to liquefied gas generators these relationships demonstrate that flow through the valve orifice of a continuous discharge valve will be totally metastable and liquid only. In theoretical terms this means that the standard incompressible discharge equation may be used to describe valve stem discharge.

The flow of a two-phase mixture through an orifice is also well defined. The simplest model is the homogeneous model of the type originally developed by Tangren *et al* (1949). This model makes the assumption of no-slip between the phases, no change in vapour/liquid ratio during passage through the nozzle and equilibrium between the phases. Fletcher (1973) demonstrated the usefulness and applicability of a homogeneous model in his development of an analytical model to describe discharge of superheated propellants through a twin orifice nozzle.

However, while the literature indicates that the sonic, or choked, velocity in a two-phase vapour/liquid mixture is readily predictable, it also shows that the critical pressure ratio at which choked flow first begins is not easily defined. Also for low quality, or low voidage, flows the theoretical models and the experimental data indicate a very steep dependence of sonic velocity on the quality of flow. Both of these factors may make it difficult to theoretically predict mass discharge rates for continuous and metered discharge systems.

#### 3. **PROJECT JUSTIFICATION**

At best the literature describing the various facets of the performance of liquefied gas metered dose aerosol generators can only be described as patchy and incomplete. The studies that have been reported are generally of an empirical and qualitative nature. They make little or no attempt to quantify the magnitude of the relationships between the various formulation variables and the performance of the generators. None of the work reported to date can be described as truly fundamental in nature.

The literature upon continuous discharge and atomisation is a little more complete. Rance (1972 & 1974) studied continuous discharge in an effort to understand the generation of hair sprays. Fletcher (1975) investigated twin-orifice atomisation for a mixture of propellants 12 and 11 and developed a valuable analytical expression for the mass discharge rate from such a system. Sher and Elata (1977) studied sprays generated from pressure canisters and developed a theoretical expression to predict the propellant droplet size produced by such a system. However, their paper is somewhat at odds with other published papers since they considered 'flashing' as the only mechanism involved in droplet generation. Fletcher (1975) and Murayama (1970 & 1971) believed 'airblast' processes were more important. It can thus be seen that the mechanisms involved in the atomisation of superheated liquids from twin-orifice nozzles are still not well understood and that further work is required.

Additionally, the use of radiolabelling/gamma camera procedures to investigate the lung deposition of aerosols generated by metered dose inhalers (Newman et al, 1989) has lead to a far better understanding of the fate of MDI clouds. Combined with work elucidating the sites of action of pharmaceutical molecules within the lung (Padfield et al, 1983) this has lead to a better definition of inhaler requirements.

The forced introduction of a new group of non-CFC propellant liquids, for use in both continuous and metered dose aerosol systems, thus offered an ideal opportunity to investigate and elucidate the mechanisms involved in the atomisation of liquefied gases, particularly with reference to metered dose aerosol production and lung delivery.

The aim of the work reported in this thesis was to develop a good understanding of the atomisation processes involved in the twin orifice atomisation of superheated liquids and to develop design criteria for metered dose inhaler systems which were firmly establish on fundamental scientific principles.

The main thrust of the work was to identify the important variables in metered dose aerosol production, to quantify their effects and to develop a fundamental understanding of the underlying processes involved in both metered discharge and metered spray formation. However, in order to develop this understanding continuous atomisation was also investigated. This was mainly to enable the development of a sound theoretical model which could then be extended to the metered process, but it also enabled the atomisation process to be studied in more detail than previously reported. As described in section 1 the following sections therefore detail 3 phases of work.

The first phase is the investigation, using empirical sizing techniques, of the main formulation and geometric variables (section 4). The second phase is the theoretical and experimental investigation of the continuous discharge and atomisation process (section 5). The third phase is the experimental investigation of the metered discharge and atomisation process and the extension of the theoretical model for continuous discharge to describe the metered process (section 6).

# 4. FACTORS INFLUENCING METERED DOSE INHALER PERFORMANCE

## 4.1 **INTRODUCTION**

- 4.2 **EXPERIMENTAL METHODS**
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### 4.3.1 LIQUID PHASE

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- 4.3.2.1 Solids Concentration
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- 4.3.4 HIGH SPEED FILMING

# 4.4 CONCLUSIONS AND DISCUSSION

# 4. <u>FACTORS INFLUENCING METERED DOSE INHALER</u> <u>PERFORMANCE</u>

### 4.1 **INTRODUCTION**

As stated in sections 1 and 3, the first phase of the experimental investigation was designed to quantify the influence of various formulation parameters upon the performance of the metered dose delivery system. This was considered necessary in order to direct the later stages of the project towards the investigation of the major variables. Although some literature exists on these aspects it was considered to be limited and incomplete. The following section will describe the test methodology used together with the results of investigations into 3 main 'formulation' variables: the liquid phase (propellant and dissolved surfactant), the solid phase (size distribution and concentration of the suspended drug) and the component geometry (metering volume and orifice dimensions).

Since the metered dose inhaler is designed to deliver drug particles to the respiratory tract, its performance must be judged against its ability to produce respirable particles.

The size of aerosol particle required in order to maximize both tracheobronchial and alveolar deposition is well documented (Gross & Hatch, 1966, Task Group on Lung Dynamics, 1966 and Stahlhofen *et al.*, 1980). Under conditions of normal tidal breathing, particles of below 10  $\mu$ m aerodynamic diameter are required in order to ensure penetration into the conducting airways, and particles of 1-5  $\mu$ m are required if alveolar deposition is to be maximized. Alveolar deposition is most likely for particles of 3  $\mu$ m aerodynamic diameter (Stahlhofen *et al.*, 1980). Thus, in principle the efficiency of a pressurized metered dose inhaler could simply be judged against these size criteria. However, as will be shown in **sections 5** and **6**, the cloud produced by a metered dose system is volatile, dynamic and the droplets may be moving at velocities of the order of 30-40 metres per second near the spray orifice. It is
therefore difficult to judge inhaler performance on a simple size basis, particularly since the size of the propellant droplets may be changing quite rapidly.

Oral deposition is a major problem with all forms of metered dose inhalers (Newman et al, 1981). Typically only 10 to 20% of the delivered cloud actually penetrates into the airways, with as little as 8% reaching the alveolar regions (Dolovich et al, 1983, Vidgren et al, 1988). This is despite the fact that the suspended drug particles are usually of the order of 1-3  $\mu$ m. However, as will be discussed in section 5, this original size distribution is not reproduced either in the original spray (made up of propellant droplets rather than drug particles) or the residual spray (made up of agglomerates formed as propellant droplets containing one or more drug particles evaporate). The high oral deposition is the result of impaction at the rear of the oral cavity, due to the high droplet velocity associated with the atomisation process and to the large size of the propellant droplets at the time of passage through the oropharynx. Because of the high velocity the impaction process is essentially governed by the Stokes number of the aerosol droplets and not simply by the droplet size. The Stokes number  $(N_{st})$  is related to the velocity (V) and the diameter (d) of the particle.

$$N_{\rm sr} \propto V.d^2$$
 4.1

Since both droplet size and velocity are changing with distance it is clear that any method designed to assess the quality of the cloud delivered from a pressurized inhaler must characterize both droplet size and velocity in a way that is relevant to the obstruction presented by oropharyngeal cavity. This can be effectively achieved in 2 ways; either by separate measurement of the diameter and velocity of the droplets as a function of distance, or by assessment of the Stokes number using a dynamic test representative of inspiratory airflow and obstruction (dimensions of the oropharyngeal cavity).

Because of simplicity and ease of use, the latter of these options was chosen for this phase of the investigations. However, data derived using the former method will be discussed in section 5. The British Pharmacopoeia (1988) describes 2 inertial impaction devices for use in the assessment of inhalation aerosols. Apparatus A, which is a glass device consisting of a 'throat' and 2 impinger stages, and apparatus B which is a metal device consisting of 'throat', an impaction stage and an absolute filter. The 'throat' sections of each device are slightly different, but each is designed to crudely represent the oral cavity and to carry out the initial assessment of Stokes number. The aerosol penetrating beyond the 'throat' is then separated into 2 size fractions. The latter of these devices was designed by the author, in the author's laboratory, and was chosen for the preliminary investigations.

## 4.2 **EXPERIMENTAL METHODS**

#### 4.2.1 AEROSOL MANUFACTURE

Metered dose inhalers were manufactured using a standard cold filling process. A known weight of micronised powder was dispersed, using a Silverson mixer, into a 500 ml beaker containing measured quantities of surfactant (sorbitan trioleate) and propellant 12. This concentrate was added to a measured quantity of propellant 114 which had been pre-cooled to a temperature of 213 K using a mixture of solid carbon dioxide and isopropyl alcohol. The suspension was mixed, using a magnetic stirrer and follower, before being filled into standard 20 ml aluminium cans. The cans were filled with 18 g aliquots of the suspension and standard metering valves (BK356, Bespak plc, King's Lynn, Norfolk), of the appropriate volume (50  $\mu$ l or 100  $\mu$ l), were then crimped into place. The canisters were leak tested in a water bath maintained at 328 K. They were then stored for 2 weeks at room temperature before testing. The storage period was to ensure that equilibrium had been established between the components of the drug suspension.

## 4.2.2 **PERFORMANCE TESTING**

Figure 4.1A is an illustration of Apparatus B, figures 4.2A and 4.2B show photographs of the apparatus. The device was calibrated using a polydispersed aerosol of carnauba wax. The wax aerosol was sampled by the impinger and split into 2 size fractions, that retained in the 'throat' and stage and that penetrating to the filter. The number and size of the wax particles captured in the 2 'size' fractions were determined using a Coulter Counter model TAII.

From the number and size information, a stage efficiency curve was constructed. Figure 4.1B presents the stage efficiency curve at a volumetric flowrate of 60 litres per minute.

The efficiency of an impactor device is usually expressed in terms of the  $d_{50}$ , or 'cut-off' diameter (Rao & Whitby, 1978). The  $d_{50}$  is defined as the size with an equal probability of capture by, or passage through, the stage. The  $d_{50}$  for apparatus B can be seen to be approximately 10  $\mu$ m.

An alternative definition of efficiency sometimes used is the inertial impaction parameter ( $\psi$ ) (Cushing *et al*, 1979), which is the ratio of the particle's stopping distance to the impaction jet diameter, or alternatively the Stokes number of the d<sub>50</sub> particle in the impaction jet.

$$\Psi = \frac{d_{50}^2 C_u V_o}{18 v D_W}$$
 4.2

Where  $C_u$  is the slip correction factor,  $\rho$  the particle density,  $V_0$  the jet velocity,  $\upsilon$  the gas kinematic viscosity and  $D_w$  the jet diameter.  $\psi$  takes the value 0.2 for apparatus B.

As described above, the device initially assesses oral deposition by capturing particles in the 'throat' section. The remaining cloud is then separated into non-respirable and respirable fractions by the impaction stage, the latter being retained upon the 'absolute' filter. The performance of a metered dose inhaler is usually expressed as 'dispersion' which is the percentage of the total



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delivered dose (ex the metering valve stem) reaching the filter of the apparatus. That is, the percentage of the dose nominally less than 10  $\mu$ m. The term 'nominally' is used because the device actually assesses the initial Stokes number of the propellant droplets before it 'sizes' the remaining cloud.

The 'dispersions' of the experimental preparations were determined using the following general procedure:-

The apparatus was assembled as in figure 4.1A and an airflow of 60 litres per minute was drawn through the device with the aid of a suitable vacuum pump. An appropriate number of actuations where discharged into the 'throat' of the impinger. The oral adaptor, impaction stage and filter where then washed with propellant 11 to dissolve the surfactant. These washings were passed through individual 0.45  $\mu$ m filters and both the filters and apparatus were allowed to dry. (This washing procedure was necessary in order to remove the surfactant which would have interfered with subsequent assay procedures). After drying, the apparatus and filter where then washed with a suitable analytical solvent quantitatively into individual volumetric flasks. The quantity of compound in each flask, and hence the quantity deposited at each location, was determined by comparing the absorbance of each solution with a calibration curve relating absorbance to concentration. The exact number of actuations tested and the particular volumes used during the wash recovery procedures was adjusted so as to maximize the sensitivity of the chemical assay procedure. (The wavelengths used, the absorbance constants and calculations are summarised in Appendix I. For an estimate of the sensitivity and reproducability of the method see Clark et al, 1990).

# 4.3 **RESULTS**

#### 4.3.1 LIQUID PHASE

## 4.3.1.1 **Propellant Vapour Pressure**

The dependence of dispersion upon the vapour pressure of the propellant mixture is illustrated in figure 4.3. The data shows the effect of

propellant vapour pressure upon 2 different solids concentrations of micronised FPL 50670. The 20 mg/ml concentration was discharged through a 50  $\mu$ l valve, the 50 mg/ml concentration was discharged through a 100  $\mu$ l valve. Propellant vapour pressure was varied by changing the relative proportions of propellant 12 to propellant 114. The concentration of surfactant (sorbitan trioleate) was maintained at 1% throughout. Maximum pressure was obtained with 100% propellant 12 (685 kPa), minimum pressure was obtained with 20% propellant 12 and 80% propellant 114 (320 kPa). Propellant 114 boils at 277 K and hence develops insufficient pressure to form a spray at room temperature.

It can be seen that as vapour pressure is increased a concomitant increase in dispersion also occurs. However, it should be noted that the improvement in dispersion value is dependant upon solids concentration (or at least solids concentration and/or metering volume). The first observation is perhaps not to surprising since, as discussed above (Teslin, 1969), an increase in vapour pressure means an increase in the energy available for spray formation. The dependence of dispersion upon solids concentration is also perhaps not too surprising. Each propellant droplet can contain more than one drug particle and as the concentration of the suspended drug is increased the probability of multiple occupation increases. On evaporation of the propellant droplet this 'multiple occupation' will be seen as a large agglomerate and thus the dispersion values will decrease. The convergence of the data at high pressures is, however, difficult to explain and indicates that dispersion is independent of solids concentration if 'pure' propellant 12 is used. This result will be discussed in more detail below.

It should be noted that the data presented in all of the following sections was obtained using a propellant ratio of 60:40 propellant 12:114. This propellant ratio is indicated in Figure 4.3 and was chosen because it represents a fairly typical formulation pressure.

## 4.3.1.2 Surfactant Concentration

Figure 4.4 summarizes the effects of the concentration of surface active agent (sorbitan trioleate, SPAN 85) on the normalized dispersion of



5 formulations containing 4 different pharmaceutical compounds. The data are expressed as "Relative Dispersion (1%)" which is the dispersion value for aparticular compound/formulation divided by the dispersion value for that compound at a surfactant concentration of 1%. "Relative Dispersion" has been used in order to eliminate the effects of formulation variables other than that of surfactant concentration and to demonstrate the fundamental relationship which appears to be independent of the suspended drug.

It can be clearly seen that increasing the concentration of surface active agent reduces the dispersion values. A concentration of 2% results in a four-fold reduction when compared to formulations containing 0%. However, in most practical valve designs the surfactant also serves as a valve lubricant and unfortunately a level of 0% is unacceptable because it can lead to valve malfunction.

The above dependence is in general agreement with previously published data. A number of mechanisms may be postulated for this dependence. These relate either to depression of the propellant vapour pressure or changes in fluid surface tension.

Depression of the propellant vapour pressure could have 3 possible effects upon the atomisation process:-

The first is to reduce the overall driving pressure available from the propellant reservoir.

The second is upon evaporation and mass transfer in the expansion chamber. Evaporation at a vapour/liquid interface could increase the surfactant concentration at the boundary and hence reduce evaporation and reduce the pressure in the expansion chamber. This could lead to a reduction in the pressure drop across the spray orifice and hence to an increase in droplet size.

The third effect is not directly related to changes in atomiser characteristics but is related to mass transfer in the developing aerosol cloud. The presence of liquids of low vapour pressure, even in very small amounts, has been shown to markedly reduce the evaporation rates of droplets

(Renninger *et al*, 1981). As the high vapour pressure component evaporates the concentration of the low vapour pressure component increases continually and causes a concomitant reduction in overall droplet vapour pressure and evaporation rate. This ever decreasing evaporation rate results in a dramatic increase in droplet lifetimes. The delayed evaporation of the propellant droplets, once they have been generated at the spray orifice, would then result in a coarser spray at the time of passage through the impinger and lower dispersion values.

The importance of these possible mechanisms will be discussed further in section 5. However, the latter of these mechanisms, that is increased droplet lifetimes, would seem the most plausible. The molecular weight of sorbitan trioleate is of the order of 1000 and hence, even at 2% w/w, the reduction in vapour pressure in the propellant reservoir would be negligible. Reduced pressure in the expansion chamber would also seem unlikely since, as will be described in section 5, reductions in expansion chamber pressure lead to increased mass flow through the valve orifice which in turn leads to an increase in the amount of propellant in the expansion chamber and a cancelling out of any pressure reduction.

Finally, it should be noted that the addition of surfactants may lower the surface tension of the propellant liquid. However, measurements of the surface tension values across a range of sorbitan trioleate concentrations and propellant formulations has shown that suface tension values are not reduced by the addition of this agent (see **Appendix IV**). In any case, a reduction in surface tension would result in a reduction in the energy needed to produce new droplet surfaces and hence would produce a finer spray. The monotonic fall of dispersion therefore cannot be explained in surface tension terms.

## 4.3.2 SOLID PHASE

#### 4.3.2.1 Solids Concentration

Figure 4.5 summarizes the effect of solids concentration upon the dispersion of 3 formulations of FPL 61369. "Relative dispersion" is again used



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to eliminate the effects of formulation variables other than solids concentration. In this particular case dispersion values are plotted relative to a solids concentration of 20 mg/ml, that is 'Relative Dispersion (20 mg/ml)'.

It can be seen that as the solids concentration is increased dispersion values fall. Over the small range studied it appears that dispersion is linearly related to solids concentration. However, the data presented may be considered as a limited subset of the data reported by Meakin and Stroud (1983) (figure 2.1) which showed that, over a much wider range of solids concentrations, dispersion is proportional to the log of solids concentration rather than being directly linearly proportional.

A simple model which considers each propellant droplet to contain a number of drug particles can be used to qualitatively explain this phenomenon. As discussed above, as solids concentration is increased the number of drug particles contained in each propellant droplet, and hence the size of the residual particle, increases. At low solids concentration multiple occupancy of droplets is unlikely, but as solids concentration increases it becomes more and more likely that each droplet will containing more than one individual drug particle. The size distribution of the residual aerosol will thus increase. To predict the exact effect of solids concentration the size distribution of both the droplet cloud and the suspended solids must be known. Reliable theoretical models have been developed to describe the atomisation of both monodispersed solids in monodispersed droplets (Raabe, 1968) and monodispersed solids in polydispersed droplets (Chan & Gonda, 1988). However, truly polydispersed systems of droplets and solids have only been studied on an empirical basis (Callingham, 1980).

Additionally, the presence of solids will affect droplet evaporation (Davis, 1989). Changes in evaporation rates, together with additional residual mass, may also affect particle momentum and hence may affect the measured respirable fraction and dispersion in a very complex way.

#### 4.3.2.2 Particle Size

Figures 4.6A and 4.6B summarize the correlation between the mass median diameter of the suspended solid and the dispersion values. Data for FPL 59002 is presented in figure 4.6A, data for FPL 50670 and salbutamol sulphate is summarized in figure 4.6B.

The particle size distribution of the suspended solids was determined by Coulter Counter in the case of FPL 50670 and salbutamol sulphate and by Joyce Loebl Disc Centrifuge in the case of FPL 59002. The Coulter Counter was used with a 50  $\mu$ m orifice tube and 3% ammonium thiocyanate in isopropyl alcohol was used as the electrolyte fluid. The electrolyte was presaturated with the particular compound under investigation. The instrument was calibrated using standard latex particles and the number split technique (Coulter Counter TAII Operators Manual, 1983).

The Joyce Loebl was used in a homogeneous light extinction mode using a mixture of liquid paraffin, cyclohexane and carbon tetrachloride as the suspension fluid. These 3 fluids were chosen so that density and viscosity could be varied independently in order to obtain optimum sedimentation conditions. A disc speed of 2000 rpm was used for all size determinations.

All 3 compounds exhibit dispersion values that show a strong dependence upon the mass median diameter of the suspended solids, although the data sets are not coincident. This lack of coincidence is, however, not too surprising since the median diameters were measured with different sizing techniques and different sizing methodologies measure fundamentally different particle parameters (Allen, 1974). It should also be remembered that the data is from 3 discrete chemical entities with individual physico-chemical properties. Additionally, as can be seen from the figure legends the solids concentrations were not the same for all the compounds tested. (The effect of solids concentration was discussed above in **section 4.3.2.1**).

The difference between the size distribution of the suspended solids and the size distribution of the propellant droplets could explain the above phenomena. No individual propellant droplet can contain a drug particle larger

Figure 4.6A The Effects of Mass Median Diameter of the Suspended Phase on the Quality of the Aerosol Cloud Delivered from a Metered Dose Inhaler



Figure 4.6B The Effect of of Mass Median Diameter of the Suspended Phase on the Quality of the Aerosol Cloud Delivered from a Metered Dose Inhaler



NB. For a definition of Dispersion see text.

than itself. Thus, as progressively finer drug particles are used, smaller propellant droplets become occupied with drug particles. Since the chemical assay procedures used to determine the dispersion values only determine the drug content in each size fraction the above mechanism could only be seen as an improvement in dispersion. The problem with testing any model based upon the stochastic nature of droplets being occupied by drug particles is that not only does the volume concentration need to be known but, as expressed above, the droplet and drug size distributions also need to be known. The impinger device used for these preliminary studies supplies insufficient information for any detailed calculations to be carried out.

#### 4.3.3 COMPONENT GEOMETRY

Figure 4.7 presents data correlating dispersion values to spray orifice diameter. "Relative Dispersion (0.56 mm)" has been used to eliminate the effects of formulation variables. Dispersion values at 0.56 mm were used to normalize the data because 0.56 mm represents what is, at present, a typical spray orifice diameter. In all the determinations reported the area of the valve stem orifice was constant at 0.88 mm<sup>2</sup> (0.53 mm diameter).

The data shows a strong correlation between spray ornice diameter and dispersion values. In simplistic terms, it is tempting to associate this relationship with the exit momentum through the spray orifice. Fletcher (1975) developed an expression relating the velocity of the aerosol cloud to the exit momentum of the spray.

$$V = \frac{C}{x} \sqrt{\frac{2 J}{\pi \rho_{air}}}$$
 4.3

Where x represents the distance from the spray nozzle,  $\rho_{air}$  is the density of air and J is the exit momentum.



NB. Relative diep. (0.58mm) = % disp. / % disp. at 0.58mm

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Since the square root of the exit momentum is given by

$$\sqrt{J} \sim C_{q_s} \frac{\pi}{4} D_s \left( \frac{\gamma r_c^{\gamma+1}}{\gamma} \rho_{ge} P_e \right)^{\frac{1}{4}}$$
 4.4

(see section 5) the velocity of the cloud at given distance would be expected to be proportional to the spray orifice diameter. Since the impinger 'Throat' measures the Stokes number, which is also proportional to velocity, the dependence upon spray orifice diameter is perhaps not too surprising. However, it should be remembered that the initial droplet size may also be dependant upon spray orifice diameter and that the ratio of vapour to liquid exiting the spray orifice will depend upon spray orifice diameter. All of these issues will be discussed further below.

#### 4.3.4 HIGH SPEED FILMING

In order to produce an initial estimate of spray discharge times a simple high speed filming procedure was adopted.

A Hycam, high speed camera operating at 600 frames per second was used to record the metered spray discharge from a number of commercial inhalers. Three 1000 watt quartz-halogen spot lamps were used to "back light" the sprays. The flumes were recorded on Tri-X 16 mm film, which was developed in a high contrast developer.

The films were examined frame by frame to determine the duration of spray generation. Because of the extremely fast onset of spray production an error in the determination of the onset of spray formation was incurred. The maximum error was equivalent to the time between consecutive frames, on the first of which the spray was absent and on the second of which it was present. Also because of poor contrast and the way in which the spray flume "fades out" an error in the determination of the end of the spray pulse had to be accepted.

However, the combined error from both these sources could not have been more than 4 or 5 frames, 6 to 8 ms at 600 frames per second. Table 4.1 and Figure 4.8 summarize the results of spray duration determinationsupon 8 commercially available metered dose inhalers.

The inhalers can be broadly divided into groups according to the volume of the metered discharge, showing that discharge times are roughly proportional to metering volume. (It should be noted that the final spray orifice diameter for all the inhalers tested was broadly similar and in the range 0.56 to 0.58 mm). Discharge times of the order of 150 to 200 ms were recorded for 100  $\mu$ l metering volumes with times of the order of 50 ms for a 25  $\mu$ l metering volume. The recorded discharge times are in general agreement with data obtained using high speed video techniques (Misuk *et al*, 1980).

In general this data indicates that mass flowrates through the final spray orifice are of the order of 0.6 to  $1 \text{ g s}^{-1}$ . Dividing by the spray orifice diameter, and allowing for the likely density of the propellant vapour mixture (Fletcher, 1975), leads to an initial spray velocity of 20 to 25 m s<sup>-1</sup>, an estimate that is again in general agreement with previously published data (Misuk *et al*, 1980 & Rance, 1974).

Although of a qualitative nature, these spray duration measurements and mass flow estimates were used to design the experimental rigs described in sections 5 & 6. They will also be discussed later in the light of more detailed measurements made on model systems.

# 4.4 CONCLUSIONS AND SUMMARY

Three areas of metered dose inhaler "formulation/construction" have been investigated, the liquid phase, which includes propellant vapour pressure and surfactant concentration, the solid phase, which includes solids concentration and the size distribution of the suspended material and inhaler "hardware", which includes the spray orifice diameter and metering volume. A number of relationships between inhaler performance and the above variables were identified. A Comparison of the Spray Durations for Eight Commercially Available Metered Dose Inhalers

Table 4.1:

Figure 4.8 Spray Duration versus Metering Volume for 8 Commercial Metered Dose Inhalers

Inhaler	Nominal Dose and Compound	Metering Volume $(\mu l)$	Spray Duration (ms)
Intal	5 mg sodium cromoglycate	100	186
Tilade	2 mg nedocromil sodium		137
Ventolin	0.1 mg salbutamol	63	71
Becloforte	0.25 mg beclomethasone dipropionate		85
Intal	1 mg sodium cromoglycate	50	74
Aarane	1 mg sodium cromoglycate + 0.5 mg reproterol hydrochloride		82
Alupent	0.75 mg orciprenaline sulphate		75
Bricanyl	0.25 mg terbutaline sulphate	25	58

Notes:

- 1. All spray orifice diameters were broadly similar (0.56 to 0.58 mm).
- Spray durations were determined from high speed films of individual sprays. Each reported value is the mean of three such determinations.



Increasing propellant vapour pressure by reducing the proportion of the less volatile component, increased the quality of the generated cloud. Increasing the concentration of the surfactant (sorbitan trioleate) decreased cloud quality. (It is interesting to speculate, based on the literature, (Lefebvre & Tregan, 1964) that the inclusion of any fluid with low volatility would produce similar reductions of quality to those associated with the inclusion of surfactant).

Increasing the concentration of the suspended phase or increasing the median diameter of the suspended material decreased cloud quality. In a qualitative sense this relationship was ascribed to the stochastic nature of the inclusion of suspended particles within the generated droplets.Cloud quality was also shown to be linearly related to spray orifice area. It would have been desirable to study the effects of valve stem orifice diameter upon spray quality, however because of difficulties in obtaining valves containing stems with different orifice diameters this variable was not investigated at this stage.

High speed filming was used to determine the duration of the visual spray pulse generated from 10 commercially available inhalers. Pulse width was shown to be broadly proportional to metering volume. The effects of the final spray orifice dimensions upon spray duration were not investigated.

The empirical relationships developed above are undoubtedly valuable in identifying and defining the effects of formulation variables upon the performance of the metered dose delivery system. A number of authors (Clark, 1989a & 1989b, Padfield *et al*, 1983) have shown that the use of relatively simple impinger systems, such as that used above, can produce data relevant to clinical efficacy and in-vivo human lung deposition patterns. However, the major drawback of such simple instruments is that data derived from them cannot be interpreted in a fundamental way. That is, because of the complex way in which these 'sizing' instruments interact with an aerosol plume, the observed trends may be due to a number of physical processes which could be taking place either at the atomiser nozzle or inside the developing cloud. Thus, having chosen the option of a "... dynamic test representative of inspiratory airflow and obstruction..." to identify the important formulation variables worthy of further study, a more restrictive and fundamental approach is required if an understanding of the underlying processes is to be developed. As intended during this phase of the experimental program, the major factors affecting metered dose inhaler performance have been identified and quantified; some of these factors relate to propellant formulation variables, some to valve/atomiser geometry and others to the suspended solid phase. From the results presented above it was considered that a number of possible lines of investigation were warranted. For example, investigation of the particle inclusion mechanism whereby solids concentration and particle size affect the dispersion values, or the dynamics and evaporation kinetics of the spray plume, would both have proved rewarding.

However, it was considered that investigation of the first 2 factors, propellant formulation and atomiser geometry would be the most fruitful. This was so because, without an understanding of the basic atomisation process, it would prove difficult to study and understand either the powder inclusion mechanism or spray plume development. The following sections thus document fundamental investigations into these aspects of superheated liquid aerosol generators.

# 5. <u>CONTINUOUS DISCHARGE</u>

# 5.1 **INTRODUCTION**

# 5.2 MASS DISCHARGE

# 5.2.1 **THEORY**

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- 5.2.1.2 Mass Discharge Through the Valve Orifice
- 5.2.1.3 Mass Discharge Through the Spray Orifice
  - 5.2.1.3.1 Sub-Critical Discharge
  - 5.2.3.2.2 Critical Discharge
- 5.2.1.4 Exit Spray Momentum
- 5.2.1.5 Expansion Chamber Conditions
- 5.2.1.6 Computer Model of Continuous Flow

#### 5.2.2 EXPERIMENTAL

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- 5.2.2.5 **Results** 
  - 5.2.2.5.1 Determination of Discharge Coefficients
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  - 5.2.2.5.3 Spray Orifice Exit Velocity
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  - 5.2.2.5.5. Expansion Chamber Pressure
  - 5.2.2.5.6 Metastability Effects in the Expansion Chamber

## 5.2.3 **DISCUSSION**

# 5.3 **ATOMISATION**

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#### 5.3.1.2 **Results**

- 5.3.1.2.1 Orifice Dimensions
- 5.3.1.2.2 Surfactant Concentration
- 5.3.1.2.3 **Propellant Vapour Pressure**
- 5.3.1.3 Discussion

## 5.3.2 DROPLET DYNAMICS

- 5.3.2.1.1 The Diffraction analyser
- 5.3.2.1.2 Experimental Apparatus
- 5.3.2.1.3 Experimental Procedures / Program

#### 5.3.2.2 Results

- 5.3.2.2.1 Surfactant Concentration
- 5.3.2.2.2 Propellant Vapour Pressure
- 5.3.2.3 Discussion

# 5.4 SUMMARY AND CONCLUSIONS

# 5. **CONTINUOUS DISCHARGE**

## 5.1 **INTRODUCTION**

As stated in section 3 the main aim of the second phase of the investigational program was to develop, and experimentally verify, a theoretical model to describe the continuous discharge process in such a way that the model could be extended to describe the more complex metered process. Additionally it was hoped that a more detailed examination of the relationship between thermodynamic conditions at the spray nozzle and the droplet size produced by various propellant liquids would lead to a better understanding of the dominant mechanisms associated with this form of liquefied gas aerosol generator.

The following sections detail the development of a computer model to describe the discharge process, an experimental program designed to validate the predictions of the computer model and a detailed experimental program designed to elucidate the dominant mechanisms involved in the droplet generation process. A number of experiments, which were carried out to determine the effects of surfactant concentration on the dynamics of the aerosol cloud are also described.

# 5.2 MASS DISCHARGE

# 5.2.1 **THEORY**

As has already been discussed in the literature survey, the only analytical model describing the flow of a saturated liquid through a twin orifice system was developed by Fletcher (1975). By making various restrictive assumptions about the geometry of the system and the thermodynamic properties of the saturated propellant mixture (60% propellant 12 and 40% propellant 114), Fletcher developed a set of analytical equations describing mass flow through the system and pressure and temperature fall across the first orifice. However, and by its flow equilibrium nature, Fletcher's model cannot be extended to describe a metering process.

It is the purpose of this section to develop, and experimentally verify, an alternative steady state model which is both less restrictive in its application and is amenable to further development in order to describe the metering process. The model will be developed in a form which is amenable to computation by standard digital computing techniques.

# 5.2.1.1 Qualitative Description of the Flow of a Saturated Liquid Through a Twin Orifice System

The continuous flow of a saturated liquid through a twin orifice system is basically a 4 stage process. Initially, saturated liquid propellant flows through the first, or valve, orifice. Then, due to the pressure drop across the orifice, the saturated liquid boils and partially evaporates in the 'expansion' chamber connecting the 2 orifices. This boiling has the effect of 'expanding' the propellant liquid into a two-phase fluid until the liquid/vapour mixture fills the chamber. The two-phase mixture, still at a pressure above ambient, then discharges through the second, or spray, orifice. Atomisation of this two-phase fluid takes place downstream of the spray orifice. Steady state conditions are reached in such a system when the single-phase mass flowrate through the valve orifice is equal to the two-phase mass flowrate through the spray orifice.

The single-phase mass discharge through the valve orifice is controlled by the pressure drop across the orifice, the orifice area and the density of the propellant.

The two-phase discharge through the spray orifice is more complicated and is controlled by the prevailing expansion chamber conditions such as the mass fraction of propellant contained in the vapour phase (mass quality), the temperature, the pressure and the ratio of the pressure to the ambient pressure down-stream of the orifice.

Provided there is sufficient residence time within the expansion chamber for equilibrium to be reached, the equilibrium discharge rate will not be affected by the expansion chamber volume. (The effects of metastability and nonequilibrium conditions will be discussed in more detail below). **Figure 5.1** describes the discharge process in a diagrammatic form.

It can be seen from this description that in order to describe the passage of a superheated liquid through a twin orifice system 3 sets of equations are required. These equations must describe mass flow through the valve orifice, mass flow through the spray orifice and the prevailing expansion chamber conditions at any time during discharge. These equations will now be developed, with consideration being given to the mass discharge equation first.

#### 5.2.1.2 Mass Discharge Through the Valve Orifice

Since the discharge through the valve orifice is to be considered as liquid phase only (see discussion below) the Bernoulli equation can be applied and the standard equation for a single phase incompressible fluid obtained.

$$\dot{m}_{v} = C_{q_{v}} \frac{\pi}{4} D_{v}^{2} \sqrt{\frac{2\rho_{I}(P_{v} - P_{e})}{1 - \left(\frac{D_{v}}{D_{e}}\right)^{4}}}$$
5.1

In practical value systems, and the experiments reported here, the value stem which constitutes the diameter of the expansion chamber is approximately 3.8 mm. Since the maximum value orifice diameter studied was 1 mm the denominator of Eq 5.1 can be neglected without much loss in accuracy (< 0.5%).

# Figure 5.1 Passage of a Superheated Liquid Through a Twin Orifice System



Therefore

$$\dot{m}_{v} = C_{q_{v}} \frac{\pi}{4} D_{v}^{2} \sqrt{2 \rho_{I} (P_{v} - P_{e})}$$
 5.2

Eq 5.2 can only be considered to apply if discharge through the valve orifice is indeed single phase and if no phase change takes place within the orifice due to the drop in pressure. Pasque (1951) developed criteria by which complete metastable single phase liquid flow can be confirmed for the flow of pure propellant 12. Pasque defined a critical pressure ratio below which vaporisation in the orifice does not occur.

$$\frac{P_e}{P_v} = 0.37 \left(\frac{W_v}{D_v}\right)^{0.2}$$
 5.3

Fauske and Min (1963) developed a similar relationship for the flow of propellant 11 through nozzles and short tubes.

$$\frac{2\left(P_{\nu}-P_{e}\right)}{\rho_{l}\dot{m}_{\nu}}A_{\nu}^{2}\left(\frac{W_{\nu}}{D_{\nu}}\right) \leq 10$$
5.4

Reference to the following experimental sections, and orifice dimensions listed in **appendix II**, will show that these criteria are never exceeded for a practical valve system provided the spray orifice to valve orifice ratio does not exceed approximately 3.5. **Eq 5.2** will thus be retained to describe flow through the valve orifice.

#### 5.2.1.3 Mass Discharge Through the Spray Orifice

Two possible discharge conditions may occur in the downstream spray orifice. The first is sub-sonic or sub-critical flow. The second is sonic or critical flow, sometimes referred to as choked or mass limiting flow. As the description of this second condition implies, it corresponds to expansion chamber pressures which are sufficient to raise the velocity of the fluid in the spray orifice to the velocity of sound in the two-phase mixture. Classically this is described as the condition where reductions in downstream pressure, and hence an increase in the pressure drop across the orifice, do not result in increase in mass flowrate. However, this does not imply that the mass discharge does not increase with increasing up-stream pressure since, even though increases in pressure only marginally affect the sonic velocity in a two-phase mixture, they do increase the average density of the discharged fluid.

Equations will now be developed to describe these 2 alternative discharge conditions together with an equation defining the expansion chamber conditions under which each will apply.

#### 5.2.1.3.1 Sub-Critical Discharge

Assuming isentropic behaviour of a truly homogeneous mixture where there is no slip between phases, no heat or mass transfer between phases and where the vapour phase can be considered to be an ideal gas (the homogeneous model) the discharge velocity of the two-phase fluid may be found using the one-dimensional Euler equation.

$$\frac{V^2}{2} = \int_{P_e}^{P_A} \frac{dP}{\bar{\rho}}$$
 5.5

Where  $\rho$  is the density of the two-phase mixture. Since specific volumes are additive:-

$$\frac{1}{\overline{\rho}} = \frac{q}{\rho_g} + \frac{1-q}{\rho_l} \qquad 5.6$$

Therefore:-

$$\frac{V_s^2}{2} = \frac{1-q}{\rho_l} (P_e - P_A) - q \int_{P_e}^{P_A} \frac{dP}{\rho_g}$$
 5.7

Now it follows from the assumption of no phase change or heat transfer in the orifice that the vapour will obey the isentropic gas equation and

$$\frac{P}{\rho_g^{\gamma}} = \text{Const}$$
 5.8

Hence at any point in the orifice

$$\frac{P}{\rho_g^{\gamma}} = \frac{P_e}{\rho_{g_e}^{\gamma}}$$
 5.9

Where the subscript e refers to expansion chamber conditions. Substitution of the above into Eq 5.7 then yields:-

$$\frac{V_s^2}{2} = \frac{1-q}{\rho_l} (P_e - P_A) + \frac{q P_e^{\frac{1}{\gamma}}}{\rho_{ge} \left(1 - \frac{1}{\gamma}\right)} \left(P_e^{1-\frac{1}{\gamma}} - P_A^{1-\frac{1}{\gamma}}\right)$$
 5.10

The mass discharge rate for non-critical flow is then:-

$$\dot{m}_s = C_{q_s} \frac{\pi}{4} D_s^2 \bar{\rho} V_s \qquad 5.11$$

Where  $\rho$  is the density of the two-phase mixture at the orifice exit and can be found from Eq 5.8 by use of Eq 5.9 where P is equal to the ambient pressure downstream of the spray orifice  $P_A$ .

#### 5.2.1.3.2 Critical Discharge

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The mass discharge under critical conditions can be obtained from Eq 5.11 by substituting the sonic velocity in the two-phase fluid for the discharge velocity. Wallis (1969) developed an equation to describe the sonic velocity in a two-phase fluid as follows

$$V_{ss} = \left[ (\alpha \rho_g + (1 - \alpha) \rho_l) \left( \frac{(1 - \alpha)}{\rho_l V_l^2} + \frac{\alpha}{\rho_g V_g^2} \right) \right]^{-1}$$
 5.12

Under the circumstances where the velocity of sound and density of the liquid phase are much higher than the vapour phase, as is the case here, Eq 5.12 may be simplified to

$$V_{ss} = \frac{V_g^2 \rho_g}{\rho_l \alpha (1 - \alpha)}$$
 5.13

Now the velocity of sound in an isentropic vapour is

$$V = \sqrt{\frac{\gamma P}{\rho_g}}$$

Therefore Eq 5.12 may be written as

$$V_{ss} = \frac{\gamma P}{\rho_g \alpha (1 - \alpha)}$$

In terms of mass fraction, or quality, as opposed to void fraction this may written as

$$V_{ss} = \sqrt{\frac{\alpha Pq}{\rho_g}} \left(1 + \frac{1 - q}{q} \left(\frac{\rho_l}{\rho_g}\right)\right)$$
 5.14

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Substitution of Eq 5.14 into Eq 5.11 then gives the mass discharge rate

$$\dot{m}_s = C_{q_s} \frac{\pi}{4} D_s^2 \bar{\rho} V_{ss} \qquad 5.15$$

Both  $\overline{\rho}$  and  $V_{ss}$  must be evaluated at the point of choking. If the subscript **cr** is used to denote the value of the variables at the point of choking then

$$\dot{m}_{s} = C_{q_{s}} \frac{\pi}{4} D_{s}^{2} \left( \frac{\gamma_{cr} P_{cr} \rho_{g_{cr}}}{q_{cr}} \right)^{\frac{1}{2}}$$
 5.16

Now since we have assumed there is no phase change during passage through the orifice

$$q_{cr} = q_e = q$$
 and  $\gamma_{cr} \approx \gamma$ 

If we define a critical pressure ratio above which Eq 5.16 can be considered to apply then

$$r_c = \frac{P_{cr}}{P_e}$$

and finally as above if the vapour obeys the isentropic gas law

$$\frac{P_{cr}^{\frac{1}{\gamma}}}{\rho_{g_{cr}}} = \frac{P_{e}^{\frac{1}{\gamma}}}{\rho_{g_{e}}}$$

Then Eq 5.16 may be written in terms of the expansion chamber conditions

$$\dot{m}_{s} = C_{q_{s}} \frac{\pi}{4} D_{s}^{2} \left( \frac{\gamma \rho_{g_{e}} P_{e} r_{c}}{q_{e}} \right)^{\frac{1}{2}}$$
5.17

Now  $P_{cr}$  cannot be equated to  $P_A$  since in general the pressure at the point of choking during critical flow will be higher than ambient. However,  $r_c$  may be found by equating Eq 5.10 for sub-critical flow to Eq 5.14 for critical flow. The point at which these equations are equal defines the pressure ratio at which the exit velocity first reaches the velocity of sound in the two-phase fluid and hence the point at which choking mass discharge first begins.

This mathematical equality is quite complex and is best expressed in terms of the critical void fraction as

$$\gamma \alpha_{cr} \left(1 + \frac{1}{\alpha_{cr}}\right)^2 = 2 \left( \left(\frac{1}{r_c} - 1\right) + \alpha_{cr} \left(\frac{\frac{1}{\gamma} - 1}{\frac{1}{c} - 1}\right) \right)$$
 5.18

Where

$$\alpha_{cr} = \frac{1 - q_e}{q_e} \left( \frac{\rho_L}{\rho_{g_{cr}}} \right)$$
 5.19

And

$$\rho_{g_{cr}} = \rho_{g_{e}} r_{c}^{\frac{1}{\gamma}}$$
 5.20

Unfortunately Eq 5.18 can not be solved analytically to obtain a value for  $r_c$  in terms of  $q_e$  and  $\rho_{ge}$ . However, it will be retained and used in a computer model were its solution will be by successive approximation.

# 5.2.1.4 Exit Spray Momentum

As will be described later in the experimental section it proved difficult to confirm spray exit velocity experimentally without the use of equipment which was unavailable. Therefore it was decided that the exit velocity should be estimated indirectly by measuring the exit momentum or exit thrust. Equations will now be developed for exit momentum in sub-critical and critical flow. Under conditions of sub-critical or non-choking flow the emergent jet can be assumed to be at ambient pressure and the exit thrust is simply

$$J = \dot{m}_s V_s \qquad 5.21$$

substitution of Eq 5.11 then yields

$$J = C_{q_s} \frac{\pi}{4} D_s^2 \overline{\rho} V_s^2 \qquad 5.22$$

Eq 5.21 leads to the experimental conclusion that the exit velocity in sub-critical flow can be found by simply measuring the exit thrust and the mass discharge rate.

Under critical conditions, as has been stated above, the emergent jet is at higher than ambient pressure and as a result a small correction term has to be added to Eq 5.21

$$J = \dot{m} V_{ss} + C_{q_s} \frac{\pi}{4} D_s^2 (P_{cr} - P_A)$$
 5.23

Where  $V_{ss}$  is found from Eq 5.14. Without much loss of accuracy  $P_{cr}$  may be replaced with  $r_c P_e$ . Therefore

$$J = C_{q_s} \frac{\pi}{4} D_s^2 (\bar{\rho} V_{ss}^2 + (r_c P_e - P_A))$$
 5.24

Again the exit velocity may be found by dividing the exit thrust by the mass flowrate. However, the correction term for the stored momentum must be subtracted first. Computation of the correction term requires a knowledge of the expansion chamber conditions and calculation of  $r_c$  using Eq 5.18.

Application of the equations describing mass discharge through the spray orifice, the exit velocity and thrust requires knowledge of the expansion chamber conditions. Equations describing expansion chamber conditions will now be developed.

#### 5.2.1.5 Expansion Chamber Conditions

Eq 5.6 relates the specific volume of the phases to the average fluid density. With a little rearrangement, however, it can be used to relate the quality of the fluid to the density of the phases and the average density of the fluid.

$$q = \frac{\frac{\rho_l}{\overline{\rho}} - 1}{\frac{\rho_l}{\rho_{g_e}} - 1}$$
5.25

In terms of expansion chamber conditions  $\rho$  is the mass of propellant in the expansion chamber divided by the expansion chamber volume. Now if the density of the liquid phase is assumed to be constant,  $\rho_1$  varies by less than 3% over the temperature range encountered in a twin orifice system, Eq 5.24 can be seen to relate quality to the mass of propellant contained in the expansion chamber and to the density of the vapour phase. It should also be noted that this relationship is independent of any assumption about either thermal or dynamic equilibrium. However, in order to use this equation to calculate quality, the density, and hence temperature, of the vapour phase must be known. An equation relating the expansion chamber temperature to the initial propellant temperature and the thermodynamic properties of the propellant will now be developed.

If the propellant discharge rate is sufficiently high then the residence time of the propellant in the expansion chamber will be short and heat flow into the propellant via the valve stem may be assumed to be negligible. Under these conditions the propellant flow may be considered to be adiabatic. For typical
temperature and discharge conditions experienced in common valve designs this assumption is fairly good. Calculations based upon equilibrium conditions and the temperature falls reported below indicate that heat flow adds less than 0.5% of the initial enthalpy of the propellant to the fluid during passage through the expansion chamber. In this case any flashing, or evaporation, of the liquid phase must take place at the expense of a temperature fall of the system.Neglecting kinetic energy changes this may be expressed in terms of the enthalpy of the system as

$$H = q_e ML + q_e C_g M\Delta T + (1 - q_e) M C_l \Delta T \qquad 5.26$$

A little rearrangement gives the temperature fall in the expansion chamber in terms of thermodynamic variables, mass quality and initial enthalpy.

$$\Delta T = \frac{E - q_e L}{q_e C_g + (1 - q_e) C_l}$$
 5.27

where  $\mathbf{E} = \mathbf{H}/\mathbf{M}$ 

Eq 5.26 has now related the temperature of the expansion chamber to thermodynamic variables, in order to complete the equation set a relationship needs to be established between the vapour density and its temperature.

If the propellant is considered to be present in the expansion chamber long enough to establish thermal equilibrium then the Clapeyron equation may be used to obtain the pressure of the vapour phase.

$$P_{e} = \mathbb{C}_{1} \exp\left(\frac{\mathbb{C}_{2}}{T_{e}}\right)$$
 5.28

Assuming the vapour obeys the ideal gas law the density of the vapour may then be found from

$$\rho_{g_{e}} = \left(\frac{\chi_{g_{e}} \mathbb{C}_{1}}{RT_{e}}\right) \exp\left(\frac{\mathbb{C}_{2}}{T_{e}}\right)$$
 5.29

Where  $\chi_{ge}$  is the average molecular weight of the propellant vapour phase, and may be found by the use of Raoult's Law for multi-component propellant systems.

Eq 5.25, 5.27 and 5.29 represent 3 equations describing 3 unknowns. Unfortunately this equation set cannot be solved analytically but it will be retained and used in the computer model where it will be solved by successive approximation.

Equations have now been developed which describe mass flow in terms of expansion chamber conditions and geometric variables and which describe expansion chamber conditions in terms of thermodynamic and geometric variables. Although this equation set is insoluble analytically it will be used in a computer model to simulate the discharge process. Figure 5.2 presents the equation set and summarizes the various thermodynamic and geometric variables in concise form. The computer model will now be described.

#### 5.2.1.6 Computer Model of Continuous Flow

Two alternative methods of solution of the above equation set are possible. The first method is to search for a solution of the equation set where the valve stem single phase discharge is equal to the spray orifice two-phase discharge. The second method is to model the discharge process from the point where the valve orifice is first opened and the expansion chamber is empty, to the point where equilibrium is reached. (Obviously air would be present in the expansion chamber initially, but since the air will be purged quite rapidly and since equilibrium will not be affected this will be ignored).



Note:  $-r_c$  may be found by solution of

$$\alpha_{cr}\gamma\left(1+\frac{1}{\alpha_{cr}}\right)^{2} = \left(\left(\frac{1}{r_{c}}+1\right)+\alpha_{cr}\left(\frac{\frac{1}{r_{c}}-1}{1-\frac{1}{\gamma}}\right)\right) \qquad Where \quad \alpha_{cr} = \frac{1-q_{e}}{q_{e}}\left(\frac{\rho_{l}}{\rho_{gcr}}\right)$$

and  $V_s$  is given by

$$v_{s} = \left(\frac{2(1-q_{e})}{\rho_{l}}(P_{e}-P_{A}) + \frac{2q_{e}P_{e}^{\frac{1}{\gamma}}}{\rho_{ge}\left(1-\frac{1}{\gamma}\right)}\left(P_{e}^{1-\frac{1}{\gamma}}-P_{A}^{1-\frac{1}{\gamma}}\right)\right)^{\frac{1}{2}}$$

Since the ultimate goal of the work reported here was to investigate metered flow, where a model will be required to describe the changing flows and conditions during metered discharge, the second method was considered to be more appropriate.

The basis of the computer model was to model the changes in mass flow and expansion chamber conditions over small but finite time intervals. Over the first time interval discharge only takes place from the valve orifice. The expansion chamber conditions as a result of this discharged propellant are then calculated. Having obtained new expansion chamber conditions the critical pressure ratio and discharge rates through the valve orifice and spray orifice are then calculated for the next time interval. Expansion chamber condition are then recalculated on the basis of the mass of propellant present in the chamber and the process is repeated until equilibrium is reached. Equilibrium is defined as numerically equal mass discharge rates for the valve and spray orifice.

Figure 5.3 presents a computer flow diagram for the computer model which was developed. The programming language used was Turbo Pascal. A comparison between the computer models predictions and experimental data will be made below.

Figure 5.4 presents a typical data set generated by the computer program. The data has been generated using propellant 12 with an initial temperature of 291.15 K. The valve stem orifice diameter was 0.259 mm, the spray orifice diameter was 0.56 mm and the expansion chamber volume was 0.189 mm<sup>3</sup>. The temperature and pressure falls under equilibrium discharge conditions are indicated by the arrows. This data set may be compared with figure 5.10 below, which is the experimental data obtained from a broadly similar orifice and volume configuration. It will be seen that the general forms of the profiles agree and that the temperature and pressure falls are similar.

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Figure 5.4 Computed Continuous Discharge Profiles

# 5.2.2 EXPERIMENTAL

The purpose of this phase of the experimental program was to validate the assumptions and the computer model presented in section 5.2.1. The object of the work was to measure, simultaneously, the thermodynamic conditions within the expansion chamber, the mass discharge rate and the exit velocity. In order to achieve this it was necessary to construct an 'instrumented' valve system in which temperature, pressure, mass flow and exit velocity could be measured. The results of the experimental program were to be compared to the predictions of the computer model described in section 5.2.1.6. The secondary aim of the work program was to verify the assumptions made in the derivation of the model, such that the model could be extended to describe metered discharge.

The experimental apparatus was thus designed to resemble, as closely as was possible, the apparatus used in the metered discharge experiments reported in section 6 below. The design of both experimental 'rigs' was therefore founded upon the design of a metered valve system. As already illustrated by section 1, a large number of metering valve designs exist. Thus, it seemed more sensible to adapt the components from an existing valve than to attempt to design an idealised valve with all the problems that that would have entailed.

The major criteria for the choice of a metering valve system for modification were 3 fold.

Firstly, the valve had to be simple. It needed to contain the basic elements, metering chamber, valve orifice and expansion chamber, in such a way that they could be easily changed, and modified to give a variety of valve orifice configurations. Secondly, it had to be possible to modify the valve so that it could be used to study continuous discharge. This was in order to ensure that the dimensions of the continuous discharge and metered discharge systems were as similar as possible.Thirdly, and very importantly for the metered discharge experiments, it was essential that the metering chamber could be 'instrumented' so that the pressure and temperature inside it could be measured during discharge. After studying many valve designs it was found that the only design which fulfilled all the above criteria was the Bespak BK 356,

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(Bespak plc, King's Lynn, Norfolk). This value is illustrated in figures 1.1, and is shown in more detail, in its modified continuous form, in figure 5.7.

## 5.2.2.1 Experimental Apparatus

The continuous flow test apparatus is shown diagrammatically in figure 5.5 and photographically in figure 5.6. The apparatus consists of 4 major components, a reservoir and instrumented valve assembly, a 5 channel amplifier with variable gain controls, a high speed analogue to digital converter and a standard IBM AT personal computer. The reservoir and 'instrumented' valve assembly is shown in more detail in figures 5.7 and figure 5.8. Figure 5.9 shows an 'exploded' view of the valve components.

The propellant reservoir was mounted on top of a brass manifold and sealed via an 'O'-ring. The reservoir was held in place by a clamp and 2 wing nuts. The volume of the reservoir was chosen to minimize the temperature fall of the bulk propellent during discharge. Calculations indicated that a 125 ml reservoir was adequate provided it was not used below 50% capacity. The base of the propellant reservoir was connected via the manifold directly to the inlet ports of the valve assembly. The inlet ports were enlarged to ensure that there was no restriction of flow prior to the valve stem orifice. By connecting the propellant pressure head was ensured. The maximum excess pressure due to the height of the propellant contained in the reservoir was 1.5 kPa which is less than 0.5% of the propellant saturated vapour pressures used during the experimental program, typically in the range 360-600 kPa.











Figure 5.8 Photograph of Instrumented Valve Assembly

Figure 5.9 'Exploded' View of Valve Components

For the continuous discharge experiments blank stems were obtained (stems without side orifices) and the metering chamber filling grooves were eliminated by filling with electrical solder. The stems were then machined to obtain a smooth outside finish. A side orifice (valve orifice) was then drilled in the stem but at a slightly higher position than would be the case for a 'metering' stem. After polishing the inside of the valve orifice using diamond paste the orifice diameter was measured using an optical microscope. The manufacture of valve stems in this fashion resulted in stems with identical internal dimensions to those which will be described below for the metering experiments. When assembled, flow through the metering chamber was eliminated giving valves that, when depressed, continually discharge liquid.

The spray orifices/actuators for the continuous flow experiments were manufactured from brass. Each actuator was machined individually and a spray orifice of the appropriate size drilled into a flat face machined on the side of the actuator button. The length of the spray orifice, rather than the length to diameter ratio, was maintained at a constant 1 mm. A spray orifice which was at right angles to the flow in the valve stem was employed for 2 reasons. Firstly, it more closely resembled current actuator designs and secondly to reduce the possibility of 'streaming' from the spray orifice. Fletcher (1975), had found that 'streaming' limited the investigation of large spray orifices if the valve and spray orifices were in line with the propellant flow.

The pressures in the propellant reservoir and spray head were monitored using Sensym SCX100 monolithic piezo transducers (Sensym Technics plc, Rugby, England). These transducers where chosen because of their compatibility with the propellant liquids to be investigated as well as for their high speed (typical response time 100  $\mu$ s), temperature compensation (better than 0.002% per deg K) and claimed linearity of response. The reservoir pressure was measured via a small bore stainless steel tube (0.25 mm); the spray head pressure was measured by direct attachment of the transducer to the base of the propellant channel.

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Temperatures were monitored using rapid response copper/constantan thermocouples (Labfacility plc, Hampton, England). Initial attempts to use 25  $\mu$ m thermocouples with the spray head failed because the shock of actuating the system broke the thermal junction. The thermocouples were thus manufactured from 76  $\mu$ m wire but the thermal junction was reduced in size after manufacture by abrasion with a carborundum stone. The response time for the thermocouples used are discussed further in section 6.

The exit thrust generated by the spray was measured using a 5 cm aluminium 'target' disc attached to the top of a PN 4155 Sensym strain gauge (Sensym Technics plc, Rugby, England). The use and interpretation of the thrust information will be discussed further below.

The outputs from the 5 sensors were fed to a purpose built 5 channel variable gain amplifier. The thermocouple inputs were connected to thermocouple amplifiers with simulated cold junctions.

Each channel had its own zero and gain control.

The outputs from the amplifier were connected to a multi-channel high speed analogue to digital converter (CED1401, Cambridge Electronics Design plc, Cambridge, England). The 1401 unit is a 12 bit analogue to digital converter capable of reading 5 inputs with a cycling time of better than 0.5 ms. The 1401 was software controlled from a standard IBM AT personal computer using purpose written computer code.

The pressure sensors were calibrated individually using 2 mercury manometers in series. The thermocouples were calibrated against a reference standard platinum resistance thermometer certified by the National Physical Laboratory (Kaye plc, Tonbridge, England). The strain gauge was dead weight calibrated in a horizontal position using small pre-weighed pieces of aluminium foil. In each case the calibration was carried out directly on the digital signal received by the computer software. This eliminated any need to establish the actual gain of the amplifiers and verified the software/1401/amplifier/sensor link. The whole of the test apparatus including computer hardware was situated inside a temperature and humidity controlled clean room.

# 5.2.2.2 Experimental Procedure

As will be seen from the experimental program described below (section 5.2.2.4) the test rig illustrated in figure 5.5 was used to test a number of valve/spray orifice combinations together with a number of propellant formulations. In each case the experimental procedures to determine the pressure and temperature falls across the valve orifice, the mass discharge rate and the exit velocity were the same.

The valve and brass manifold were assembled using the appropriate valve stem. The reservoir was cooled using a mixture of solid carbon dioxide and isopropyl alcohol. During cooling, the filling aperture in the canister was covered with aluminium foil to prevent condensation of water vapour inside the can. When the canister was sufficiently cool, it was filled from a bulk reservoir containing the propellant mixture to be tested. Care was taken during the filling process to ensure that the head space in the canister and the pressure port were filled with propellant vapour. After filling, the valve assembly and manifold were placed on top of the reservoir and were secured in place with the aid of the clamp and wing nuts. The assembly was then inverted into the test position and allowed to warm up.

During warming, the temperature of the apparatus was monitored by the can temperature sensor. When the temperature was above the dew point the assembly was dried and weighed. Weighings were carried out upon a 4 place analytical balance (Mettler AK160).

The sensor leads were then connected and a check run to confirm that all the sensors were functioning correctly. When the reservoir temperature had reached 291 K data acquisition was started via a keyboard instruction on the IBM PC. (291 K was chosen because although in general the temperature controlled environment was maintained at 293 K the small but finite difference between ambient temperature and the 'rig' temperature allowed reasonably

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accurate control over the discharge temperature without necessitating extremely rapid experimentation). Approximately 1 second after the start of data acquisition discharge was initiated by depression of the spray head/actuator. The discharge was maintained for approximately 10 seconds and was timed accurately with the aid of a digital stop watch. Data acquisition was timed to run for the first 5 seconds of the discharge because preliminary experimentation had shown that 5 seconds was sufficient for equilibrium conditions to be reached. After discharge was complete the sensors were disconnected and the assembly was re-weighed.

The raw sensor data, which was automatically stored as a data file on the hard drive of the PC, was then converted to absolute values using a purpose written computer program. These data were then analysed using Lotus 1-2-3; the appropriate equilibrium section of the discharge was chosen and the pressure and temperature falls across the valve orifice, and the exit thrust determined. The mass discharge rate was found from the weight difference and the discharge time. The expansion chamber pressure was also noted since this was required in order to determine the exit velocity from the exit thrust measurements (Eq 5.24).

A typical experimental discharge profile is shown in figure 5.10. This may be compared with the computer simulated profile shown in figure 5.4. It should be noted that the time axis has been extended in figure 5.10 and that the spray orifice used was slightly larger than for the computer simulation. However, the general form of the profiles together with the absolute values of pressure and temperature fall, etc., show reasonable agreement.

## 5.2.2.3 Interpretation of Exit Thrust Measurements

Preliminary experiments with the thrust transducer had indicated that provided the 'target' remained at a distance from the spray nozzle such that the 'target' disk was always of larger diameter than the expanding spray plume a constant level of thrust was obtained. (This was expected theoretically since momentum would be expected to be conserved in such an expanding spray). However, once the 'target' became smaller than the spray plume diameter, the



Figure 5.10 Experimental Discharge Profiles

thrust levels would be expected to, and did in practice, diminish. Figure 5.11 presents the peak thrust as a function of the distance between the spray orifice and target disk for a 5 cm target and a variety of spray nozzles. A 100  $\mu$ l valve and propellant 12 were used throughout.

The theoretical curve shown in figure 5.11 was derived in the following way :-

A number of authors (for example Rance, 1974, Shuen *et al*, 1985, and Solomon *et al*, 1985) have shown both theoretically and experimentally that the radial velocity profile of an expanding droplet-laden jet is of the form

$$V_r = V_x \exp\left(\frac{-2r}{x\tan\theta}\right)$$
 5.30

Where **r** is the radial distance from the spray axis, **x** is the distance from the origin of the spray and  $\theta$  is the half angle of expansion of the spray. Now the thrust on the 'target' disk can be equated to the sum of the momentum in each radial element **dr**. The thrust on each element being

$$T_{dr} = V_r \frac{dm_r}{dt} = 2\pi r \rho_r V_r^2 dr$$

The total thrust is then

$$T = 2\pi \rho_x \int_0^{R_s} r V_r^2 dr \qquad 5.31$$

Where  $\rho_x$  is the average density of the spray plume at distance x and Rs is the radius of the 'target' disk.  $\rho_x$  is assumed to be independent of r and at more than a few diameters downstream of the orifice it may be considered to be that of air.



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Figure 5.11 The relationship between Distance and Peak Thrust for a Variety of Spray Orifice Diameters

Substitution of Eq 5.30 into Eq 5.31 and integration gives

$$T = 2\pi \rho_{air} V_x^2 \frac{\sigma^2}{4} \left[ 1 - \exp\left(\frac{-2Rs^2}{\kappa^2}\right) \right]$$
 5.32

Where  $\kappa = x \cdot \tan \theta$ .

Now Fletcher (1975) has shown, by assuming that the velocity profiles for both the propellant droplets and the vapour within the spray are of the same Gaussian form as Eq 5.30, that

$$V_x \approx \frac{1}{x} \sqrt{\frac{2J}{\pi \rho_{air}}}$$
 5.33

Where J is the momentum at the nozzle exit.

Thus with substitution of Eq 5.33 into Eq 5.32 and a little rearrangement it can be shown that

$$T = J \left[ 1 - \exp\left(\frac{-2Rs^2}{x^2 \tan^2 \theta}\right) \right]$$
 5.34

Townsend (1956) showed that  $\theta$  takes the value 5.7° for an expanding air jet. Fletcher (1975) showed that this half angle was also generally applicable to flashing jets produced from twin-orifice systems.

The theoretical expression shown in figure 5.11 assumed a value of  $5.7^{\circ}$  for  $\theta$ . It can be seen that the theoretical curves predict a constant level of thrust measurement up to 10 cm from the spray origin. After this point a diminishing level of thrust is predicted. The experimental data agrees well with the theoretical predictions up to a distance of 5 cm however, after 5 cm the measured thrust level falls faster than expected. It should be remembered

however, that the above analysis takes no account of the effect of the presence of the 'target' upon the spray plume.

In fact the presence of the disk would be expected to force the spray plume to diverge with a greater half angle than that of a free plume. Thus, it would be expected that the thrust fall would be steeper than predicted. However, both the theoretical model and the experimental data show that provided thrust is measured within 5 cm of the spray nozzle a constant level is obtained.

The distance at which the 'target' is placed from the spray nozzle is thus not crucial to the accuracy of thrust measurement. As described above a distance of 3 cm was used for all the experimental determinations.

In order to verify the use of thrust measurement as a basis for assessing exit velocity from a nozzle the velocity of sound in nitrogen gas was determined using a critical nozzle and the thrust transducer described above. The results are described in **Appendix II**; suffice to say here that the experimental values obtained from thrust measurement showed very good agreement with published data.

# 5.2.2.4 Experimental Program

The variables chosen for experimental investigation were the valve/spray orifice ratio, the propellant type and mixture and the surfactant concentration. The valve/spray orifice ratio was studied using a nominal combination of 5 valve orifice diameters and 4 'instrumented' spray orifices. This enabled 20 combinations to be fully investigated and covered a valve/spray orifice ratio range of between 0.29 and 3.94. In addition to the 4 'instrumented' spray nozzles a further 5 plastic 'non-instrumented' orifices were used. However, because of the lack of instrumentation these plastic nozzles could only be used for the determination of mass discharge rates. Their inclusion was valuable because it confirmed that the material of construction of the spray nozzles was unimportant which in turn adds support to the adiabatic assumption presented in section 5.2.1.5 above. The particular diameters used and the diameter ratios obtained are summarized in Appendix III. Also shown in Appendix III are the orifice discharge coefficients, the determination of which will be described in section 5.2.2.5. below.

The propellants investigated included 2 'current' CFC's, propellant 12 and 114 and 2 'new' HFC's, propellants 134A and 227. Propellant 12 was used individually and in a 60/40 blend with propellant 114. The 60/40 combination was chosen as it represented what is at present a typical formulation pressure and because its saturated vapour pressure was similar to 227. Propellants 134A and 227 were used individually. **Table 5.1** lists the propellants studied together with their chemical names and physical properties. Since values of enthalpy of vaporisation for mixtures of propellants 12 and 114 were not available from the literature they have been calculated on the basis of mole fraction and the values for the individual components. The values of specific heat capacity and enthalpy of vaporisation reported in **table 5.1** are for a temperature of 291.15 K. In calculations using the computer model, the variation of these values with temperature was taken into account by using published enthalpy tables for each propellant.

For propellant 12, the table published by Haywood (1976) was used, for propellant 114, the values were calculated from data reported by Herridge *et al* (1988) and for propellants 134A and 227, data supplied by the manufacturers was used (Imperial Chemical Industries, 1989 & Hoechst Chemicals, 1991).

The effect of surfactant concentration was investigated using sorbitan trioleate (SPAN 85) in 60/40 blends of propellants 12 and 114. However, initial investigations covering a range of 0.25% to 2% by weight failed to show any detectable effect on either the mass discharge rate or the pressure and temperature falls across the valve orifice. It was thus concluded that Span 85 concentration had little or no effect upon atomizer pressures and no further investigations were performed during this phase. This lack of effect is perhaps not surprising since the molecular weight of Span 85 is of the order of 1000 and that even at 2% by weight the mole fraction would only be 0.0015. Its effect on vapour pressure etc. would thus be expected to be minimal.

TABLE 5.1 Physical Properties of Propellants and Propellant Mixtures used for the Continuous Discharge Experiments

Propellant	Chemical Name	Structure	
12	Dichlorodifluoromethane	CCl <sub>2</sub> F <sub>2</sub>	
114	1.2 Dichlorotetrafluoroethane	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	
134A	1.1.1.2 Tetrafluoropropane	CF <sub>3</sub> CFH <sub>2</sub>	
227	1.1.1.2.3.3.3 Heptafluoropropane	CF <sub>3</sub> CHFCF <sub>3</sub>	

	12	60/40 12/114	134A	227	
LIQUID PROPERTIES					
Density (kg/m <sup>3</sup> )	1292	1351	1260	1412	
Molecular wt.	1209	1409	1020	1700	
Enthalpy of Vaporisation (J/kg)	165.9	161.39	212.4	110.95	
Specific Heat Capacity (kJ/kg/K)	0.993	0.992	1.436	1.109	
Boiling Point at STP (K)	242.85	249.75	245.7	275.85	
VAPOUR PROPERTIES					
Ratio of Specific Heats	1.11	1.13	1.11	1.12	
Specific Heat Capacity (kJ/kg/K)	0.662	0.670	0.849	0.565	
Claperyon Constants $\mathbb{C}_1$ (x10 <sup>9</sup> )	2.263	2.131	5.242	4.986	
$\mathbb{C}_{2}(x10^{3})$	-2.432	-2.486	-2.674	-2.773	
Saturated Vapour Pressure (gauge kPa)	566.4	441.51	576.84	402.9	

In all, the combinations of valve/spray orifice and propellant formulations allowed the investigation of 80 discharge conditions for each of which temperature and pressure fall, mass discharge rate, and exit velocity were determined. The results of these experiments will now be discussed.

## 5.2.2.5 Experimental Results

#### 5.2.2.5.1 Determination of Discharge Coefficients

In order to compare the discharge profiles predicted by the model with the experimental data, the empirical discharge coefficients for the valve and spray orifices need to be determined. It would have been possible to carry out completely separate experiments to determine them, however the method chosen was to use the discharge equations developed in section 5.2.1.2 and 5.2.1.3 to calculate them from the actual experimental discharge data.

Equation 5.2 states that the mass flow through the valve orifice is proportional to the area of the orifice times the square root of the product of the fluid density and differential orifice pressure, the constant of proportionality being the discharge coefficient. Thus a plot of mass flow against this square root function should produce a straight line whose gradient is the discharge coefficient.

**Figure 5.12** shows this plot for all the data obtained from the 5 valve orifices. It can be seen that for any individual orifice the plot is linear. However the gradient, and hence the discharge coefficient, falls as the orifice diameter increases. This fall may, at first sight, seem surprising, however it should be noted that the valve orifice does not discharge into a free space; it discharges directly onto the opposite face of the interior of the valve stem. Also, typical Reynolds numbers for the valve orifice are of the order of 2000 and reference to Perry (1958) shows that the discharge coefficient for even a free non-restricted orifice can vary dramatically in this Reynolds number region. It should also be noted here that the observed decrease of discharge coefficient cannot be taken as evidence of vaporisation in the orifice and violation of Pasque's criteria (**Eq5.3**). Since, with the constant wall thickness stems used in



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these experiments, L/D decreases as D increases and Pasque's criteria shows that vaporisation is less likely, not more likely, as L/D decreases.

Figure 5.13 presents valve orifice discharge coefficient as a function of valve orifice diameter and as a function of the valve orifice to valve stem diameter ratio.

For the spray orifice, Equation 5.17 states that the mass discharge is proportional to the area of the orifice times the square root of a number of the physical parameters within the expansion chamber. Figure 5.14 shows a plot of mass flow against the square root of these parameters for all the data obtained with the 4 spray orifices. In order that the validity of Equation 5.17 was not compromised by metastability effects within the expansion chamber ( see section 5.2.2.5.5 below ), the density of the vapour phase was calculated using the Ideal Gas Law together with the measured expansion chamber temperatures and pressures rather than from the Clapeyron relationship. It can be seen that the gradients for all the orifices are reasonably linear and of the same value. Thus, the discharge coefficient for the valve orifices is 0.78. This linearity also lends limited validation to equation 5.17.

# 5.2.2.5.2 Mass Discharge

Figure 5.15 presents the mass discharge data for the 4 propellants under investigation. The ordinate represents mass flowrate in kg/sec, the abscissa is expressed as the ratio of the discharge diameter of the spray orifice to the discharge diameter of the valve orifice; valve orifice diameter is used as a parameter.

The term discharge diameter is defined as the product of the square root of the discharge coefficient and the geometrical diameter of the orifice. Discharge diameter has been used in order to correct for the effects of the decrease in the valve orifice discharge coefficient detailed in section 5.2.2.5.1.

This particular choice of abscissa was made for 2 reasons. The first is that in a continuous equilibrium discharge system the expansion chamber conditions would be expected to be the same for a given ratio regardless of the



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C) 60:40 Propellant 12/114





absolute diameters of orifices themselves. The second is that the ratio of the discharge diameters has the property that it tends to zero when the valve orifice is large and only the spray orifice is present and that it tends to infinity when the spray orifice is large and only the valve orifice is present. In either of these cases the twin orifice system approximates to a single orifice, and provided Pasque (Eq5.3) or Fauske (Eq5.4) conditions are met, the mass discharge rate would be expected to asymptote to the value for discharge of liquid propellant under its own saturated vapour pressure.

This asymptotic behaviour is perhaps better visualized in figure 5.16 where the discharge rate has been expressed as mass flow per unit area (specific discharge) with valve orifice and spray orifice used as parameters. Also shown is the specific mass discharge for liquid propellant only through a single orifice. It can be seen, as would be expected, that the specific discharge does indeed asymptote to liquid/single orifice flow at zero and infinity. Also shown in the figure are the theoretical predictions of the computer model. In general it can be seen that the theoretical predictions are quite good although there appears to be a tendency to overestimate the specific mass flow through the spray orifice at low discharge orifice ratios. There also appears to be some spread in the experimental discharge values.

However, it was stated above that the discharge diameter ratio was a suitable choice of abscissa for an equilibrium discharge process. In fact, as will be shown below, discharge through a twin orifice system is in general metastable and the degree to which equilibrium is reached depends, amongst other things, upon the residence time in the expansion chamber and hence upon the absolute mass flowrate. Some of the spread of the experimental discharge values may thus be explained by variations in the degree of metastability experienced with different valve orifice configurations. Metastability will be discussed further in section 5.2.2.5.5.





/ Cqs/Cqv · Ds/Dv



#### 5.2.2.5.3 Spray Orifice Exit Velocities

The exit velocities for the 4 propellant systems, as determined using the thrust transducer described in section 5.2.2.3 and calculated from Eq 5.24, are presented in figure 5.17. Also shown on the figures are the theoretical exit velocities based upon choked sonic flow as described by Eq 5.14. The theoretical limit of sonic or choked flow is indicated by an arrow. This limit represents the point at which the expansion chamber pressure falls below the critical pressure ratio as expressed by Eq 5.18. The ratio of the discharge diameters is again used as the abscissa.

It can be seen that over the range investigated the data does appear to confirm that the exit velocities for the various propellant/orifice systems are indeed close to the choked or sonic values. The exit velocities for the high vapour pressure propellants are of the order of 5 to 10 m/sec greater than those for the lower pressure systems. However, the large scatter of the experimental values is rather disappointing and is probably due to the inherent variability of this method of exit velocity determination.

#### 5.2.2.5.4 Temperature Fall Across the Valve Orifice

Figure 5.18 presents the computer generated and experimental temperature falls across the valve orifice for the 4 propellants and various orifice combinations. The abscissa is again expressed as discharge diameter ratio, the ordinate is the temperature fall in Kelvin. The second ordinate is the approximate expansion chamber quality. Quality was calculated using a re-written, simplified, linear form of Eq 5.27. Without much loss of accuracy, the enthalpy of the vapour and the reduction in liquid mass may be ignored.

$$q_e = \frac{C_l \Delta T}{L + C_g \Delta T + C_l \Delta T} \approx \frac{C_l}{L} \Delta T$$

Also shown in the figures are the maximum possible temperature falls, that is the temperature fall which would lower the propellant temperature to its boiling point at atmospheric pressure.



















C) 60:40 Propellant 12/114



D) Propellant 227

C) Propellant 134A



It can be seen that at low discharge diameter ratios where low quality flows would be expected, the experimental and theoretical values are in reasonable agreement. However, as the diameter of the spray orifice becomes large in comparison to that of the valve orifice and the expected temperature falls increase, the experimental values are less than predicted by the equilibrium theory. The discrepancy between the experimental values and the theoretical values increases as the predicted fall increases. This discrepancy is a manifestation of metastable flow. The propellant has insufficient time during its passage through the expansion chamber to produce enough vapour to reach equilibrium conditions.

The departure from equilibrium increases with increasing temperature fall because in general large temperature falls mean high quality flows, and high quality flows result in short residence times within the expansion chamber. Short residence times mean less time to reach equilibrium and an increase in metastability. Metastability will be discussed in more detail below.

# 5.2.2.5.5 Expansion Chamber Pressure

Figure 5.19 presents the experimental and theoretical values of expansion chamber pressure for the 4 propellants under investigation. Curves showing the theoretical pressure fall, including the metastability correction described below, are also presented.

It can be seen that the measured values are generally lower than predicted by the equilibrium model. This discrepancy is again a manifestation of metastable flow. Metastability can be expressed in terms of either a failure to reach the predicted temperature fall, as a result of insufficient evaporation and vapour formation, or as a failure to reach the predicted pressure. In general, in metastable flow the experimental pressure would be expected to be less than either the experimental saturated vapour pressure or the predicted equilibrium pressure. However, since the temperature of the vapour would be higher than the equilibrium value (because the temperature does not have time to fall as far as predicted), the discrepancy between the equilibrium pressure and the experimental pressure would not be expected to be as great as the discrepancy

#### Figure 5.19 Expansion chamber Pressure A) Propellant 12

B) Propellant 134A





C) 60:40 Propellant 12/114







between the measured and predicted temperature falls. This will be discussed further below.

#### 5.2.2.5.6 Metastability Effects

The heat and mass transfer processes by which evaporating propellant approaches equilibrium in the expansion chamber of a twin orifice system are undoubtedly very complex. Thus, although a fundamental approach to the explanation of the discrepancies between the equilibrium theory and the experimental data reported in the above sections would have been desirable, an empirical approach was the only practical option at this stage.

In general, the heat and mass transfer processes involved in such an approach to equilibrium would be expected to be of exponential form. The degree to which equilibrium is reached would be expected to depend on the residence time of the propellant within the expansion chamber.

At zero residence time there is no time for evaporation to take place and the ratio of the experimental expansion chamber pressure to the theoretical equilibrium pressure would be zero. This is so since by definition there would be no time for any propellant to evaporate. Conversely at infinite residence time the ratio would be expected to be 1, since by definition the equilibrium point must be reached in an infinite time. An exponential equation of the following form would thus seem appropriate.

$$\frac{P_e}{P_T} = 1 - \exp\left(\beta_{me}R_t\right)$$
 5.35

Where  $\beta_{me}$  is a constant incorporating the heat and mass transfer coefficients and the surface area to volume ratio of the propellant during its passage through the chamber, and  $\mathbf{R}_t$  is the theoretical residence time. Attempts to fit the experimental data to this equation proved difficult and resulted in low correlation coefficients. An equation of the following form was found to be more appropriate.
$$\frac{P_e}{P_T} = 1 - \alpha_{me} \exp(\beta_{me} R_t)$$
 5.36

Where  $\alpha_{me}$  is an additional constant.

This latter form was found to be necessary in order to correct for the second order effect of the residence time not being equal to that predicted theoretically on the basis of equilibrium flow and also to correct for the fact that the surface area to volume ratio of the propellant during passage through the chamber would depend upon the quality of flow.

The above equation obviously leads to the paradox that it predicts a finite level of metastability for a zero residence time. Its application therefore must be restricted to the range of residence times encountered in the experimental program.

A similar argument to that presented above can also be used to develop an empirical equation to describe the effects of metastability upon the experimental temperature falls. In this case an equation of the following form was found to be appropriate.

$$\frac{\Delta T_e}{\Delta T_T} = 1 - \gamma_{me} \exp(\delta_{me} R_t)$$
 5.37

Where  $\gamma_{me}$  and  $\delta_{me}$  are constants,  $\Delta T_{e}$  is the experimentally measured fall and  $\Delta T_{T}$  is that predicted by the equilibrium model.

Table 5.2 presents the values of the various coefficients for the four propellant systems together with the correlation coefficients and the range of theoretical residence times covered by the experimental data. It can be seen that even for equations of the above form the correlation coefficients are rather weak, although acceptable.

Propellant	P <sub>e</sub> /P <sub>T</sub>			$\Delta T_e / \Delta T_T$			R <sub>t</sub> Range
	$\alpha_{\rm me}$	$\beta_{\rm me}$	r <sup>2</sup>	Ϋ́me	δ <sub>me</sub>	r <sup>2</sup>	(ms)
12	0.35	22.3	0.79	0.37	5.7	0.78	21 - 647
134A	0.29	18.2	0.64	0.44	8.3	0.75	35 -556
60:40 12:114	0.41	26.6	0.61	0.61	10.0	0.81	42 - 761
227	0.48	20.0	0.80	0.74	11.8	0.87	47 - 794

TABLE 5.2 Summary of Empirical Constants for Metastability Corrections

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Note.  $r^2$  is the correlation coefficient

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It can also be seen, as evidenced by the larger negative exponential coefficients, that as discussed above, metastability has a less dramatic effect on expansion chamber pressures than on expansion chamber temperature falls. It should also be noted that the values of the coefficients for all the propellants are very similar.

#### 5.2.2.6 Discussion

The discharge of a propellant liquid through a twin orifice nozzle system has been successfully modelled using, in the first instance, equilibrium thermodynamics. At spray to valve orifice diameter ratios of below about 1.5 the equilibrium model predicts the conditions within the expansion chamber and the mass discharge rates extremely well. However, at diameter ratios greater than 1.5 the discrepancy between theory and experiment steadily grows. The experimental expansion chamber pressures and the valve orifice temperature falls are less than predicted. The mass discharge prediction however is still reasonably good.

This discrepancy between equilibrium theory and experiment is explained as metastable flow. The discharge is in fact a quasi-equilibrium state since there is insufficient time, during passage through the expansion chamber, for complete evaporation to occur and equilibrium to be reached. An empirical relationship between temperature and pressure metastability and residence time has therefore been developed. It was found that no correction was necessary for the mass discharge data. This is probably because metastability has two effects on the mass discharge equations. It reduces the expansion chamber pressure and vapour density which appear on the denominator of **Eq 5.17**, but it also reduces the quality of flow which appears in the numerator of **Eq 5.17**. The net effect, although positive, is therefore quite small.

The data reported in the above sections will now be used to relate the expansion chamber and nozzle exit conditions to the droplet size produced during the continuous atomisation process. The empirical correction terms developed in section 5.2.2.5.6 will be retained for use in the computer model describing the metering process which will be detailed in section 6.

### 5.3 **ATOMISATION**

The literature describes 2 major mechanisms which may be involved in atomisation from twin orifice liquified-gas generators. The first, and possibly the most favoured, although on very limited experimental evidence, is explosive bubble growth or 'Flashing'. The second is so called 'airblast' atomisation where the aerodynamic break-up of liquid ligaments is caused by dynamic forces between the vapour and liquid phases. The purpose of the work reported in this section was to relate the experimental data on expansion chamber pressures and temperatures to the droplet size generated at the spray orifice and thereby elucidate which atomisation mechanism, or mechanisms, are dominant.

In order to do this a reliable method of assessing the initial droplet size produced by the atomiser was needed. Initial attempts at droplet sizing were made using a Malvern 2600HSD laser diffraction size analyser. It was intended that the drop size would be measured at a number of points along the spray axis and the data would then be extrapolated back to the orifice exit to give an estimate of the initial droplet size. However, because of its limited operational window and lack of resolution (see below **section 5.3.2**), its general application to the experimental investigation had to be abandoned and a more fundamental approach was adopted. The limited data obtained using the Malvern did, however, produce some interesting insights into the effects of surfactant concentration and propellant vapour pressure on the development of the spray plume. A limited amount of data will thus be presented below.

The second approach to determining the droplet size produced at the spray nozzle was to use propellants containing known amounts of dissolved surfactant and then to size the residual aerosol when the propellant had completely evaporated. The spray was discharged into a large holding vessel, where complete evaporation was allowed to take place, and then sampled via an APS33B aerodynamic particle sizer in order to determine the residual particle size distribution. Simple calculation then allowed an estimate of the initial droplet diameters. This technique was used to investigate the effects of orifice diameter, propellant vapour pressure and surfactant concentration upon the initial droplet diameter produced by the atomiser. A full description of the apparatus, experimental method and results is presented below.

#### 5.3.1 INITIAL DROPLET DIAMETERS

#### 5.3.1.1 Experimental Apparatus

#### 5.3.1.1.1 The Aerodynamic Particle Sizer

The aerodynamic particle sizer, or APS, was developed by Remiarz et al (1977) as a high resolution aerosol sizing instrument to assess aerosol particles in the size range 0.5 to  $15\mu$ m. The instrument was a direct development from earlier work by a number of authors (for example Dahneke & Flachsbart, 1972 or Agarwal & Fingerson, 1979) who used laser doppler velocimetry to measure the velocity of particles as they exited an accelerating nozzle. The APS uses a twin beam laser velocimeter to measure the time of flight of aerosol particles as they exit an accelerating nozzle; the air velocity at the nozzle exit is approximately 150 m/sec. A timer is triggered when the particle passes through the first beam and is halted when it traverses the second beam. The time taken to travel between the two beams is dependent upon the deceleration of the particle and hence upon its inertia and aerodynamic diameter. At small particle diameters, 0.5  $\mu$ m, the resolution of the instrument is easily better than 0.1  $\mu$ m (Remiarz, 1977). At large diameters the resolution is poorer but still better than 1  $\mu$ m at a diameter of 25  $\mu$ m.

The high resolution and monotonic calibration function of the instrument (Baron, 1986) made it an almost ideal choice for investigating the residual sprays from twin orifice atomisers. However, the instrument does exhibit some non-ideal characteristics.

Firstly, in order to avoid coincidence problems within the velocimeter, particle concentrations must, in general, be below 200 particles per cubic centimetre. Particle concentrations in typical spray clouds are many orders of magnitude greater than this and a dilution system, based on a standard diluter and large volume sampling chamber, had to be employed in order to reduce concentrations to an acceptable level (see below section 5.3.1.1.2.).

Secondly, it has been shown by Griffiths et al (1986) that the acceleration of liquid droplets in the nozzle of the APS can result in shape

distortion and an overestimate of true droplet diameter. Since the residual aerosol from the sprays investigated in this thesis do indeed consist of surfactant liquid droplets this was initially a cause for concern. However, underestimation of droplet diameter is limited to droplets greater than approximately 5  $\mu$ m aerodynamic diameter and only increases at about 1.5 percent per micron thereafter. As will be seen below, most of the residual aerosols sized as part of this investigation have mass median diameters in the range 2 to 6  $\mu$ m it was therefore felt sizing errors due to droplet distortion represented a very small source of error.

A third error is related to so called phantom particle counts which may arise in the APS for a variety of reasons. The most important in the context of this study is the triggering of only one of the APS's two velocimeter beams. This effect will be discussed in more detail below (section 5.3.1.2).

#### 5.3.1.1.2 The Experimental Rig

Figure 5.20 shows the experimental arrangement for the residual particle size measurements carried out using the APS33B. A 60 litre holding vessel incorporating an 8 cm injection port and a 4 cm sampling port was placed on top of a 100:1 aerosol diluter (Model 3320, TSI Incorporated, St Paul, USA). The diluter was in turn stacked on top of an Aerodynamic Particle Sizer (Model 3310 TSI Incorporated St Paul, USA). The model 3310 APS has an operational size range of 0.5 to 30  $\mu$ m. The 100:1 diluter reduces the aerosol concentration by isokinetically sampling 1 percent of the incoming air and then recombining this sampled air with the remaining 'by-pass', air after the 'by-pass' air has been filtered (Remiarz and Johnson, 1984).

The manufacturers of the instrument incorporate a correction for the sampling efficiency of the diluter in the computer software which calculates the size distribution of the test aerosol. The whole apparatus, including the aerosol generator, described above in section 5.2.2.1, was contained in a temperature controlled environment which was maintained at 291 + - 1K.



Figure 5.20 Photograph of the Residual Droplet Test Rig

#### 5.3.1.2 Experimental Procedures

The experimental procedure consisted of discharging a 1 second aerosol burst into the holding vessel, waiting approximately 5 seconds for evaporation to occur and then drawing the aerosol into the APS for analysis. A minimum of 150,000 droplets where counted for each determination and each determination was repeated 5 times for each atomiser/formulation configuration. The 5 second delay period was estimated by investigating various delay times and finding the minimum time which produced a stable aerosol size distribution.

Because of the large numbers of fine droplets produced in residual aerosol sprays the APS velocimeter had to be operated at reduced gain. This was in order to reduce the number of phantom counts produced by fine particles triggering only one of the two measurement beams. Triggering of only one beam results in the instruments timer running until the random arrival of the next particle. Since the arrival of the next particle is completely random, this results in a wide range a flight times being computed and spurious particles are 'generated' across the whole of the operating size range. While this presents very few problems if data is analysed as number distributions it can grossly distort the weight distribution calculated from the number data. Reducing the gain means that fewer single beam events occur and this reduces the number of spurious counts. This in turn results in a weight distribution which is more truly representative of the sampled aerosol. Lowering the photomultiplier gain also raises the lower size threshold of the machine and fewer fine particles are counted. However, since these fine particles represent only a very small percentage of the weight of the sampled aerosol it was considered that this would not unduly reduce the accuracy of the computed weight distributions.

#### 5.3.1.3 Experimental Program

As described above the experimental program was designed to elucidate the dominant mechanisms in the atomisation process. The main problem with this program, from a theoretical point of view, as will be explained below, is that the major atomisation variables are not truly independent in a twin orifice system of this type.

Thus, a number of formulation variables, as well as physical variables, were `investigated in order to enable the atomisation mechanism to be delineated.

The saturated vapour pressure of the propellant was varied by using mixtures of propellant 12 and 114 ranging from 100 percent 12 to 20:80 propellant 12:114. The droplet size produced by propellants 134A and 227 were also investigated. The effects of the valve orifice dimensions and valve to spray orifice ratio were investigated using 6 spray orifice diameters (4 instrumented metal, 2 plastic) and 3 valve stem diameters. The effects of surfactant concentration was also examined using various concentrations of sorbitan trioleate in both pure propellant 12 and 40:60 propellant 12:114. The formulations used, together with the physical properties relevant to atomisation are summarised in **Table 5.3**. The orifice diameters and discharge ratios are summarised in **Appendix III**.

#### 5.3.1.4 Results

#### 5.3.1.4.1 Orifice dimensions

Figure 5.21 and figure 5.22 present the effects of spray to valve orifice diameter ratio for 2 propellant mixtures, pure propellant 12 and 40:60 propellant 12/114 respectively; valve orifice diameter is expressed as a parameter. The surfactant concentration was 2% w/w in both mixtures. The right hand ordinate is the residual mass median diameter as measured by the APS33B and the left hand ordinate is the initial droplet diameter calculated from the following relationship :-

$$d_{i} = \frac{d_{r}}{\sqrt{\rho_{s}}} \left(\frac{\rho_{s}}{\rho_{l} w}\right)^{\frac{1}{3}}$$
 5.38

		Propellant Formulation <sup>1,2</sup>					
		12	80:20	60:40	40:60	134A	227
Liquid density	kg/m <sup>3</sup>	1330	1358	1394	1429	1260	1412
Surfactant <sup>3</sup>		Span85	Span85	Span85	Span85	Peg300	Peg300
% w/w		2.0,1.0 0.5,0.25	0.25	0.25	2.0,1.0, 0.5,0.25	2.0	2.0
Surface tension <sup>4</sup>	mN/m	9.2	9.8	10.3	10.5	8.8	7.9
Viscosity	cP	0.26	-	-	-	0.23	-
Saturated Vapou Pressure	r kPa	566.4	508.4	441.5	367.8	576.8	402.9
Saturated Vapou density	r kg/m <sup>3</sup>	28.1	25.8	23.1	20.2	28.1	25.6

# TABLE 5.3 A Summary of the Physical Parameters Relevant to Atomisation forVarious Propellant Formulation

1. All values quoted at 291K

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- 2. Values for all variables except surface tension obtained from :-ICI technical notes (1989)
  ICI KLEA 134a Preliminary Data sheet (1990)
  Hoechest Aktiengesellschafts (1991)
- 3. Density of Sorbitan trioleate (Span85) =  $950 \text{ kg/m}^3$ " of Peg300 =  $1120 \text{ kg/m}^3$
- 4. Surface tension is not dependant upon 'surfactant' concentration (see Appendix IV)

Ø ဖ 2 0 4 4 Residual MMAD (um) × Valve Orifice Daimeter Figure 5.22 The Effect of orifice ratio on Initial and Residual Droplet Diameter (40:60 Prop. 12:114, 2% w/w Span 85) **0.259mm** 0.589mm 1.006mm  $\diamond$ თ ×  $\triangleleft$ Х  $\diamond$  $\triangleleft$ Cqs/Cqv • Ds/Dv  $\diamond$ × N  $\diamond$ ⊲ ×  $\triangleleft$ Initial MMAD (um) 4 +/- 1 SD 0  $\triangleleft$ 0 ⊲ ю 0 30 25 20 15 10 5 ο œ Θ 2 0 4 Residual MMAD (um) Valve Orifice Daimeter Figure 5.21 The Effect of orifice ratio on Initial and Residual Droplet Diameter (Propellant 12, 2% w/w Span 85) +/- 1 SD 0.259mm 0.589mm 1.006mm თ ы .  $\diamond$  $\diamond$ Cqs/Cqv • Ds/Dv 2 0 •  $\diamond$ Initial MMAD (um)  $\diamond_{\Box}$ с С 0 30 25 20 15 ę S 0

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Where  $\mathbf{d}_{i}$  is the initial median volumetric diameter,  $\mathbf{d}_{r}$  is the residual median aerodynamic diameter,  $\boldsymbol{\rho}_{s}$  is the density of the surfactant liquid,  $\boldsymbol{\rho}_{i}$  is the density of the propellant and  $\mathbf{w}$  is the weight fraction of surfactant contained in the original propellant solution. (The concentrating effect of vapour evaporation in the expansion chamber, before atomisation, is estimated to produce a maximum error of less than 5 percent in the calculation of the initial droplet diameter and has thus been ignored for the purposes of data presentation). Each data point is the mean of 5 determinations. The standard deviation for each test condition was broadly similar and a typical +/- 1 standard deviation is shown in the top right hand corner of both figures.

It can clearly be seen from these figures that for both propellant systems the initial droplet diameter exhibits a broad minimum, the position of which depends on the diameter of the valve orifice. It can also be seen, that the lower vapour pressure propellant produces a coarser spray. These observations are in line with the Malvern investigations reported below.

Figure 5.23 presents similar data for the HFC propellants 134A and 227. In this case the dissolved non-volatile agent is PEG300. It should also be noted that only the initial droplet diameters are presented in figure 5.23 since the bracketed term on the right hand side of Eq 5.38 is different for each propellant formulation.

In a qualitative sense these curves are similar to those reported by Tsuda (1989) shown in **figure 2.6**. Tsuda used a Malvern analyser to assess the droplet size produced from a kerosene/butane mixture sprayed from a twin orifice nozzle. He measured the droplet diameter 50 cm downstream of the spray orifice. The general form of the curves presented in Figures **5.21**, **5.22** and **5.23** would thus appear to be a characteristic feature of atomisation from twin orifice liquefied-gas generators. The mechanisms leading to this form will be discussed below.





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#### 5.3.1.4.2 Surfactant Concentration

**Figure 5.24** presents the effect of surfactant concentration, in the range 0.25 to 2% by weight, upon the initial droplet diameter generated from pure propellant 12 and a mixture of 40:60 propellant 12:114. The valve orifice diameter for these determinations was 0.26 mm and the spray to valve orifice diameter ratio was approximately 1.

It can be seen that increasing the surfactant concentration marginally decreases the initial median droplet diameter. However, this decrease is quite small in comparison to the standard error of measurement and may in fact be an artifact of the sizing and calculation method. This postulate is supported by the fact that the addition of sorbitan trioleate to these propellant formulations does not alter surface tension values (Table 5.3) and in tests reported in section 5.2.2.4 did not affect expansion chamber pressures or temperature falls. This conclusion is also in line with sizing data obtained by Malvern diffraction analyser reported in section 5.3.2 below.

#### 5.3.1.4.3 Propellant Vapour Pressure

The initial droplet diameters for propellant vapour pressures in the range 180 to 460 kPa gauge, are shown in **figure 5.25A** and **5.25B**. **Figure 5.25A** presents the data with discharge diameter as the abscissa and saturated vapour pressure as a parameter. Figure 5.25B presents the data with saturated vapour pressure as the abscissa and discharge diameter ratio as a parameter. The valve orifice diameter for these determinations was 0.26 mm. Perhaps not surprisingly it can be seen that initial mass median droplet diameter decreases as vapour pressure increases.

Also shown in **figure 5.24B** are regression lines for each spray to valve orifice ratio showing that initial droplet diameter is proportional to an inverse power of the propellant saturated vapour pressure (See section 5.3. below).

Figure 5.24 The Effect of Span Concentration on Initial Droplet Dia. (Dv - 0.259mm, Ds/Dv - 1.67, 12:114)



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800 600 Figure 5.25B The Effect of Propellant Vapour Pressure on Droplet Diameter (Dv • 0.259mm, 12:114, 0.25% Span 85) 400 200 10 - 4 Cq#/Cqv • D#/Dv Initial MMAD (um) 2.18 2.84 3.76 1.64 . 0 +0 0 0 0 0 0 0 0 ن م 35 30 25 20 15 4 × □ॳ• Figure 5.25A The Effect of Propellant Ratio on Droplet Diameter (Dv = 0.26mm, 12:114, 0.25% Span 85) ო Х + ×  $\Box \diamond$ +2 × Ø +. Propellant Ratio W/W Initial MMAD (um) 60:40 80:20 40:60 20:80 100 . + ×  $\diamond$ 0 404 35 30 25 20 15 10 ō ŵ

Vapour Pressure (kPa)

Cqs/Cqv • Ds/Dv

$$d_i = \frac{\mathbb{C}_3}{P_s^n}$$
 5.39

In each case the correlation coefficients for the regression lines were better than 0.93 indicating a good fit to the data.  $\mathbf{n}$  varied from 0.46 to 0.52 depending upon orifice ratio.

In general, the above equation would also be expected to hold if the expansion chamber pressure is substituted for the saturated vapour pressure. This is so since for all the orifice diameter ratios tested the degree of evaporation and hence the pressure in the expansion chamber is approximately proportional to the original vapour pressure (see Section 5.2).

It should also be noted here that the width of the droplet size distributions, as measured by the geometric standard deviations (GSD) of the aerosol clouds, showed no particular trend with either vapour pressure or any of the other formulation/geometric variables. The clouds were in general very polydispersed for all the experiments, with GSD's ranging from 1.75 to 2.4.

#### 5.3.1.5 Discussion

The main problem associated with attempts to delineate the atomisation mechanism involved in twin orifice liquefied-gas generators is that the key atomisation variables are not, and can never be, independent. For example, it was shown in section 5.1 that when evaporation takes place within the expansion chamber it does so adiabatically. Thus, the propellant must undergo a temperature fall in the expansion chamber proportional to any increase in quality of the flow. Hence quality and temperature, and thus the degree of superheat of the emerging liquid, are related. Higher quality flows are generated at the expense of lower superheats.

Additionally, because the density and pressure of the vapour phase are related to temperature, via either the Claperyon equation or the Ideal Gas Law, expansion chamber pressure and vapour density also fall as the quality of flow increases.

In general terms, the absolute value of all of the thermodynamic variables will fall as the quality of the flow increases.

Now since the quality of flow at the spray nozzle increases with spray orifice to valve orifice ratio (see section 5.2 above), and since the degree of superheat decreases with increasing spray orifice to valve orifice ratio it is tempting to believe that 'airblast' atomisation and 'Flashing' should show an opposite dependence upon the discharge diameter ratio. This is so because 'airblast' mechanisms become more efficient with higher quality flows, whereas 'flashing' mechanisms becomes less efficient with decreasing superheat (see section 2). However, in reality, because vapour density and atomiser pressure are also major variables in 'airblast' atomisation, and since both of these decrease with increasing quality, it is actually very difficult to use this type of simple argument to explain either the shape of the curves shown in figure 5.21, 5.22 and 5.23, or to ascribe unequivocally an atomisation mechanism.

However, some clues to the atomisation mechanisms and an explanation for the shape of the droplet size curves observed in both this study, and that reported by Tsuda (figure 2.6), may be found in the pressure dependence reported in figure 5.24 and in the work of Lefebvre (1988) reported in section 2 (figure 2.4).

It will be recalled that Lefebvre used non-flashing liquids and atomised true homogeneous vapour/liquid mixtures through small single orifices. This work is important in the context of the present study because in Lefebvre's study flow through the spray nozzle would have been qualitatively similar to that investigated here, but bubble growth and 'flashing' downstream of the spray nozzle would not have occurred. Lefebvre showed that droplet size was very dependant upon the quality of flow through the spray nozzle and upon the atomiser pressure. The quality dependence is in indicated in **figure 2.4B**. The curve presented in the figure was added to Lefebvre's original data by the current author. It shows that the initial droplet diameter is proportional to an inverse power of the quality of the flow.

$$d_i = \frac{\mathbb{C}_4}{q^{0.44}}$$
 5.40

The correlation coefficient for all of Lefebvre's data was 0.94.

If it is assumed that the atomisation mechanism in Lefebvre's study is similar to that reported here for twin-orifice liquefied-gas generators, that is it is assumed that 'airblast' type mechanisms are involved, then the general form of the droplet size/spray orifice ratio curves may be explained by summing the effects of increasing quality, identified by Lefebvre, with those of decreasing of expansion chamber pressure identified above. That is, the shape of the curves in **figure 5.21**, **5.22** and **5.23** is the result of the competing effects of increasing quality of flow and decreasing atomiser pressure. At low orifice discharge ratios the quality of flow increases rapidly and reduces droplet size. At higher orifice discharge ratios, where the effect of increasing quality only marginally improves droplet size, the decrease in pressure becomes important. Combining Eq 5.39 and **5.40** and casting the equation in dimensionless form thus yields a general correlation which fits all the data in **figure 5.21**, **5.22** and **5.23**.

$$d_i = \frac{\mathbb{C}_5}{q_e^m \left\{\frac{P_e - P_A}{P_A}\right\}^n}$$
 5.41

where n is 0.46, m is 0.56 and  $C_5$  is 8.02. This equation together with the droplet data from the above figures is presented in figure 5.26. The correlation coefficient for the data was 0.94 and in general it can be seen that the agreement is good, especially when the errors in the droplet size determinations are considered.

The shift in the minimum droplet diameter to lower orifice ratios as the valve orifice diameter increases is now explained as the effects of metastability. The larger the valve orifice the greater the discharge rate and the shorter the residence time within the expansion chamber. As evidence by Eq 5.34 and 5.35 the shorter the residence time the greater the effect of metastability and the





lower the expansion chamber pressure. Thus, the effect of the pressure term in the above equation becomes greater at lower orifice ratios and the droplet size increases at smaller discharge ratios. When viewing Eq 5.41 it must also be remembered that decreasing pressure also means a concomitant decrease in vapour density. However, because of the similar vapour densities generated by most propellant systems and the almost linear relationship between expansion chamber pressure and vapour density, it was not possible to delineate the effects of vapour pressure and density as a separate variables.

It is now possible to postulate a physical atomisation mechanism. It will be remembered that all of the 'airblast' correlations reported in section 2 showed that droplet size was inversely proportional to a power of the Weber number. This implies that it is the relative velocity between the liquid and vapour phase, together with the vapour density, that controls droplet size. However, in the system under discussion here there is, in principle, no initial velocity between the liquid and vapour. Indeed, one of the major assumption in the equilibrium discharge model presented above is that there is zero velocity slip between the phases. Additionally it has been shown that the exit velocity from twin-orifice liquefied gas generators is choked, or sonic. Exit velocity is therefore fairly constant over a wide diameter ratio and hence does not decrease with reducing expansion chamber pressure in a manner similar to conventional airblast atomisers.

All of the developments of efficient 'airblast' atomisers to date have been based on the principle of squeezing a liquid ligament to as small a diameter as possible before it is allowed to break into droplets. It is thus instructive to ask how with this current atomiser, which is very efficient by modern standards (Lefebvre, 1987), this squeezing may occur. One of the possible mechanisms is that the rapid expansion of the vapour phase between the ligaments squeezes and shears them to generate droplets. This effect, together with the more conventional 'airblast' mechanism is illustrated in **figure 5.27**. It is worth noting here that both Lefebvre (1987) and Soloman (1978) in their investigations on 'aerated' sprays preferred to talk about the gas bubbles embedded in the liquid phase 'exploding'. However, since the void fractions in these generators usually exceeds 50% then the vapour would be expected to be





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## Figure 5.27 Aerodynamic Shear in Conventional 'Airblast' and Homogneous (twin orifice) Atomisers

the continuous phase and bubble flow would appear to be an inappropriate description of atomiser conditions. It can now be seen why atomiser pressure, quality and vapour density are important variables in this type of system. In effect the quality and pressure of the flow controls the energy available for release on exit from the nozzle. The vapour density then comes into play via the Weber number as the gas expands and shears the ligaments into droplets. This may also explain the rapid spray expansion observed by Fletcher (1973) and Oza (1969) (see section 2).

However, as stated above, the degree of superheat of the emergent ligaments also decreases with increasing quality of flow and it is difficult without further evidence to state unequivocally that 'airblast' is the only mechanism responsible for droplet generation. Calculation of the bubble growth rates, using Eq 2.10 for the propellant systems under test does show that bubble growth may just be rapid enough to disrupt the ligaments before they break via aerodynamic forces. However, the standard bubble growth models are based on an infinite heat source maintaining the degree of superheat throughout the bubble growth period. In reality with a 'flashing' liquid where a large amount of the liquid phase 'flashes' superheat is 'used-up' during flashing and the degree of superheat continually decreases as the bubbles grow. Eq 2.10 thus needs modification to give the instantaneous growth rate  $dC_{r}/dt$ .

$$\frac{dC_T}{dt} = 2 \sqrt{\frac{3}{\pi}} \alpha_k \frac{\rho_l}{\rho_g} \frac{C_p}{L} \left( T_i - (N \ 4 \frac{\pi}{3} \ R_b^3 \ \rho_g \ L) \right)$$

5.42

Where  $T_i$  is the initial temperature, N is the bubble density and  $R_b$  is the bubble radius. The actual growth times for the bubbles are then found by integration. Unfortunately the bubble density for these systems is unknown. However estimates based on the work of Edwards (1968) for water show that N is likely to be of the order of 10<sup>8</sup> to 10<sup>9</sup>. Using this value and performing the necessary numerical integration of Eq 5.42 suggests the growth times may be increased by as much as 10 percent for the range of qualities investigated here. The expansion of the vapour phase as it exits the nozzle would produce cooling due to adiabatic expansion. The temperature of the vapour phase being given by the vapour expansion ratio.

$$\frac{T_A}{T_e} = \left\{ \frac{v_e}{v_A} \right\}^{\alpha - 1}$$
 5.43

Since up to 20 percent of the propellant's mass may be in the vapour phase this represents a considerable heat sink and cooling effect.

In summary, the observed trends in droplet diameter show many similarities with previous observation on 'non-flashing' homogeneous vapour/liquid atomisers. Thus, although calculations indicate that bubble growth rates may be fast enough to contribute to atomisation it is believed that 'airblast' processes are dominant. Some proposals for further experimental investigation designed to settle this point will be described in **section 8**. It should also be noted that the correctness, or otherwise, of the arguments presented in the foregoing paragraphs does not detract from the value of **Eq 5.37** which is correct regardless of the mechanisms involved.

#### 5.3.2 **DROPLET DYNAMICS**

In section 5.3.1 a correlation relating the initial droplet diameter produce by a twin-orifice atomiser to the thermodynamic variables within the expansion chamber was proposed. The dynamics of plume development and the kinetics of droplet evaporation will now be considered.

#### 5.3.2.1 Experimental Apparatus

#### 5.3.2.1.1 Diffraction Analyser

The technique of using the diffraction pattern produced by an array of droplets to estimate diameter has been known for many years (Schmidt, 1945). However, it was not until the late 1970's and the advent of powerful

desk-top computers that the diffraction analyser as we now know it was described by Swithenbank (1977). The diffraction analyser uses the intensity distribution of the Fraunhoffer diffraction pattern produced by spray droplets as they pass through an incident monochromatic light beam, to calculate droplet size. Fine droplets diffract light at high angles whereas large droplets diffract light at low angles. The analysis of the angular light intensity can thus be used to determine droplet size. In the commercial instrument (Malvern 2600HSD) an expanded He-Ne laser beam is used as the incident light source and a Fourier transform lens is used to focus the diffracted light onto a purpose built annular detector.

The main advantages of this type of instrument are that it is quick, non-intrusive and the velocity of the droplets as they pass through the light beam has no effect on the diffraction information (Dodge et al, 1987). These attributes make it ideal for investigating liquid spray systems (Dodge, 1987). However, it does suffer from a number of limitations in the context of the investigations reported here.

When attempting to 'view' close to the nozzle exit it is found that in addition to the diffraction produced by the droplets, the turbulent vapour phase produces large amounts of refraction. This refraction has the effect of spreading the incident light beam and 'fogging' the low angle diffraction information. This in turn results in either a severe limitation in the operational size range of the instrument, the necessary acceptance of 'ghost' large droplets, or it restricts the use of the instrument to distances at which the entrainment of air has reduced the turbulent refractive index changes to an acceptable level. This in effect means that the diffraction analyser cannot successfully be used at a distance closer than about 8 to 10 cm from the spray nozzle exit. It is interesting to note here that this effect also probably precludes the use of laser holography to investigate this type of spray system, since similar 'fogging' of the phase information contained within a hologram would also occur close to the nozzle exit.

The second limitation is upon the maximum distance at which the diffraction analyser can be used. In order to avoid vignetting of the diffracted light the whole of the width of the droplet spray must remain within the focal length of the focusing lens. This means that the spray can not be measured `once its width has increased beyond the focal length of the lens. Additionally, since the cross sectional area of the spray increases with distance the proportion of the plume viewed by the diffraction analyser decreases. Hence, the intensity of the scattered light falls with a concomitant increase in signal to noise ratio and a reduction in the accuracy of the size determination.

These phenomena together restrict the operation of the instrument to a window extending over a range of approximately 8 cm to 24 cm from the spray orifice exit.

#### 5.3.2.1.2 Experimental Rig Design

Figure 5.28 shows the experimental arrangement for the droplet size determinations using the diffraction analyser. The pressure canister was maintained at right angles to the laser beam by means of an adjustable retort clamp. The distance from the beam to the spray orifice exit was varied by moving the retort along a horizontal 'distance' arm. During each determination the spray was prevented from re-entering the measurement zone by extracting the 'waste' aerosol via a wide necked funnel attached to a high volume vacuum cleaner. Because the forward velocities of the droplets were very high, no attempt was made to compensate for any horizontal settling in the cloud during transit to the beam.

#### 5.3.2.2 Experimental Procedures/Program

Each determination started with actuation of the aerosol spray followed by a 1 second delay to allow the system to come to equilibrium. After the delay, the measurement was initiated via the computer keyboard. A 100 mm lens was employed throughout and 100 measurement sweeps were averaged before the standard Fraunhoffer diffraction, 'liquid droplet spray', model was used to de-convolute the diffraction image. As stated above, only a limited number of investigations were performed before it was realised that the instrument lacked the necessary resolution to give an accurate estimate of what was happening at



Figure 5.28 Photograph of the Diffraction Droplet Test

the spray orifice exit. These investigations involved determinations with a single orifice ratio and various propellant and surfactant concentration.

#### 5.3.2.3 Results

Figures 5.29 and 5.30 present the results of the Malvern investigations. Each result is the mean of 5 determinations; a typical +/-1 standard deviation error bar is shown in the top right corner of the figure 5.30. Also shown in the figures are a set of empirical curves, the derivation of which will be described below in section 5.3.2.4.

#### 5.3.2.3.1 Surfactant Concentration

Figure 5.29 shows the effect of distance and surfactant concentration (Span 85) upon the droplet size produced by a 60:40 mixture of propellant 12:114. It can be seen that droplet size decreases with increasing distance. The rate at which this decrease occurs is related to surfactant concentration and shows that larger proportions of surfactant result in slower evaporation rates. This is consistent with the non-volatile dissolved surfactant continually reducing the vapour pressure of the droplets as evaporation progresses and its mole fraction increases (Podzimek & Saad, 1975 and Renninger et al, 1981). Additionally the data shows that higher surfactant concentrations asymptote to larger droplet sizes. This latter effect is due to higher initial concentrations of surfactant producing larger residual droplet diameters. The data is also consistent with the view that the surfactant concentration has very little effect upon the initial droplet diameter produced at the spray nozzle. The asymptotes shown in the figure are for an initial droplet diameter of approximately 15  $\mu$ m (This will be discussed further below).

#### 5.3.2.3.2 Propellant Vapour Pressure

Figure 5.30 shows the effect of distance and propellant vapour pressure upon the droplet size produced by a 1% solution of surfactant (sorbitan trioleate). It can be seen that reducing the vapour pressure of the propellant increases both the asymptotic diameter and the rate at which droplet



size decreases with distance. This indicates, as would be expected, that lower vapour pressures result in slower droplet evaporation rates, but it also shows that lower vapour pressures produce coarser initial sprays. (This point will be discussed in more detail below).

#### 5.3.2.4 Discussion

It can be seen from **figure 5.29** and **5.30** that there is enormous difficulty in attempting to extrapolate droplet size data back to the spray origin and this is why this technique was abandoned. Firstly, the Malvern does not appear to have sufficient resolution and secondly the rate of evaporation and hence the slope of the extrapolation seems to be both distance and formulation dependant. It also shows how difficult it would be to use measurements at a single point within the spray as a 'characteristic' of the droplet size produced at the spray nozzle. However, the data does give some interesting insight into how the vapour pressure and surfactant concentration affect the developing cloud. The effect of surfactant concentration seems to be mainly restricted to changing droplet evaporation rate and residual diameters. Vapour pressure, on the other hand, appears to affect both the initial droplet diameter and the evaporation rate. Lower vapour pressures not only produce coarser sprays but they also entail longer evaporation times.

The empirical curves shown figures 5.29 and 5.30 were derived using the following considerations.

For a pure propellant droplet of low volatility embedded in free space, evaporation takes place in a way which ensures that droplet surface area decreases linearly with time (Hinds, 1980).

5.44

$$d t^2 = constant$$

In addition Fletcher (1973) has shown that the velocity of the cloud ' issuing from a twin orifice atomiser is inversely proportional to the distance from the spray origin.

$$V = \frac{dx}{dy} \propto \frac{1}{x}$$
 5.45

Integrating Eq 5.45 and combining the results with Eq 5.44 then shows that a 'simple' droplet would decrease in diameter in direct proportion to the distance travelled from the spray origin.

With the current system however, the situation is far more complex than this 'simple' case. The vapour field in which the droplet is embedded is, in general, Gaussian (Fletcher, 1973) and the propellant is highly volatile in nature. Also the droplets contain dissolved non-volatile agents (surfactants) which have the effect of continually reducing the propellant vapour pressure, and hence the evaporation rate, as the droplets decrease in size (Podzimek & Saad, 1975). The non-volatile component also results in residual droplets being formed.

The evaporation of propellant droplets within an expanding aerosol flume is thus very complex. However, in general, the droplets would be expected to decrease in size at an ever decreasing rate as the residual droplet diameter is approached. Hence an exponential model is appropriate. Also, by analogy with the 'simple' case described above, distance from the spray origin would to be a suitable choice of variable for the exponent. The curves presented in **figure 5.29** and **5.30** were thus of the following exponential from.

5.46

$$(d_x - d_r) = (d_i - d_r) \exp(-\lambda t)$$

Where  $d_i$  is the initial volume median droplet diameter,  $d_x$  is the droplet diameter at a distance x from the spray origin,  $d_r$  is the residual droplet diameter and  $\lambda$  is an evaporation rate constant which depends upon the propellant formulation.

Since (see Eq 5.38)

$$d_r = d_i \left(\frac{\rho_l w}{\rho_s}\right)^{\frac{1}{3}} = d_i \phi$$
5.47

Eq 5.46 may be simplified to

$$d_x = d_i (\phi + (\phi - 1)\exp(-\lambda t))$$
5.48

Table 5.4 summarises the value of  $\lambda$  and  $d_i$  obtained from regression analysis of the experimental data for the various formulations investigated. As would be expected it can be seen that  $\lambda$  decreases with increasing surfactant concentration or with decreases in propellant vapour pressure. Also it should be noted that the initial droplet diameters presented in Table 5.4 are around 15 to 20 percent smaller than the values obtained from the studies using the APS33B. This discrepancy is probably inherent in the different sizing strategies used by the 2 instruments.

The correlation coefficients for each curve are also summarised in the table. As can be seen, with the exception of the data obtained with pure propellant 12, the empirical curves fit the experimental data quite well. However, despite this good fit care should obviously be taken in the application of **Eq 5.47** because of the of the limited nature of the data upon which it is based. (The poor fit with the propellant 12 is because data could not be obtained any closer than 8 cm to the spray nozzle).

# TABLE 5.4 Evaporation Rate Constants for Various Propellant Formulations(Eq 5.46)

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For	mulation		2	3
Propellant	Surfactant <sup>1</sup> conc. w/w%	λ	r <sup>2</sup>	d <sub>i</sub>
60:40 12:114	0.25	- 0.22	0.95	15
"	0.5	- 0.19	0.99	11
17	1.0	- 0.15	0.95	11
11	2.0	- 0.13	0.93	11
12 only	1.0	- 0.26	0.76	11.7
60:40 12:114		- 0.15	0.95	15
20:80 12:114	n	- 0.14	0.97	19.8

- 1. Sorbitan trioleate.
- 2. Linear regression correlation coefficient.
- 3. Data on 60:40 12:114 was obtained by assuming the same initial diameter for the aerosol cloud (see section 5.3.1.4.2).

## 5.4 SUMMARY AND CONCLUSIONS

Section 5 describes a theoretical and experimental investigation into the continuous discharge and atomisation of superheated propellant liquids through twin orifice nozzle assemblies.

Section 5.2 details the dynamics of the discharge through a twin orifice nozzle. A computer model, developed to describe the thermodynamics of mass discharge, is presented. The model, based in the first instance upon equilibrium thermodynamics, was successfully validated with experimental data. However, in order to improve the overall range of the agreement between the model and the experimental data a small empirical metastability correction was required in the final computer code. The computer model is thus capable of predicting the spray nozzle exit conditions given the geometry of the system and the thermodynamic properties of the propellant.

Section 5.3 describes an investigation into the atomisation process. In section 5.3.1 an APS33B aerodynamic sizer was used to investigate residual spray diameters. A correlation relating the calculated initial volume median diameter of the spray to the orifice exit conditions was developed. In section 5.3.2 a limited investigation using laser diffraction allowed the development of an empirical expression to describe droplet evaporation within the spray plume.

The investigations into the discharge and atomisation from a continuous twin orifice atomiser have thus successfully related the 3 phases of spray production. The computer model can be used to predict spray orifice exit conditions and the 2 empirical correlations can then be used to describe the developing spray. These relationships will discussed further in section 7 where they will be used to develop a quantitative understanding of the empirical observations reported in section 4.

In addition to the above relationships, an understanding of some of the underlying atomisation phenomena has been developed. The droplet size produced by an atomiser of this type appears to be the result of the competing influences of increasing quality of flow (mass fraction evaporated) and falling atomiser pressure. The falling pressure is a result of the adiabatic evaporation

which in itself is responsible for increasing the quality of the flow. The relationship governing the atomisation process is similar to that governing the homogeneous atomisation of non-superheated gas/liquid mixtures. The data therefore suggests that the atomisation process is aerodynamic in nature and not due to 'flash' boiling as has hitherto been postulated.

## 6. **METERED DISCHARGE**

## 6.1 **INTRODUCTION**

### 6.2 MASS DISCHARGE

#### 6.2.1 **THEORY**

- 6.2.1.1 Qualitative Description of Metered Discharge
- 6.2.1.2 Discharge from the Metering Chamber
- 6.2.1.3 Discharge from the Expansion Chamber
- 6.2.1.4 Metering Chamber Conditions
- 6.2.1.5 Expansion Chamber conditions
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#### 6.2.2 EXPERIMENTAL

- 6.2.2.1 Experimental Apparatus
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- 6.2.2.4 Results
  - 6.2.2.4.1 Determination of Discharge Coefficients
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  - 6.2.2.4.5 Peak Exit Velocities
- 6.2.2.5 Discussion
# 6.3 **ATOMISATION**

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# 6.3.1 INITIAL DROPLET DIAMETERS

- 6.3.1.1 Experimental Apparatus
- 6.3.1.2 Experimental Procedure
- 6.3.1.3 Experimental Program
- 6.3.1.4 Results
  - 6.3.1.4.1 Orifice Dimensions
  - 6.3.1.4.2 Surfactant Concentration
  - 6.3.1.4.3 Propellant Vapour Pressure

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6.3.1.5 Discussion

# 6.4 SUMMARY AND CONCLUSIONS

# 6. METERED DISCHARGE

# 6.1 **INTRODUCTION**

The main aim of the work reported in this thesis was to investigate, on a quantitative basis, the metered atomisation of saturated liquids. To this end the following sections detail the extension of the continuous discharge model, developed in section 5, to describe the metered discharge process. Also described are investigations designed to confirm that similar atomisation mechanisms are involved in both metered and continuous atomisation.

# 6.2 MASS DISCHARGE

## 6.2.1 **THEORY**

# 6.2.1.1 Qualitative Description of Metered Discharge Through a Twin Orifice System

The metered discharge of a saturated liquid through a twin orifice system differs from the continuous discharge process described in section 5 in two major ways. The first is that propellant-flows through both the valve and spray orifices are, in general, two-phase. The second is that the pressure and temperature within the metering reservoir exhibit a monotonic fall as the discharge progresses and the metering chamber empties.

Figure 6.1 shows a schematic diagram of metered discharge. Initially, when the valve stem is depressed the situation is as shown in figure 6.1a. The metering chamber is full at the ambient temperature and at the saturated vapour pressure of the propellant; the expansion chamber is empty, accept for air, at ambient temperature and atmospheric pressure. The sudden release of the pressure as the valve orifice opens results in a single phase discharge from the metering chamber. This initial single-phase flow quickly turns to two-phase





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flow as the propellant boils and vapour is generated to fill the voidage left in the chamber. The discharged propellant then enters the expansion chamber and undergoes further boiling as it attempts to fill the chamber and displace the air. Finally, a high quality two-phase flow emerges from the spray orifice.

As discharge progresses the quantity of propellant in the metering chamber decreases and, as vapour is generated to fill the voidage, the temperature and pressure fall. Conversely, because the low quality flow from the metering chamber into the expansion chamber is larger than the high quality flow through the spray orifice, the quantity of propellant in the expansion chamber increases. This situation prevails until the two flows become equal, at which point the peak expansion chamber pressure occurs (figure 6.1b). It should be noted that the situation of equal flows does not imply equal quality of flow since the discharge areas of the two orifices may be different.

After the point of maximum expansion chamber pressure the spray orifice discharge becomes greater than the flow from the metering chamber and the expansion chamber temperature and pressure begin to decline (figure 6.1c). Eventually the situation is reached where only propellant vapour is present and vapour discharges continues until atmospheric pressure is reached.

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From this general description it can be seen that the equations developed in section 5 to describe the expansion chamber conditions and mass discharge from the spray orifice during continuous flow should be applicable to metered flow. However, in contrast to continuous flow two sets of equations are required, one to describe the metering chamber conditions and valve orifice discharge and the other to describe the expansion chamber conditions and spray orifice discharge. These equations will now be developed. The metastability correlations developed in section 5 will be included in this equation set in order to correct for non equilibrium conditions. Their applicability will be discussed further below.

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## 6.2.1.2 Discharge from the Metering Chamber

In general, as is described above, the discharge from the metering chamber will be two-phase. However, the initial discharge, when the valve is first opened, must be considered to be single-phase. The initial discharge will thus be given by Eq 5.2

$$\dot{m}_{v} = C_{qv} \frac{\pi}{4} D_{v}^{2} \sqrt{2\rho_{l}(P_{m} - P_{A})}$$
 6.1

Where  $P_A$  is ambient pressure (approx 101 kPa). After a very small amount of discharge, bubbles will begin to grow within the metering chamber and two-phase flow will quickly develop. (It assumed here that bubbles will grow uniformly throughout the metering volume and that as a consequence the two-phase fluid will discharge as a homogeneous mixture). During this initial discharge phase the expansion chamber pressure will, in general, be low and the pressure fall across valve orifice will exceed the critical pressure ratio. Discharge will thus be described by Eq 5.17.

$$\dot{m}_{\nu} = C_{q\nu} \frac{\pi}{4} D_{\nu}^{2} \left( \frac{\gamma \rho_{gm} P_{m} r_{c}^{\frac{\gamma+1}{\gamma}}}{q_{m}} \right)^{1/2}$$

$$6.2$$

Where  $r_c$  can be found from the application of Eq 5.18 to the prevailing metering chamber conditions. After this initial phase the pressure in the expansion chamber will rise, the critical pressure ratio will no longer be exceeded and Eq 5.11 can be used to describe the discharge.

$$\dot{m}_{v} = C_{qv} \frac{\pi}{4} D_{v}^{2} \overline{\rho_{m}} \left( 2 \frac{1 - q_{m}}{\rho_{l}} (P_{m} - P_{e}) + \frac{q_{m} P_{m}^{\frac{1}{\gamma}}}{\rho_{gm} \left( 1 - \frac{1}{\gamma} \right)} \left( P_{m}^{1 - \frac{1}{\gamma}} - P_{e}^{1 - \frac{1}{\gamma}} \right) \right)^{\frac{1}{2}} 6.3$$

This equation will then continue to apply to the value orifice throughout the remainder of the discharge since the metering chamber and expansion chamber pressure fall concomitantly.

# 6.2.1.3 Discharge from the Expansion Chamber

Discharge from the expansion chamber during the metering process will always be two-phase. Initially the expansion chamber pressure will be low and Eq 5.11 will apply.

$$\dot{m}_{s} = C_{qs} \frac{\pi}{4} D_{s}^{2} \overline{\rho_{e}} \left( 2 \frac{1 - q_{e}}{\rho_{l}} (P_{e} - P_{A}) + \frac{q_{e} P_{e}^{\frac{1}{\gamma}}}{\rho_{ge} \left( 1 - \frac{1}{\gamma} \right)} \left( P_{e}^{1 - \frac{1}{\gamma}} - P_{A}^{1 - \frac{1}{\gamma}} \right) \right)^{\frac{1}{2}} \quad 6.4$$

As the expansion chamber pressure increases, the critical pressure ratio will be exceeded and the flow will become critical. Under these conditions discharge will be described by Eq 5.11.

$$\dot{m}_{s} = C_{qs} \frac{\pi}{4} D_{s}^{2} \left( \frac{\gamma \rho_{ge} P_{e} r_{c}^{\frac{\gamma+1}{\gamma}}}{q_{e}} \right)^{1/2}$$

$$6.5$$

The point at which Eq 5.11 first applies can again be found by application of Eq 5.18 using the prevailing expansion chamber conditions. In general critical flow will be maintained throughout the majority of the discharge with flow only reverting to sub-critical conditions during the final phase of pressure decay.

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## 6.2.1.4 Metering Chamber Conditions

If it assumed, as with the continuous discharge model described in section 5, that discharge from the metering chamber is adiabatic and that thermal and dynamic equilibrium are maintained, then the prevailing metering chamber conditions can be found using a similar set of equations to those described in section 5.2.1.5. Thence the metering chamber quality is given by

$$q_{m} = \frac{\frac{\rho_{l}}{\overline{\rho_{m}}} - 1}{\frac{\rho_{l}}{\overline{\rho_{gm}}} - 1}$$

$$6.6$$

The fall in temperature of the metering chamber is given by

$$\Delta T = \frac{E_m - q_m L}{q_m C_g - (1 - q_m) C_l}$$
6.7

And the density of the vapour phase is given by

$$\rho_{gm} = \left(\frac{\chi_{gm}C_1}{R T_m}\right) \exp\left(\frac{C_2}{T_m}\right) \qquad 6.8$$

As in section 5.2.1.5, these equations describe the prevailing metering chamber conditions provided the initial temperature and the mass within the metering chamber are known. Discharge from the metering chamber can then be calculated provided the expansion chamber pressure is known. No attempt was made to correct for metastability in the metering chamber. This was primarily because it was felt to be unnecessary since the flow from the metering chamber was predominantly low quality.

# 6.2.1.5 Expansion Chamber Conditions

Expansion chamber conditions are a little more complex than those within the metering chamber since initially the expansion chamber is full of air and at atmospheric pressure. Although this air will be purged from the expansion chamber during the early phase of discharge, it never-the-less needs to be taken into account in a computer model.

The basis of its inclusion in the model is that Dalton's Law of Partial Pressures applies. This means that the air and propellant vapour components can be considered as separate entities for computation of pressure but that they can be combined for the calculation of enthalpy and temperature falls. One further stipulation is that the air is removed from the expansion chamber along with the vapour phase of the propellant discharge and in direct proportion to its percentage by mass. Calculations based on these assumptions show that a negligible amount of air is present when peak expansion chamber pressures are reached.

In order to include the presence of air within the expansion chamber Eq 6.8 was modified to include the enthalpy contribution from the air component.

$$\Delta T = \frac{E' - q_e L}{q_e C_g - (1 - q_e) C_l}$$
6.9

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Where

$$E^{I} = E_{propellant} + E_{air}$$

The expansion chamber pressure was then calculated as the sum of the vapour pressure of the propellant and the pressure of the air at the prevailing expansion chamber temperature.

$$P_{e} = C_{1} \exp\left(\frac{C_{2}}{T_{e}}\right) + \frac{M_{air} R T_{e}}{v_{g} \chi_{air}} \qquad 6.10$$

Where  $V_g$  is the volume of the vapour phase and is given by

$$v_g = v_e - \frac{(1 - q_e)M_e}{\rho_l}$$
 6.11

A pseudo quality and vapour density were then defined for use in the metering expansion chamber discharge equations. This pseudo quality, q', and pseudo density,  $\rho_{g'}$ , were calculated by assuming that the bulk properties of the vapour were the same as that of the propellant alone and that the vapour mass was the sum of the mass of vapour and the mass of air.

$$q'_{e} = \frac{q_{e} M_{e} + M_{air}}{M_{e} + M_{air}}$$

$$6.12$$

$$\rho_{ge}^{\ \ } = \frac{q_e M_e + M_{air}}{v_g} \tag{6.13}$$

These assumption obviously introduce errors into the model but they have the advantage of allowing the application of the single component two-phase discharge model. Since the mass of air within the expansion chamber decreases rapidly and since a negligible amount of air is present when peak conditions are reached, it was felt that these assumption did not severely limit the applicability of the model.

#### 6.2.1.5 Metastability effects

Section 5.2.2.5.5 developed 2 empirical equations to allow correction of the expansion chamber conditions obtained from the equilibrium model for the

effects of metastability. In metered flow, metastability will generally exist in both the metering and expansion chambers. However, as discussed above, because the flow from the metering chamber is predominately low quality (for example even when the metering chamber contains only 5% of its original mass the quality will still be as low as 1.5%) the effects of metastability would be expected to be much less than those in the expansion chamber. Thus metastability in the metering chamber was neglected.

Eq 5.34 and Eq 5.35 were cast in terms of the theoretical residence time within the expansion chamber. For inclusion in the metering model the residence time was calculated as an average and was defined as

$$\overline{R}_{t} = \frac{2 \ Vol_{e} \ \overline{\rho}}{\dot{m}_{v} + \dot{m}_{s}}$$

$$6.14$$

Equations have now been developed to describe the mass flows and thermodynamic conditions with the metering and expansion chambers. Pseudo qualities and vapour densities have been defined in order to facilitate the application of single component two-phase discharge equations to the flow from the spray orifice. These equations are summarized in concise form in Figure 6.2 A computer model designed to solve this equation set will now be described.

#### 6.2.1.6 Computer Model of Metered Flow

The basis of the computer model was to use the equations describing the thermodynamic conditions in the metering and expansion chambers to calculate the mass flows through the valve and spray orifices. The mass flows were modeled over small, but finite, time intervals and the effects of changing amounts of propellant within the chambers were then fed back into the thermodynamic equation set in order to re-calculate the discharge rates.

Over the first time interval discharge from the spray orifice was assumed to be zero and discharge from the metering chamber into the expansion chamber was



valve orifice  $D_v$  ,  $A_v$  ,  $C_{qv}$ 

$$\begin{aligned} q_e &= \frac{\rho_e}{\rho_e} - 1\\ \frac{\rho_e}{\rho_e} - 1\\ T_i - T_T &= \Delta T_T &= \frac{E' - q_e L}{q_e C_e} + (1 - q_e) C_i\\ T_i - T_T &= \Delta T_T &= \frac{E' - q_e L}{q_e C_e} + (1 - q_e) C_i\\ \rho_{ee} &= \frac{X_{ee} C_1}{R T_T} \exp\left(\frac{C_2}{T_T}\right)\\ \rho_{ee} &= \frac{X_{ee} C_1}{R T_T} \exp\left(\frac{C_2}{T_T}\right)\\ \rho_{ee}^{T} &= \frac{Q_e}{M_e} + \frac{M_{air}}{M_{air}}\\ \rho_{ee}^{T} &= \frac{Q_e}{M_e} + \frac{M_{air}}{M_{air}}\\ \rho_{ee}^{T} &= \Delta T_T (1 - \gamma_{me} \exp(\delta_{me} R_i))\\ P_e &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_e &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i)\\ P_e &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_E &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_E &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_E &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_E &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_E &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_E &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i) \\ P_E &= P_T (1 - \alpha_{me} \exp(\beta_{me} R_i$$

Spray orifice D<sub>s</sub> , A<sub>s</sub> , C<sub>qs</sub> Where  $r_{cm}$  and  $r_{ce}$  may be found by application of Eq 5.18 and  $v_{v}$  and  $v_{s}$  can be found by application of Eq 5.10

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assumed to be single phase. After this initial discharge new metering and expansion chamber conditions were calculated and the next discharge iteration progressed in line with the two-phase flow equations. This process was repeated over many iterations thus allowing the complete discharge profiles to be calculated.

Figure 6.3 presents a computer flow diagram for the metered discharge model. As with section 5, the computing language was Turbo Pascal. A comparison between the models predictions and the experimental data will be made below. Figure 6.4 presents a typical computed profile. The data has been generated for a 100  $\mu$ l valve with nominally similar valve and spray orifice dimension and a spray orifice diameter of 0.26 mm. It may be compared with the experimental profile shown in figure 6.8.



Metering and Expansion Chamber Pressures

Metering & Expansion Chamber Temperature





Exit Momentum & Velocity



Figure 6.4 Theoretical Profiles for Metered Discharge

Propellant 12 100uL Valve Ds = 0.26mm Ds/Dv = 1

# 6.2.2 EXPERIMENTAL

The experimental investigations reported in section 5.2.2 were aimed at validating the continuous discharge computer model and at developing metastability corrections for inclusion in the metered discharge model. The experimental work reported in this section was performed in order to validate the metered discharge model described in section 6.1. over a wide range of formulation and geometrical variables.

Because the metastability corrections used in the above metering model were derived from continuous discharge experiments it was obviously essential that the design of the metered discharge test rig closely resembled that of the continuous test rig. This was achieved by using essentially similar components for the 2 valve systems. The only major difference was the position of the orifice in the valve stem.

The experimental apparatus and program will now be described.

#### **6.2.2.1 Experimental Apparatus**

The metered flow test apparatus is shown diagrammatically in figure 6.5. It can be seen that in general its design and layout is the same as the continuous flow test rig. The main exception to this is the design and construction of the 'instrumented' valve assembly. Figure 6.6 and figure 6.7 present the valve assembly in more detail. Figure 6.8 shows an 'exploded' view of the metering valve components.

The propellant reservoir was a 350 ml canister pre-filled with the test formulation. The base of the canister was 'capped' with a wide bore (1 mm) continuous discharge valve (Precision Valve UK, Peterborough, England).

The stem of the reservoir canister was connected to the brass valve assembly manifold via an 'O'-ring seal.





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![](_page_198_Figure_0.jpeg)

Figure 6.8 'Exploded' View of Metered Valve Components

![](_page_198_Picture_2.jpeg)

Figure 6.7 Photograph of Instrumented Metered Valve Assembly When held in the depressed state by appropriate laboratory clamps the test formulation was delivered to the small reservoir above the metering valve. As with the continuous discharge apparatus described in section 5.2.2. this configuration ensured a negligible excess pressure due to the propellant 'head'.

Metering stems containing an appropriate range of orifice sizes were manufactured from blank stems. The orifices were drilled and polished using diamond paste. The final size of the orifice was determined by optical microscopy. Manufacture of the metering stems using this method ensured essential similarity to those used in the continuous discharge experiments.

The spray orifice/actuators for the metered discharge experiments were the same as those used for the continuous discharge experiments.

The pressure inside the metering chamber was again monitored using a Sensym SCX100 monolithic pressure transducer (Sensym Technics, Rugby, England). Because of the limited access to the metering chamber wall the pressure sensor had to be connected via a small bore stainless steel capillary (1 mm bore, 2.5 cm length). Initial experiments showed that the use of such a capillary did not significantly reduce the response time of the sensor (see below) or increase the metering volume. However, great care had to be taken when priming the metering chamber in order to avoid air being trapped in the tube since trapped air would resulted in excess pressure. The pressure within the spray head was monitored in the same way as described in section 5.2.2.

The response time of the pressure senor, with capillary attached, was measured using an exploding balloon. An inflated balloon was attached to the open end of the capillary tube. The balloon was 'popped' and the rate of pressure decay monitored. The 'half life' response time was shown to be better than 0.2 msec (see Appendix III).

Temperatures were monitored via copper/constantan thermocouples as described in section 5.2.2. The response times of the reduced volume thermocouples were estimated by plunging them into cooled liquids. The thermocouples were equilibrated at room temperature and then plunged into liquids maintained at temperatures below ambient. The exponential

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temperature decay of the thermocouple outputs were monitored via the hardware of the test rig and the temperature decay half life estimated (see **Appendix III**). The half-lives were typically of the order of 2-5 msec.

The exit thrust was measured using the same equipment as described in section 5.2.2.

As with the continuous discharge rig, the analogue outputs from the sensors were feed to an IBM AT personal computer via variable gain amplifiers and a CED 1401 high speed analogue to digital converter. The sensors were calibrated in the same way as those used in the continuous discharge experiments.

## 6.2.2.2 Experimental Procedure

The experimental apparatus described above was used to study a variety of system variables including propellant formulation, valve and spray orifice diameter and metering volume. In each case the experimental procedure to determine the thermodynamics of the discharge was essentially similar.

The valve and brass valve assembly manifold were loosely assembled as shown in **figure 6.6** using the appropriate metering chamber and valve stem. The valve assembly was then placed on top of the propellant reservoir/canister and the assembly was depressed. This resulted in vapour being discharged from the canister and a purging of the air from the valve assembly. After 1 or 2 seconds the valve assembly was tightened and the assembly was inverted into the test position. Approximately 10 to 20 metered discharges were then released in order to completely purge the system.

After allowing the assembly to warm up to a few degrees below the test temperature the pressure and temperature were measured via the interface and computer software. If the pressure recorded was higher than the saturated vapour pressure of the propellant under test the apparatus was agitated and the purging procedure repeated in order to eliminate air from both the capillary tube and the brass valve assembly reservoir. This procedure was generally repeated until a suitable saturated vapour pressure reading was obtained.

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All the sensor leads were connected and a blank run performed to confirm the integrity and continuity of data acquisition. When the test temperature had been reached (291 K), data acquisition was initiated via a microswitch and simultaneously a metered discharge was initiated by manual depression of the spray orifice/actuator. (Automatic initiation of the discharge had been investigated but showed no better reproducibility than manual discharge). The raw sensor data was stored directly into a disc file and was processed in a similar way to the data obtained during the continuous discharge experiments.

A typical experimental discharge profile is shown in figure 6.9. This may be compared with the computer generated profile shown in figure 6.3. It can be seen that the profiles are broadly similar. However a number of differences are apparent.

Firstly, the experimental metering chamber pressure fall at the beginning of the discharge is sharper than predicted by the model. This is probably due to the bubble idle time discussed in section 2 and hence to metastability affects. The computer model did not attempt to take into account metastability within the metering chamber.

Secondly, the initial experimental expansion chamber temperature fall is not as steep as predicted by the computer model. This is probably due to lack of response time of the copper/constantan thermocouples, although this may be aggravated by poor thermal transmission between the propellant and thermocouple due to the high vapour content of the propellant.

Thirdly, the experimental exit velocity profiles are generally higher than those predicted by the computer model, although the general form of the curves is in good agreement.

#### Metering and Expansion Chamber Pressures

Metering & Expansion Chamber Temperature

![](_page_202_Figure_2.jpeg)

![](_page_202_Figure_3.jpeg)

Exit Momentum & Velocity

![](_page_202_Figure_5.jpeg)

Figure 6.9 A Typical Experimental Profile for Metered Discharge

Propellant 12 100uL Valve Ds = 0.26mm Ds/Dv = 1 The data also shows that the theoretical sonic velocity, Eq 6.1, based on the measurements of expansion chamber pressure and temperature is higher than that determined from the thrust measurements, Eq 6.4. This discrepancy would indicate, contrary to the assumptions made in the computer model, that a small amount of slip is occurring between the vapour and liquid phase. This slip is, however, calculated to be only of the order of 3% of the average exit velocity has little effect on the computation of the mass discharge profiles and does not invalidate the computer model. Further experimental data on peak exit velocities will be presented below.

## 6.2.2.3 Experimental program

The variables chosen for experimental investigation were essentially similar to those investigated during the continuous discharge program with the addition of metering volume.

Two metering volumes were used nominally 100  $\mu$ l and 50  $\mu$ l. The valve/spray orifice ratio was studied using 4 valve orifice diameters and 3 spray orifice diameters. This combination of metering volumes and orifices allowed the investigation of 24 discharge conditions for each propellant formulation. The particular valve and spray orifice diameters used are summarised in **Appendix IV**. Also shown are the discharge coefficients for each orifice. The determination of the discharge coefficients will be discussed below.

The range of propellant and surfactant variables investigated were the same as those used in the continuous discharge experiments. The thermodynamic properties of the propellants are summarised in table 5.1.

The effect of surfactant concentration was investigated using 60/40 blends of propellants 12/114 and a surfactant (sorbitan trioleate) concentration of from 0.25% to 2%. As with the continuous discharge experiments surfactant concentration had no measurable effect on metering or expansion chamber pressures and temperatures. A surfactant concentration of 0.25% was used throughout the investigation reported below.

In all, approximately 100 experimental discharge profiles were measured. The results of this experimental program will now be compared with the prediction of the computer model. For simplicity and for reasons which will become apparent in section 6.4 the following discussions will mainly be restricted to consideration of the peak expansion chamber conditions.

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## 6.2.2.4 **Results**

### 6.2.2.4.1 Determinations of Discharge Coefficients

It can be seen from Eq's 6.3 and 6.4 that, as with the case of continuous discharge, the value of the valve and spray orifice discharge coefficients need to be known before the discharge profiles can be calculated.

The discharge coefficient for the metered valve orifices were determined by reference to section 5.2.2.5.1 and figure 5.13. The geometric diameter of each orifice was measured by optical microscopy and the discharge coefficient was read from the ordinate of figure 5.13. Although the data used to construct figure 5.13 was determined using continuous discharge valves this procedure was felt to be valid for 2 reasons. Firstly, the data presented in figure 5.13 was determined for a variety of orifices and for a variety of flow conditions (qualities). Secondly the valve stem geometry used in both valves is essentially similar. The only difference between the two valves is the position of orifice in reference to the longitudinal axis of the stem. In the metering valve the valve orifice is approximately 1 mm closer to the discharge end of the stem (see figure 6.8 and 5.9).

The discharge coefficients for the spray orifices were determined in section 5.2.2.5.1 and illustrated in figure 5.14. The discharge coefficient was found to be 0.78 regardless of the geometric diameter of the orifice.

#### 6.2.2.4.2 Pulse Shape and Width

Figures 6.10a to 6.10d present a comparison between the experimental expansion chamber pressure profiles and the predictions of the computer model for 4 spray orifice diameters. The propellant was propellant 12, the metering volume was 100  $\mu$ l and valve orifice diameter is used as a parameter. The ordinate is gauge pressure the abscissa is elapsed time in milliseconds. Care should be taken when viewing the figures to note that the time axis for figure 6.10c and 6.10d is twice as long as the time axis in figure 6.10a and 6.10b.

![](_page_206_Figure_0.jpeg)

•

![](_page_206_Figure_1.jpeg)

![](_page_206_Figure_2.jpeg)

![](_page_206_Figure_3.jpeg)

300

B) Experimental Data Spray Orlfice Diameter 0.6mm

![](_page_206_Figure_5.jpeg)

Theory

![](_page_206_Figure_7.jpeg)

![](_page_207_Figure_0.jpeg)

Theory

![](_page_207_Figure_2.jpeg)

![](_page_207_Figure_3.jpeg)

Theory

Expansion Chamber Pressure (kPa Gauge) Time (ms)

It can be seen that, in general, the model predictions show reasonable agreement with the experimental data, both in terms of pulse height and width.

The data also show that for any given valve orifice diameter increasing the spray orifice diameter decreases the expansion chamber pressure and slightly increases the pulse width. This increase in pulse width may at first sight seem slightly paradoxical in that increasing the area of the spray nozzle should result in a higher mass discharge. However, increasing the spray orifice diameter results in more evaporation in the expansion chamber and a higher quality flow in the spray nozzle as well as reduced expansion chamber pressures. This increase in quality reduces the average density of the spray orifice discharge and, since the flow is choked, this results in a decreased mass discharge rate from the spray nozzle. This effect is to some extent offset by low expansion chamber pressures giving rise to higher mass flows from the metering chamber. However, since valve orifice discharge is also two-phase, the metering chamber discharge can also become choked, and hence limited, if the expansion chamber pressure falls below the critical level.

The effect of decreasing the valve orifice diameter can be seen by comparing **figures 6.10a to 6.10d**. It can be seen that decreasing the valve orifice diameter dramatically increases the pulse width. This effect is perhaps better illustrated in **figure 6.11** where the model predictions for a spray orifice diameter of 0.39 mm and a varying valve orifice diameter are compared with the experimental data. It can be seen that increasing the valve orifice diameter from 0.25 mm to 1.00 mm results in a five fold decrease in pulse width.

Similar data, and similar agreement between model predictions and experiment, was found for the 3 remaining propellant formulations and for the 50  $\mu$ l metering volume.

It would have been desirable to compare the experimental and computed pulse widths directly, however, the rather ragged nature of the experimental pressure pulses made it extremely difficult to determine an accurate end point. Hence the data was only compared in the qualitative fashion described above.

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![](_page_209_Figure_0.jpeg)

Theoretical Profiles

![](_page_209_Figure_2.jpeg)

Comparing the computed pulse width for 100  $\mu$ l and 50  $\mu$ l discharges of a 60:40 mixture of propellants 12 and 114 with nominally similar valve and spray orifice diameters of 0.6 mm showed that pulse width was approximately proportion to volume and the average discharge rate was 0.75  $\mu$ l/msec. This value is in reasonably good agreement with the high speed filming work reported in section 4.3.4, where the valve and spray orifices were of nominally similar dimensions. It also indicates that the average discharge rate is, as would be expected, slightly longer than that found during the continuous discharge experiments using similar conditions. This adds further weight to the validity of the computer model.

## 6.2.2.4.3 Peak Expansion Chamber Pressures

Figure 6.12a to 6.12d present a comparison of the peak experimental expansion chamber pressures and the predictions of the computer model for 4 propellant systems using a 100  $\mu$ l valve; valve orifice diameter is used as a parameter. The abscissa is the orifice discharge ratio, the ordinate is gauge pressure. It can be seen that the peak pressure falls monotonically with increasing spray orifice diameter (increasing orifice discharge ratio) and that the rate of fall, in terms of discharge ratio, is more rapid for larger valve orifice diameters. As would be expected the rate of fall is higher and the absolute pressure values are lower for the lower vapour pressure propellants.

Figures 6.13a to 6.13b present similar data to the above for a 50  $\mu$ l metering volume. In general, the overall peak pressures are slightly lower than those for the 100  $\mu$ l metering volume and the rate of pressure fall with increasing valve or spray orifice diameter slightly higher.

The agreement between the model and the experimental data is remarkably good.

In order to elucidate the effects of metering volume on peak expansion chamber pressures it is interesting to compare the peak pressures reported in figures 6.12 and 6.13 with those for continuous flow illustrated in figure 5.19. Figure 6.12 Peak Expansion Chamber Pressure Veraus Discharge Diameter Ratio for a 100ul Valve

A) Propellant 12

![](_page_211_Figure_2.jpeg)

![](_page_211_Figure_3.jpeg)

C) 60:40 Propellant 12:114

![](_page_211_Figure_5.jpeg)

![](_page_211_Figure_6.jpeg)

![](_page_211_Figure_7.jpeg)

Figure 6.13 Peak Expansion Chamber Pressure Versus Discharge Diameter Ratio for a 50ul Valve

A) Propellant 12

![](_page_212_Figure_2.jpeg)

![](_page_212_Figure_3.jpeg)

C) 60:40 Propellant 12:114

![](_page_212_Figure_5.jpeg)

![](_page_212_Figure_6.jpeg)

![](_page_212_Figure_7.jpeg)

It can be seen that the effect of valve orifice diameter is far more dramatic for the metered spray systems than for the continuous system. The variations in pressure caused by variations in valve orifice diameter with the continuous systems are entirely limited to reducing the residence time and increasing metastability. Whereas increasing the valve orifice diameter with a metered system not only increases metastability, it also changes the balance of flows between the 2 orifices. For any given orifice discharge ratio increasing valve orifice diameter means increasing spray orifice diameter and a higher rate of mass discharge. Hence, since propellant will be discharged from the spray orifice more rapidly less propellant will be left in the system at peak pressure and hence more evaporation will be needed to fill the expansion chamber volume and the peak pressure will be lower. The effects of metering volume on peak pressure, temperature and the atomisation efficiency will be discussed in more detail below.

### 6.2.2.4.4 Peak Expansion Chamber Temperatures and Quality

Figures 6.14a to 6.14d present the experimental and theoretical peak temperatures for the 4 propellants under test and a 100  $\mu$ l metering volume. Spray orifice diameter has again been used as a parameter. Figures 6.15a to 6.15d present similar data for a 50  $\mu$ l metering volume. In the case of the 50  $\mu$ l data a number of experimental points for the largest spray orifice diameter have been omitted because the response time of the thermocouples was too slow to allow accurate determination. The abscissa in the figures is discharge diameter ratio, the ordinate is temperature fall. Also shown as a second ordinate is the peak expansion chamber quality. This has been calculated using the simplified enthalpy expression described in section 5.2.2.5.4. It can be seen that a reasonable agreement exists between theory and experiment. Larger temperature falls are recorded for the higher vapour pressure propellants. It should also be noted that, as with continuous discharge, propellant 227 exhibits the lowest temperature falls. Figure 6.14 Peak Expansion Chamber Temperature and Quality Versus Diameter Ratio for a 100uL Valve A) Propellant 12

![](_page_214_Figure_1.jpeg)

![](_page_214_Figure_2.jpeg)

C) 60:40 Propellant 12:114

![](_page_214_Figure_4.jpeg)

D) Propellant 227

B) Propellant 134A

![](_page_214_Figure_6.jpeg)

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Figure 8,16 Peak Expansion Chamber Temperature and Quality Versus Diameter Ratio for a 60uL Valve A) Propellant 12

![](_page_215_Figure_1.jpeg)

![](_page_215_Figure_2.jpeg)

C) 60:40 Propellant 12:114

![](_page_215_Figure_4.jpeg)

D) Propellant 227

B) Propellant 134A

![](_page_215_Figure_6.jpeg)
This is so because the ratio of the enthalpy of vaporisation to specific heat is some 50% higher than the other propellants. This means that higher quality flow can be generated for less evaporation and hence a lower temperature fall. The effects of this thermodynamic ratio on atomiser efficiency will be discussed below.

The data show that, in line with the continuous discharge experiments, the peak pressure within the expansion chamber falls with increasing discharge diameter ratio whereas the peak quality of flow increases. The pressure fall and quality increase is, however, more marked for the metered system.

#### 6.2.2.4.5 Peak Spray Orifice Exit Velocities

The peak exit velocities as measured by the thrust transducer technique, for both the 100  $\mu$ l and 50  $\mu$ l metering volumes, are summarised in figures 6.16A to 6.16D. The abscissa is discharge diameter ratio, the ordinate is average exit velocity. An arrow marks the approximate limit of critical flow. A theoretical curve is also shown in the figures. However, this curve can only be considered to be approximate because, with metered discharges, there is not a single unique relationship between exit velocity and orifice discharge ratio.

The exit velocities were calculated by rearranging Eq 5.24 and substituting the peak expansion chamber conditions.

$$v_{s} = \sqrt{\frac{\frac{J_{p}}{A_{s}} - r_{c}(P_{ep} - P_{A})}{\frac{\overline{\rho_{p}}}{\overline{\rho_{p}}}}}$$

$$6.15$$

Where the average density,  $\rho_{p}$ , is found from the following relationship.

Figure 6.16 Exit Velocity for a Metered Twin Orifice Atomiser







C) 60:40 Propellant 12:114

D) Propellant 227



$$\overline{\rho_{ep}} = \frac{q_{ep}\rho_l}{1 - \left(\frac{1 - q_{ep}}{q_{ep}}\right)\left(\frac{\rho_l}{\rho_{gep}}\right)}$$

$$6.16$$

And  $q_{ep}$ , the peak quality of flow, is calculated from the experimental peak temperature fall by rearranging Eq 5.27.

$$q_{ep} = \frac{\frac{E}{\Delta T_p} - C_l}{C_g - C_l + \frac{L}{\Delta T_p}}$$

$$6.17$$

In general the experimental data shows reasonable agreement with the theoretical predictions. As with the data presented in section 5 the exit velocities were higher for the higher pressure propellant systems. The exit velocities for the higher pressure propellants also tended to increase as the orifice discharge ratio and spray orifice diameter increased and the flow tended to single phase vapour discharge.

## 6.2.2.4.6 Discussion

The metered discharge of a saturated liquid propellant from a twin orifice metered atomiser has been successfully modelled using a combination of equilibrium thermodynamics and empirical metastability corrections. With only minor discrepancies, the computer model has shown reasonable agreement with experimental data.

The peak exit conditions generated in a metered atomiser are similar to those experienced in the continuous atomisers reported in section 5. However, because of their finite supply of propellant the pressure and temperature falls are more dramatic with the metered system.

The data presented above will now be used to relate peak expansion chamber conditions to the droplet size generated from metered atomisers.

## 6.3 **ATOMISATION**

The aim of this section of the experimental investigations was to confirm that similar atomisation mechanisms were involved in both continuous and metered sprays and to develop a similar correlation for metered atomisation to that developed in section 5.3 for continuous discharge. The initial investigations, designed to determine the initial droplet diameters and to shed light on the atomisation mechanism, were therefore carried out using the APS33B and the experimental rig described in section 5.3.2.

However, as with the continuous discharge experiments an investigation into the plume dynamics was considered useful. Initial attempts to use laser diffraction techniques proved fruitless, primarily because of synchronisation problems between spray actuation and the droplet size measurement sequence. However, the investigations were also hampered by the lack of both time and sizing resolution described in section 5. Because of these problems attention turned to the phase doppler technique described by Bachalo (1984) which in principle was capable of excellent time, size and spacial resolution. Unfortunately, due to limited availability of the phase doppler instrumentation, it only proved possible to carry out very limited investigations using this technique. Because of the limited nature of these studies the results are described in section 8, 'Suggestions for Further Work', and are presented in full in Appendix VII, rather than being presented here.

## 6.3.1 INITIAL DROPLET DIAMETER

#### 6.3.1.1 Experimental Apparatus

The experimental rig used to study the initial droplets diameters produced by the metered sprays was essentially that used for the continuous discharge studies and is shown in **figure 5.22**. The only change in design was to substitute a 10 litre holding vessel for the 50 litre vessel used in the continuous spray experiments in order to compensate for the lower aerosol concentration produced by the metered sprays.

#### 6.3.1.2 Experimental Procedure

The experimental procedure consisted of filling the metered flow test apparatus described in section 6.2.2.1 with the propellant formulation under test. After allowing the apparatus to reach equilibrium temperature (291 + /- 1 K), 2 actuations were discharged into the 10 litre vessel. After waiting approximately 5 seconds for complete evaporation to occur, the aerosol was drawn through the APS33B and its size distribution determined. A minimum of 150,000 particles were counted for each determination and each determination was repeated 5 times.

Initial investigation showed similar problems to the continuous discharge experiments, in that large numbers of very small particles were present. The APS33B was thus operated at reduced gain as described in section 5.3.1.

#### 6.3.1.3 Experimental Program

The experimental program was designed to confirm that the processes involved in metered atomisation were similar in nature to those involved in continuous sprays. It was also designed to elucidate any differences between the 2 spray systems. Propellant vapour pressure was investigated using a range of mixtures of propellant 12 and propellant 114. Surfactant concentration was studied using sorbitan trioleate in the concentration range 0.25% to 2% by weight in both propellant 12 and a 40:60 mixture of propellant 12 and 114. The effects of orifice dimensions were investigated using 4 spray orifice diameters and 3 valve orifice diameters. The exact diameters and the discharge ratios are summarised in **Appendix VII**. In essence, the experimental program was similar to that described in section 5.3.1.3 but was slightly more restrictive due to its confirmatory nature.



#### 6.3.1.4 **Results**

#### 6.3.1.4.1 Orifice Dimensions

Figures 6.17A, 6.17B present the effects of spray to valve orifice ratio for 2 metering volumes for propellant 12. The right hand axis is residual median diameter as measured by the APS33B, the left hand axis is the initial droplet diameter calculated using Eq 5.36. The abscissa is the orifice discharge ratio. Valve stem orifice diameter has been used as a parameter. Each data point is the mean of 5 determinations. A typical standard deviation is shown in the top right hand corner of figure 6.17A.

It can be seen that the initial droplet diameter shows a similar dependence to that demonstrated by the continuous discharge process described in section 5.3. However, it proved impossible to carry out determinations with diameter ratios in excess of 2.88 because 'spluttering' occurred. That is the aerosol failed to deliver a 'crisp' shot with the result that very large propellant droplets were seen to form at the spray orifice exit. This failure to function correctly at high discharge diameter ratios is, bearing in mind the pressure and temperature data presented in section 6.2, undoubtedly due to the more rapid pressure fall associated with the metering process. (see section 6.3.1.5 below).

#### 6.3.1.4.2 Surfactant Concentration

The effects of the inclusion of surfactant in the propellant phase is illustrated in figure 6.18. The ordinate is initial droplet diameter, calculated from Eq 5.36, the abscissa is surfactant concentration w/w%. It can be seen that the initial droplet diameter shows a very similar trend to the data reported in section 5.3.1.4.2. Reference to Table 5.3 again shows that increasing the surfactant concentration does not change surface tension values and hence the trend cannot be explained in terms of surface tension phenomena. A similar explanation to that given in section 5.3.1.4.2 may also be plausible here.



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#### 6.3.1.4.3 Propellant Vapour Pressure

The effects of propellant vapour pressure are presented in figures 6.19A and 6.19B. Figure 6.19A presents the variation of initial droplet size with discharge diameter ratio, propellant formulation is used as a parameter. It was not possible to indicate the residual droplet diameters because of variations in the density of the propellant mixtures. Figure 6.19B presents the variation of initial droplet diameter with the saturated vapour pressure of the propellant, discharge diameter ratio is used as a parameter. It again proved difficult to investigate discharge diameter ratios in excess of 2.88. Indeed, with a 20:80 mixture of propellant 12 and 114 'spluttering' was observed at discharge diameter ratios in excess of 2.2.

However, it can be seen that both of these graphs show similar trends to the continuous discharge data reported above and that a similar saturated vapour pressure dependence exists for both continuous and metered discharge.

#### 6.3.1.4.4 Metering Volume

The effects of metering volume upon initial droplet diameter are summarised in **figure 6.20**. The valve orifice diameter used for the determinations was 0.25 mm. For comparison data obtained during the continuous discharge experiments is also presented.

Again it can be seen that similar trends are observed with both the metered and continuous systems. In general, the droplet size produced from the metered system is slightly coarser than that produced by continuous atomisation. The data also indicates that smaller metering volumes produce coarser sprays. These observations can probably be ascribed to the lower expansion chamber pressure experienced in metered discharge, see section 6.2 above.

## 6.3.1.5 Discussion

It is apparent from the data presented in the preceding sections, that atomisation from metered volumes of propellant exhibits the same trends and dependencies as continuous discharge. The major differences between the 2







systems are that the expansion chamber pressures fall more rapidly with increasing discharge diameter ratio in the metered system. This results in slightly coarser sprays and an inability of the metered system to function at diameter ratios greater than approximately 2.8.

Examination of the width of the size distributions generated by the 2 types of system, as expressed by the geometric standard deviation, showed that the sprays produced by the metered systems are also more polydispersed. As with the continuous system there was no trend in GSD with orifice ratio or pressure, but the GSD range was larger. GSD's ranged from 1.75 to 2.4 for continuous sprays and 1.95 to 2.6 for metered sprays. This increase in polydispersity would to some extent be expected since in a metered pulse droplets are generated under continually varying atomiser conditions. However, it is difficult to assess here whether this slight increase in polydispersity is physically significant.

Figure 6.21 combines the data from continuous discharge and metered discharge in a single pressure/quality correlation. For the metered discharge data peak expansion conditions have been used. At low discharge diameter ratios (where the quality of flow is low and the expansion chamber pressure is high) reasonable agreement exits. At large discharge diameter ratios the agreement is seen to be much poorer, with the metered system generating 'finer' droplets than the continuous system. However, the correlation equation developed in section 5.3 is still satisfactory provided  $C_5$  takes the value 1.82 (correlation coefficient of 0.83).

It is at present difficult to explain why the metered system generates 'finer' droplets than the continuous system. However, this effect may be due to a number of phenomenon. It may be possible that 'spluttering' was occurring at the higher diameter ratios and that the coarse droplets were retained inside the aerosol sampling chamber rather than being sized by the APS33B. It may also be possible that the aerodynamic forces experienced at the leading edge of the metered spray may cause more efficient droplet break-up. Calculations of the limiting Weber number for secondary atomisation (Hass, 1964), however, would suggest that this is not the case. At a limiting Weber number of approximately 5, the limiting droplet size for a typical propellant is around 100  $\mu$ m.



Figure 6.21 Droplet Correlation for Mixtures of Propellant 12 and 114 for Continuous and Metered Flow

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Finally, droplet collisions and coagulation may be more marked in the continuous system. Droplet coagulation would obviously lead to a 'coarser' spray.

It should be noted here, however, that the value of the droplet correlation equation is not dependant upon the correctness, or otherwise of these explanations.

## 6.4 SUMMARY AND CONCLUSIONS

Section 6 describes a theoretical and experimental investigation into the metered discharge and atomisation of a superheated propellant liquids through twin orifice valve assemblies.

Section 6.2 details the dynamics of the metered discharge process. In section 6.2.1 the computer model presented in section 5.2 was extended to cover metered discharge. Empirical corrections for the effects of metastability within the expansion chamber, also developed in section 5.2, were incorporated in the metered computer model. Section 6.2.2 describes an experimental program designed to validate the computer predictions. An acceptable agreement between theory and experiment was found. The computer model is thus capable of predicting the expansion chamber, and hence spray nozzle exit, conditions from thermodynamic and geometrical parameters.

Section 6.3 presents the results of an investigation into the metered atomisation process. In general it was found that the trends and relationships observed with continuous atomisation were also observed with metered atomisation.

However, when the metered pulses were characterised by the peak expansion chamber conditions, it was found that for low discharge diameter ratios (< 2) the droplet size produced by a metered system agreed reasonably well with the data obtained for continuous sprays. Conversly, at high discharge diameter ratios (equivalent to low expansion chamber pressures and high quality flow) it was found that the drop size produced by the metered process was 'finer' than that produced by the continuous system. However, the droplet correlation function developed in **section 5.3** could still be used provided the constant of proportionality ( $C_s$ ) was modified. Possible reasons for the discrepancy between the 2 systems where postulated.

## 7. <u>SUMMARY AND CONCLUSIONS</u>

The main aim of the project described in this thesis was to develop a quantitative and fundamental understanding of the metered atomisation of superheated propellants. The project was undertaken in order to gain a fundamental understanding of the factors affecting the efficiency of the metered dose inhaler inhalation drug delivery system. To this aim, 3 phases of experimental and theoretical development have been carried out.

The first phase (section 4) used an empirical sizing technique to investigate major formulation and atomiser variables. The apparatus used for the investigations was a single stage inertial impactor designed to represent the upper portion of the human airways. With this apparatus, it was shown that adding non-volatile excipients, or reducing the vapour pressure of the propellant liquid, reduced the 'dispersion' of the metered aerosol cloud. (For a definition of the term 'dispersion' see section 4). In terms of the geometry of the atomiser, increasing the diameter of the spray orifice was also shown to reduce 'dispersion' values. Increasing the concentration of the suspended solids or increasing the mass median diameter of the suspended material also reduced dispersion. The effects of these variables upon 'dispersion' are summarised in Table 7.1.

Attempts were made to ascribe these observations to the physical processes involved in atomisation. However, because of the empirical nature of the impinger device no definitive conclusions could be drawn.

As a result of the empirical observations reported in section 4 the second phase of the investigational program (section 5) used more fundamental techniques to study continuous atomisation from twin orifice valve assemblies. A continuous spray process was chosen for this second phase because it offered an opportunity to study an 'equilibrium' process before tackling the more complex metered systems. During this phase the experimental program was restricted to studying atomiser geometry and liquid formulation variables. The solids phase was not investigated because it was felt that a fundamental understanding of superheated liquid atomisation was required, before the more complex suspension variables could be investigated. Initially, a

# TABLE 7.1 A Summary of the Effects of Formulation Variables upon the'Dispersion' of the Aerosol Cloud Produced from Metered Dose Inhalers

Formulation Variable	Effect upon Dispersion <sup>1,2</sup>		
Spray orifice diameter	Inversely proportional to spray orifice diameter	$\approx 1/D_s$	
Propellant vapour pressure	Proportional to the square root of pressure	$\approx P_e^{1/2}$	
Surfactant concentration	Inversely proportional to surfactant concentration	≈ 1/W	
Suspended solids concentration	Inversely proportional ≈ 1/Ln(W to Log of solids concentration		
Suspended solids size	Proportional to particle size	$f(D_p)$	

- 1. For a definition of the term 'Dispersion' see section 4.
- 2. f() means a function of the variable in parentheses.

computer model was developed to describe the thermodynamics of the discharge process. Experimental investigations were then performed to validate the computer model. Knowledge of the spray orifice exit conditions was then used to construct an empirical correlation between the droplet size produced at the atomiser nozzle and the geometric and thermodynamic variables of the system. By analogy to previously published data on the atomisation of non-superheated homogeneous gas/liquid mixtures, it was concluded from the form of this correlation that the likely mechanism of droplet formation was aerodynamic shear rather than 'flash' boiling as has hitherto been postulated. A short investigation using diffraction sizing techniques was also performed in order to estimate the droplet evaporation rates within the developing cloud.

Section 6 went on to extend the continuous discharge model to describe metered flow. A study of the droplet size produced by metered atomisers revealed that the relationships governing the droplet size produced from a metered spray were essentially the same as those for continuous discharge. The only major difference between the 2 systems was that the metered system showed a sharper reduction in atomiser pressure with increasing spray orifice diameter. This reduction is primarily due to the finite supply of propellant with the metered system.

It is now possible to combine the relationships developed in section 5 and 6 to explain, in a semi-quantitative way, the observations of section 4 and to highlight the effects of the major formulation variables.

It was stated in section 4 that in order to understand the interaction of the cloud produced by a metered dose inhaler with the upper portion of the human airways, it is necessary to measure not only droplet size but also droplet velocity. This is so, because it is the relaxation distance of the droplet which controls deposition probability in the oropharynx and not just the droplet size. The probability of impaction is proportional to the product of the velocity and the droplet diameter squared. It was stated above that the velocity of the cloud produced by a continuous spray system has been shown, by Fletcher (1975), to be inversely proportional to the distance from the spray origin.

$$v = \frac{C}{x} \sqrt{\frac{2 J}{\pi \rho_{air}}}$$

$$4.3$$

It was also shown that for a continuous system, or for a metered system at any point during its discharge cycle, section 5.2.1.4, that the exit momentum, J, could be expressed in terms of the spray orifice geometry and exit velocity.

$$J = C_{q_s} \frac{\pi}{4} D_s^2 (\bar{\rho} v_{ss}^2 + (r_c P_e - P_A)) \simeq C_{q_s} \frac{\pi}{4} D_s^2 \bar{\rho} v_{ss}^2 \qquad 5.24$$

Combining Eq 4.3 with 5.24 and substituting for  $v_{ss}$  from Eq 5.41 then gives an expression for the velocity of the cloud, down-stream of the spray orifice, in terms of expansion chamber conditions.

$$v = \frac{C_6 D_s}{x} \sqrt{\frac{r_c P_e}{\rho_{ge}}} \left\{ \left(1 + \frac{(1 - q_e)}{q_e}\right) \left(\frac{\rho_{ge}}{\rho_l}\right) \right\}^3$$
7.1

Where

$$\mathbb{C}_6 = \mathbb{C}\sqrt{\frac{C_{q_s} \gamma_c \rho_l}{2 \rho_{air}}}$$

In section 5.3.1.5 an empirical expression was developed to relate the initial median droplet diameter produced at the spray orifice to the expansion chamber conditions.

$$d_i = \frac{\mathbb{C}_5}{q_e^{n} P_e^{m}}$$
 5.41

Where  $\mathbf{n}$  and  $\mathbf{m}$  are approximately 0.5.

In section 5.3.2.4 a further empirical expression was developed to describe the decrease in volume median diameter of the spray as it travels away from the spray nozzle.

$$d_x = d_i (\phi + (1 - \phi) \exp(-\lambda x))$$
5.48

Where

$$\phi = \left(\frac{\rho_p w}{\rho_s}\right)^{\frac{1}{3}}$$
 5.47

Combining Eq 5.41 and 5.46 thus gives an expression for the volume, or mass, median droplet diameter of the spray as a function of expansion chamber conditions and distance down-stream of the spray orifice.

$$d_x = \frac{C_5}{q_e^n P_e^m} (\phi + (1 - \phi) \exp(-\lambda x))$$
7.2

(Care should be taken here in the use of Eq 7.2 because the initial droplet diameter correlation and the evaporation constants were determined using fundamentally different sizing technique. However, Eq 7.2 will be retained because it is qualitatively correct and it will help elucidate a number of important factors).

Finally if Eq 7.1 and 7.2 are combined with Eq 4.1 an approximate expression for the average deposition probability of the aerosol cloud (based on the deposition probability of the median droplet size) can be obtained.

$$Deposition \propto \frac{C_7 D_s}{x q_e} \sqrt{\frac{r_c}{\rho_{ge} P_e}} \left\{ \left(1 - \frac{(1-q_e)}{q_e}\right) \left(\frac{\rho_{ge}}{\rho_l}\right) \right\}^3 (\phi + (1-\phi) \exp(-\lambda x))^2$$

Strictly speaking, this expression is only approximate and is only applicable to continuous sprays, however because of the similarity in behaviour of the metered and continuous systems it can be used in a qualitative sense to explain the observations summarised in table 7.1.

7.3

#### **Spray Orifice Diameter**

Eq 7.3 shows that, all other things being equal, the probability of deposition in the 'throat' of an impinger, or oropharynx of the airways, is directly proportional to the spray orifice diameter  $D_s$ . Larger spray orifice diameters lead to higher deposition and hence lower 'dispersion' values. Reference to Table 7.1 and section 4.3 confirms that the 'dispersion' values obtained from the impinger apparatus are indeed proportional to spray orifice diameter. Obviously this is an oversimplification since changing the spray orifice diameter will result in changes in expansion chamber pressure and the quality of flow through the spray nozzle. However, over the range investigated in section 4.3 (discharge diameter ratios of 0.71 to 1.43) these effects would be expected to be small.

#### **Propellant Vapour Pressure**

Changing the vapour pressure of the propellant can be seen to affect 2 terms in Eq 7.3. The first term involves the inverse of the square root of the expansion chamber pressure, the second term involves the evaporation rate constant,  $\lambda$ .

Since, for any given discharge diameter ratio, the expansion chamber pressure is roughly proportional to the saturated vapour pressure of the propellant the first term implies that deposition probability decreases inversely with the square root of propellant vapour pressure. However, the evaporation rate constant also decreases with increasing propellant vapour pressure, see section 5.3. Thus the combined effect of the 2 terms means that 'dispersion' should increase slightly faster than the inverse square root of the propellant vapour pressure. Reference to Table 7.1 and section 4.3 shows this to be the case.

### Surfactant Concentration

It was stated in sections 5 and 6 that the surfactant concentration has a negligible affect on atomiser exit conditions. It was also shown that surfactant concentration has very little effect on the initial droplet size generated at the spray orifice. It can be concluded from these observations that the effect of surfactant concentration on the variables contained in Eq 7.3 is limited to changing the value of  $\mathbf{F}$  and the evaporation rate constant,  $\lambda$ . Substitution of values for  $\mathbf{F}$  and  $\lambda$  into the last term of Eq 7.3, over the range of concentrations investigated in section 4, shows that 'dispersion' should increase with decreasing surfactant concentration and should approximately quadruple over the range 0 to 2 percent. Reference to section 4 shows that this is indeed the case.

Finally, it can be concluded that the effective relaxation distance for the aerosol particles produced from a metered superheated spray can be used as a key measure of aerosol quality.

## 8. **SUGGESTIONS FOR FURTHER WORK**

## 8.1 INTRODUCTION

- 8.2 SUSPENDED SOLIDS
- 8.3 METASTABILITY
- 8.4 **DROPLET KINETICS**
- 8.5 **DROPLET SIZE CORRELATIONS**

#### 8.1 INTRODUCTION

In terms of the main objective of the project stated in section 3, that is to develop a quantitative understanding of the metered atomisation process, a great deal of progress has been made. For example a theoretical model, and associated computer software, has been developed to describe the metering process and predict atomiser exit conditions. A correlation function relating atomiser exit conditions to the initial droplet size produced at the spray orifice has also been proposed. However, there have been a number of areas highlighted during this project which have only been investigated on an empirical basis. Some of these areas, for example the effects of the solids phase on inhaler performance, were not studied in detail because it was felt that a fundamental understanding of the underlying atomisation process was required before this could successfully be achieved. Some other areas such as droplet evaporation kinetics within the developing spray plume were only investigated on an empirical basis because of a lack of adequate experimental techniques. These areas will now be reviewed and some suggestions for further work will be made.

## 8.1 SUSPENDED SOLIDS

Section 4.3.2 highlighted the effects of the concentration and particle size of the suspended solids upon the performance of the metered dose delivery system. However, because of the empirical nature of the sizing apparatus no fundamental conclusions could be drawn. The suspended solids phase was not investigated on a more fundamental basis because it was felt that superheated liquid atomisation needed to be understood before any real progress could have been be made. In the light of the work presented in this thesis the way is now open for a more fundamental study of the effects of the solid phase. Further, such a study would be valuable not only in terms of metered dose inhaler performance, but also in relation to other forms of suspension atomisation for respiratory therapy (eg. steroid nebuliser suspensions).

## 8.3 METASTABILITY

Metastability was investigated during the investigations into continuous atomisation, section 5. Empirical correlations were developed which described metastability in terms of the residence time of the propellant within the expansion chamber. These correlations were essentially based on the single valve design used in these studies and only covered a narrow range of residence times. It would be far more desirable to place the calculation of metastability on a sound theoretical basis and to extend the correlations to other valve designs and expansion chamber residence times. The area of metastability has been studied extensively in terms of pipe flow but has not been investigated in any detail on the small scales experienced in conventional 'aerosol' valves.

## 8.4 **DROPLET KINETICS**

The velocity and droplet size profiles of continuous sprays produced by superheated liquids has been investigated by a number of authors (eg. Fletcher, 1975, Rance, 1972). The evaporation of the propellant droplets within such a spray plume from a continuous generator was investigated in section 5.3. The extension of these investigations to metered sprays requires an instrument capable of high data capture rates, a large dynamic range and a capability of the simultaneous measurement of both velocity and droplet size.

One such instrument is the phase Doppler analyser. Preliminary results from a PDPA system are presented in **Appendix AVII**. It can be seen from these that this type of instrument has tremendous capabilities, both for looking in detail at 'free' plumes and possibly for looking at the dynamics of plumes expanding into confined spaces. Using casts of the human oropharyx and a PDPA it may now be possible to investigate the interaction between the plume and the upper portion of the human airways. This type of study could result in improved mouthpiece of spray orifice design.

## 8.5 **DROPLET SIZE CORRELATION**

It was stated in section 5.3 that the main problem in trying to delineate the atomisation mechanism in a twin orifice atomiser, is that the expansion chamber variables such as quality, superheat, vapour density and pressure are not independent. It would thus appear that further work on this type of system is unlikely to produce data any more conclusive, or comprehensive, than that presented above.

However it may be possible, using a 'vapour tap' valve, to vary the thermodynamic conditions in an more independent manner. It will be recalled from section 2 that a 'vapour tap' valve has a third orifice leading into the expansion chamber. This third orifice is directly connected to the vapour 'head' in the canister. Thus, by manipulating the 3 orifice diameters it may be possible to de-link the quality, temperature and pressure of the flow in the expansion chamber. The computer model and experimental methods described in section 5 could then be extended to describe the operation of a 'vapour tap' system. It may then be possible to extend the droplet correlation developed in section 5 and to gain further insight into the atomisation process.

To date only empirical studies have been performed on 'vapour tap' systems. However, as evidence by the work of Tsuda (1989), reported in section 2, there would seem every possibility that the extension of the concepts presented above would lead to a better understanding of the atomisation process.

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## **APPENDIX I**

## ANALYTICAL VALUES AND CALCULATIONS FOR DISPERSION TESTING

## Analytical Values :-

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Compound	Solvent	Buffer	λ max (nm)	E <sub>1cm,1%</sub>	No. Shots
FPL59670	Dist. Water	Disodium hydrogen orthophosphate	326	166.5	10
FPL59002	Dist. Water	Trisodium citrate dihydrate	253	869.6	5
FPL61369	Dist. Water	Trisodium citrate	331	566.7	10
Salbutamol Sulphate	Dist. Water	none used	278	56.4	50

NB. E  $_{1cm,1\%}$  refers to the absorbance value of a 1% solution when contained in a 1cm silica cell.

**Calculations** :-

mgs at location

$$mg = \frac{Absorbance \times Volume \times 10}{E_{1cm.1\%}}$$
(AI.1)

Dispersion

$$Dispersion = \frac{mg \ reaching \ filter}{mg \ total \ recovery}$$
(AI.2)

#### **APPENDIX II**

## THE USE OF EXIT THRUST TO DETERMINE THE VELOCITY OF SOUND IN NITROGEN GAS

## **INTRODUCTION**

In order to verify the use of thrust, or exit momentum, measurements as a basis for the estimation of nozzle exit velocities a number of experiments were performed using nitrogen gas. Under conditions were the up-stream pressure exceeds the critical pressure ratio the flow of nitrogen through a nozzle will be choked and equal to its sonic velocity. The use of nitrogen gas at nozzle pressures exceeding this critical level thus offered an opportunity to verify the velocity calculations based on thrust measurements.

In order to carry out the necessary measurements and calculations the orifice discharge coeffcient of the experimental nozzles needed to be known. The experimental investigations were therefore divided into 2 phases. The first phase involved the measurement of the discharge coefficients of the nozzles, the second phase involved the measurement of the exit thrust produced and the calculation of the sonic velocity.

## **MEASUREMENT OF DISCHARGE COEFFICIENTS**

#### Theory

BS 1042 defines the theoretical equation for the mass discharge rate, Q, of a compressible fluid through an orifice, or nozzle, as :-

$$Q = C_q A \sqrt{\frac{\gamma+1}{P_u \rho_u \gamma R_c^{\gamma}}}$$
(AII.1)
Where  $C_q$  is the discharge coefficient, A is the area of the orifice,  $P_u$  is the up-steam absolute pressure,  $\rho_u$  is the density of the gas and  $R_c$  is the critical pressure ratio.  $R_c$  represents the maximum ratio of down-stream to up-steam pressure which ensures choked, or sonic, flow. For a gas  $R_c$  may be defined in terms of the ratio of the specific heats,  $\gamma$ .

$$R_{c} = \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma}{\gamma - 1}}$$
(AII.2)

The discharge coefficient,  $C_q$ , can thus be found from Eq AII.1 by measuring the mass discharge rate under conditions were the experimental pressure ratio is less than  $R_c$ .

#### Experimental

Figure AII.1 presents a schematic diagram of the experimental arrangement used to determine the discharge coefficients of the 4 orifices to be used in the nitrogen velocity determinations. A vacuum pump was used to reduce the pressure on the downstream side of the orifice. The flow of air through the nozzle was measured on the up-stream side with the aid of pneumotachograph and micromanometer (Furness Controls plc, Bexhill, England). The down-stream pressure was monitored using a mercury U-tube manometer.

#### Results

The results of the critical flow determinations are presented in figure AII.2. The abscissa is presented in terms of the pressure fall across the nozzle, the ordinate is mass discharge rate in kg/sec.

It can be seen that as the down-stream pressure is reduced the mass flowrate initially increases. However, as the critical pressure ratio is approached the mass flow becomes choked and the mass discharge rate plateaus. Also shown in **figure AII.2** are the mass discharge rates for the 4 orifices calculated from **Eq AII.1** assuming a  $C_q$  of 1. The ratio of the experimental mass discharge



#### Figure All.1 The Measurement of the Spray Orifce Discharge Coefficients

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to this calculated value gives the value of the discharge coefficient. Table AII.1 presents a summary of the values of Cq for the 4 orifices, it can be seen that the average value is 0.78. This mean value was used in all the calculation of the exit velocity.

Orifice number	Discharge coefficient
A	0.76
В	0.79
С	0.81
E	0.76
Mean	0.78

## Table AII.1 Summary of nozzle discharge coefficients as Determined usingCritical Flow

#### DETERMINATION OF THE VELOCITY OF SOUND IN NITROGEN GAS

#### Theory

Eq 5.23 defines a theoretical expression relating the exit thrust from a choked nozzle to the pressure at the point of choking and the sonic exit velocity.

$$J = C_{q} A_{c} V_{c}^{2} + A_{c} (P_{c} - P_{amb})$$
(AII.3)

Where J is the exit momentum, or thrust,  $A_c$  is the area at the point of choking,  $V_c$  is the choked, or sonic discharge velocity,  $P_c$  is the pressure at the point of choking and  $P_{amb}$  is the pressure down-stream of the nozzle.

As in section 5.2.1.4 the value of  $P_c$  may be expressed in terms of the up-stream pressure conditions by making use of the critical pressure ratio  $R_c$ .

.

$$P_c = R_c P_u \tag{AII.4}$$

Also, in line with section 5.2.1.4, the density of the gas at the point of choking may be found in terms of the up-stream pressure and temperature by assuming isentropic flow and making use of the ideal gas equation.

$$\rho_{c} = R_{c}^{\frac{1}{\gamma}} \rho_{u} = R_{c}^{\frac{1}{\gamma}} \frac{\chi P_{u}}{R T_{u}}$$
(AII.5)

Were x is the molecular weight of the gas and  $T_u$  is the up-stream temperature. With very little loss of accuracy  $A_c$  may be assumed to be equal to the area of the orifice A.

$$A = C_q \frac{\pi}{4} D_s^2$$

Were  $D_s$  is the geometric diameter of the orifice.

Substituting Eq AII.4, AII.5 and AII.6 into AII.3 and performing a little rearrangement then allows the determination of the exit velocity.

$$V_{c} = \sqrt{\left(\frac{J - C_{q} \frac{\pi}{4} D_{s}^{2} (R_{c} P_{u} - P_{amb})}{C_{q} \frac{\pi}{4} D_{c}^{2} R_{c}^{\frac{1}{\gamma}} P_{u} \chi}\right)} R T_{u}$$
(AII.7)

Since in choked flow the exit velocity is sonic this should be equal to the velocity of sound in the nitrogen gas.

#### Experimental

Figure AII.3 presents a schematic diagram of the experimental arrangement used to measure the exit thrusts and sonic velocities. The up-stream pressure and temperature,  $P_u$  and  $T_u$ , where measured by mercury U-tube manometer and a copper/constantan thermocouple respectively. The exit thrust, J, was measured using 5cm target disk attached to a micro force transducer (Sensym Technics, Rugby, England). Nitrogen gas was supply from a high pressure cylinder.

The exit thrusts from each of the 4 nozzles were measured for a range of up-stream pressures and for a number of nozzle to transducer target spacings. It was found that provided the target disk was within 5cm of the nozzle a constant level of thrust was experienced (see section 5.2.2.3). All the measurements used for the velocity determination were therefore performed at a nozzle to transducer spacing of 5cm.

#### Results

The results of the application of Eq AII.7 to the experimental values of pressure, temperature and thrust determined for the 4 nozzles is shown in figure AII.4. Also indicated in the figure are the value of the critical pressure, the region over which the exit flow would be expected to be sonic, the 'best known' value for the velocity of sound in nitrogen and the theoretical isentropic sonic velocity  $V_{ci}$ .

$$V_{ci} = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\gamma R T}$$
(AII.8)

As can be seen, bearing in mind that 3 experimental values each with thier associated experimental error had to be measured for each velocity calculation, the agreement between the experimental values and the 'best known' value, obtained from the 'CRC, Handbook of Chemistry & Physics, 72 Edition', is extremely good.



#### Figure All.3 The Determination of Exit Velocty from Thrust Measurements

1. Handbook of Chemistry & Physics, CRC

#### CONCLUSION

The velocity of sound in nitrogen gas has been successfully determined using exit thrust, or exit momentum, measurement. This lends weight to the use of the technique for the determination of the exit velocities of the two-phase flow mixtures encountered in superheated liquid aerosol generators.

#### REFERENCES

CRC (1988),'Handbook of Chemistry and Physics', 72nd Edition

### **APPENDIX III**

### ORIFICE DISCHARGE RATIOS FOR CONTINUOUS DISCHARGE EXPERIMENTS

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## A. Instrumented Spray Orifices

			Orifice discharge Ratio				
Orifice Number	Valve	Orifice D <sub>v</sub>	1	2	3	4	5
Spray	Diameter (mm)		0.259	0.420	0.589	0.823	1.005
Orifice D <sub>s</sub>		Discharge Coeff.	0.78	0.72	0.67	0.59	0.48
1	0.294	0.78	1.13	0.72	0.53	0.41	0.36
2	0.479	0.78	1.85	1.18	0.87	0.66	0.61
3	0.598	0.78	2.31	1.47	1.08	0.83	0.75
4	1.023	0.78	3.94	2.53	1.87	1.42	1.30

## **B.** Plastic Spray Orifices

			Orifice discharge Ratio				
Orifice Number	Valve	e Orifice D <sub>v</sub>	1	2	3	4	5
Spray	Diameter (mm)		0.259	0.420	0.589	0.823	1.005
Orifice D <sub>s</sub>		Discharge Coeff.	0.78	0.72	0.67	0.59	0.48
A	0.425	0.78	1.64	1.05	0.78	0.59	0.53
В	0.565	0.78	2.18	1.40	1.03	1.01	0.71
С	0.725	0.78	2.80	1.79	1.32	1.01	0.92
D	0.975	0.78	3.76	2.41	1.78	1.36	1.23
E	1.147	0.78	4.43	2.84	2.10	1.60	1.45

Note.

Orifice Discharge Diameter Ratio = 
$$\sqrt{\frac{C_{qs}}{C_{qv}}} \times \frac{D_s}{D_v}$$

#### **APPENDIX IV**

## THE MEASUREMENT OF THE SURFACE TENSION OF PROPELLANT LIQUIDS

#### INTRODUCTION

As can be seen from the literature search presented in section 2 of this thesis, the surface tension of a liquid is one of the major physical properties which affects atomisation efficiency. Thus, since a number of formulations, with and without 'surfactant', were used in the experimental investigation of superheated liquid atomisation, it was desirable that the surface tension of the formulations be known.

Measuring the surface tension of a low boiling point propellant is particularly difficult since it has to be maintained under pressure in order to ensure it remains in the liquid state. This pressure constraint resulted in the capillary rise technique being chosen as the best experimental option since it could easily be adapted to application inside a pressure vessel. The capillary rise technique is in general considered to be one of the most accurate of all methods (Adamson, 1990). Indeed over the years many refinements to the simple single capillary methods have been developed. For example Stansfield (1958) and more recently McLure & Neville (1979) have made use of multiple capillaries in order to avoid the error associated with the uncertainty in the measurement of the level of the liquid reservoir. Mclure & Neville also used a twin telescope cathetometer and moved the capillary tubes and reservoir in order to avoid errors associated with viewing the capillary through many layers of optically imperfect glass (ie. dewar and water bath walls). Mclure estimated that their measurements were accurate to 0.05mNm<sup>-2</sup>

In the experiments described below no attempt was made to reach this degree of accuracy. A simple estimate of reproducibility using a single capillary showed it to be better than +/-0.4mNm<sup>-2</sup>. Comparison of experimental data with published values also showed reasonable agreement. The simple

#### AIV.1

single capillary technique was thus felt to have sufficient accuracy for the present study.

#### THEORY

The phenomena of capillary rise has been used for the determination of the surface tension of liquids for many years. The basis of the technique is a force balance between the surface tension force on the wall of a circular capillary tube and the weight of a column of fluid which this force will support. The surface tension force around the periphery of the capillary tube is

$$F_t = \pi D \gamma \cos \omega$$
 (AIV.1)

Where **D** is the diameter of the capillary tube,  $\gamma$  is the fluid surface tension and  $\omega$  is the angle of contact between the fluid and the capillary wall. This upward force is balanced by the total weight of the column of liquid in the capillary. Because of the shape of the liquid meniscus this weight is extremely difficult to determine experimentally. Rayleigh (1915) derived an expression for the weight of fluid column based on the assumption that the meniscus was essentially spherical.

$$W = \pi \frac{D^2}{4} \Delta \rho g(h + \frac{D}{6} + \frac{0.1288D^2}{4h} + \frac{0.1312D^3}{8h^2} \dots) \quad (AIV.2)$$

Where **h** is the height of the meniscus above the liquid reservoir,  $\Delta \rho$  is the buoyancy corrected density of the liquid and **g** is the acceleration due to gravity. The term **D**/6 represents a correction for the weight of the meniscus, the remaining terms represent correction for slight deviation from sphericity. Equating **Eq AIV.1** and **Eq AIV.2** and a little rearrangement then yields an expression for the surface tension.

$$\gamma = \frac{D\Delta\rho g}{4\cos\omega}(h + \frac{D}{6} + \frac{0.1288D^2}{4h} + \frac{0.1312D^2}{8h^2} + ...)$$
(AIV.3)

This approximation is valid provided that the meniscus is nearly spherical, that is when D/2 << h. When this is not the case the non-spherical shape of the meniscus needs to be taken into account when calculating the weight of the column. It is found that in the case of a non-spherical meniscus an exact solution for the column weight is not possible and a number of numerical approximations have been developed (see for example Sugden, 1921).

The surface tension values presented below were calculated using Eq AIV.3 because application of the numerical correction to the particular geometry employed in the experimental apparatus resulted in a correction of less than 1 percent.

#### EXPERIMENTAL

#### Apparatus

As stated above in order to measure the surface tension of the propellant formulations at close to ambient temperature it is necessary to maintain them under pressure. Figure AIV.1 presents a schematic diagram of the pressure cell used for this purpose. The pressure cell was made from pyrex glass. At the top of the cell a screw clamp and 2 'O-ring' seals enabled the affixation of a standard 1" continuous discharge valve. This valve was used to charge the cell with the particular formulation under test. Inside the cell a micro capillary (Volupette pipet, Dade Corp, Miami Florida) and mercury thermometer were held in an vertical position by a PTFE support. The pressure cell was enclosed in a perspex sleeve for safety and the whole apparatus was placed in a temperature controlled water bath (+/- 0.5 K).

**D** and **h** were measured with a travelling microscope (Vickers Instruments, York, England) to an accuracy of 0.01 mm.



## FIGURE AIV.1 CAPILLARY APPARATUS FOR THE MEASUREMENT OF SURFACE TENSION

Enlarged View of Capillary and Pressure Cell



#### Methods

As is always the case when making a determination of surface tension it is essential that all traces of foreign materials are removed from the glassware. This was achieved in the present investigations by initially washing the glassware with chromic acid and then rinsing with distilled water. After being allowed to dry, and then between every subsequent measurement, the glassware was rinsed with carbon tetrachloride and then propellant 11. Finally the glassware was rinsed with the propellant under test. Pure propellants were measured first followed by increasing concentration of sorbitan trioleate. The HFC propellants were measured last.

In each case the cleaned apparatus was assembled as shown in **figure AIV.1**. In the first instance the valve seals were left uncompressed so that introduction of propellant through the inlet valve resulted in air being purged from the pressure cell. After a few seconds the seals were tightened and approximately 20 ml of the propellant under test was injected into the cell.

After filling, the cell was allowed to reach equilibrium at the test temperature (as evidenced by a stationary meniscus). The apparatus was then tilted to ensure the meniscus flowed to a position higher in the capillary tube than its rest position. On returning the apparatus to its upright position the meniscus flowed back to its equilibrium position. Since the propellant liquids used in this study readily wetted the glass capillary this ensured a 'falling meniscus' and a zero angle of contact. The travelling microscope was then used to determine the location of the liquid reservoir level and the base of the 'spherical' meniscus. The height of the meniscus, **h**, was then calculated by simple subtraction. The mean internal diameter of the liquid capillary, **D**, was measured using the travelling microscope and was the mean of 4 diameter determinations.

#### RESULTS

#### Reproducibility

In order to estimate the reproducibility of the single capillary technique and to estimate the error associated with the problem of measuring the meniscus position through layers of optically imperfect glass and perspex, a series of 6 surface tension determinations were carried out upon pure propellant 12. Each determination was carried out with a different volume of propellant in the pressure cell and hence with a different meniscus and reservoir position. These experiments showed that the determination was reproducible to a level of +/-0.4mNm<sup>-2</sup> (standard deviation based on n-1).

Following the reproducibility experiments the surface tension of a number of pure propellants was measured across a range of temperatures. These data together with the 'best known' values are presented in **figure AIV.2**. It can be seen that all the propellants tested show a rise in their surface tension of approximately 10 percent from 293 -273 K. The experimental values at 293 K also appear to be in good agreement with the 'best known' values.

#### Effect of Propellant Mixture and 'Surfactant' Concentration

**Tables AIV.1** and **AIV.2** summarise a series of determinations designed to investigate the effect of mixing propellant 12 and propellant 114 and the effects of adding various concentrations of sorbitan trioleate to various propellant mixtures. **Table AIV.3** Summarises the effects of adding PEG300 (polyethylene glycol) to propellants 134A and 227.

It can be seen from table AIV.1 that there is a slight increase in surface tension as the proportion of propellant 114 in a mixture of propellant 114 and propellant 12 is increased, however the increase is quite small.

It can be seen from **Table AIV.2** that the addition of sorbitan trioleate to either propellant 12 of propellant 114:12 mixtures has no measurable effect on the surface tension values. Also **table AIV.3** shows that the addition of PEG300 to either propellant 134A or 227 has a similar lack of effect.

#### AIV.6



TABLE AIV.1The Surface Tension of Mixtures of Propellant 12 and<br/>Propellant 114

Propellant Ratio 12:114	Surface Tension $\gamma$ mNm <sup>-2</sup>
20:80	10.9
40:60	10.5
60:40	10.3
80:20	9.8
100:0	9.2

Figure AIV.2 The Surface Tension of Selected Pure Propellant as a Function Temperature

## TABLE AIV.2 The variation in surface tension of formulations of Propellant 12and 40:60 propellant 12:114 containing sorbitan trioleate

	Surface Tension $\gamma$ mNm <sup>-2</sup>		
Sorbitan trioleate concentration W/W %	Propellant 12	40:60 Propellant 12:114	
0.0	8.9	10.3	
0.1	9.1	10.2	
0.25	9.2	10.5	
0.5	8.9	10.5	
1.0	9.1	10.7	

Table AIV.3 The variation in surface tension of formulations of propellant 134Aand propellant 227 containing PEG 300

	Surface Tension γ mNm <sup>-2</sup>				
PEG 300 concentration W/W %	Propellant 134A	Propellant 227			
0.0	8.5	7.5			
0.25	8.8	7.9			

#### CONCLUSIONS

An experimental capillary cell has been developed to facilitate the measurement of the orthobaric surface tension of propellant liquids. The technique has shown reasonable reproducibility and experimental values for a number of pure propellants have shown reasonable agreement with published values.

The experimental data shows that high proportions of propellant 114 in mixtures of propellant 12:114 result in slightly higher values of surface tension. More importantly the data also shows that the term 'surfactant' when used to describe either sorbitan trioleate or PEG300 in solution in propellants is a total misnomer. The inclusion of either of theses materials in propellant formulations does not reduce surface tension values.

Extracts from Tables AIV.1 to AIV.3 are presented in table 5.3 in section 5.3 where the effects of sorbitan trioleate and PEG concentrations on atomiser efficiency are discussed.

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#### APPENDIX V

#### PRESSURE AND TEMPERATURE SENSOR RESPONSE TIMES

#### INTRODUCTION

In order to verify the suitability of the pressure and temperature transducers for use in the metered discharge test apparatus it was necessary to estimate their response times. The response times of the thermocouples were estimated by 'rapid immersion' in a boiling propellant mixture. The response times of the pressure sensors were estimated using an 'exploding' balloon technique.

#### **MEASUREMENT OF THERMOCOUPLE RESPONSE TIMES**

#### Theory

The temperature response of a thermocouple, to an abrupt step wise temperature fall, can normally be modeled by a simple mono-exponential decay.

$$(T_t - T_f) = (T_i - T_f) \exp(-Kt)$$
 (AV.1)

Where  $T_i$  is the initial temperature of the thermocouple,  $T_t$  is the new equilibrium temperature of the thermocouple, t is time and  $T_t$  is the temperature at any time t. K is known as the time constant.

#### Experimental

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The response times of each of the copper/constantan thermocouples was measured by rapid immersion in a boiling mixture of 20:80 propellant 12 and propellant 114 (T = 283K).

The thermocouples were allowed to equilibrate in air at room temperature. After reaching equilibrium they were plunged into the boiling propellant and the temperature fall monitored via the electronics and computer system described in section 5.3. The CED 1401 analogue to digital converter was run at a conversion rate of 500 Hz.

#### Results

The experimental response curves are shown in **figure AV.1**. Because the conversion from the digital values received from ADC to absolute temperature is essentially linear the response curves have been left in their raw digital form.

It can be seen that the thermocouples all exhibit the expected mono-exponential decay. Table AV.1 summarises the rate constants and time for 50% response,  $t_{1/2}$ . The 50% response times were typically 5 to 6 ms.

#### MEASUREMENT OF PRESSURE TRANSDUCER RESPONSE TIMES

#### Theory

The response time of a piezo pressure transducer is, in general, of the same exponential form as the response curves for the thermocouples described above. However, as will be seen below, the particular transducers used during the experimental work reported in this thesis had response times far shorter than could be measured by the high speed electronics described in section 5.3.

#### Experimental

The response times of the 3 pressure transducers were assessed by attaching an inflated balloon to their inlet pressure ports and then bursting the balloon with a sharp implement. The pressure fall, as indicated by the transducers, was then monitored via the electronics described in section 5.3.

	Time constant (K)	t <sub>1/2</sub> (ms)
Thermocouple 1	109.8	6.3
Thermocouple 2	105.5	6.6
Thermocouple 3	131.8	5.2

## Table AV.1 Thermocouple Response Time Data





#### Results

The pressure response curves are shown in figure AV.2. It can be seen that after the initial pressure rise as the balloon is pierced the pressure decay takes less than 2 ms. This is in line with the manufacture's claim of an 0.1 ms response time. It should be noted that transducer 3 was tested with a stainless steel inlet port attached (see section 5.3.2).

#### DISCUSSION

The data indicate that both types of transducer are suitable for use in the metered discharge experiments. It would have been desirable to have slightly 'faster' thermocouple response times but, as explained in section 5.3, the particular design chosen was a compromise between response time and robustness.



#### AV.5

#### **APPENDIX VI**

### ORIFICE DISCHARGE RATIOS FOR METERED DISCHARGE EXPERIMENTS

IF

			Orifice discharge Ratio				
Orifice Number	Valve	Orifice D <sub>v</sub>	1	2	3	4	5
Spray	Diameter (mm)		0.251	0.393	0.632	0.866	0.955
Orifice D <sub>s</sub>		Discharge Coeff.	0.78	0.74	0.66	0.59	0.52
1	0.294	0.78	1.17	0.77	0.51	0.39	0.38
2	0.479	0.78	1.91	1.25	0.82	0.64	0.61
3	0.598	0.78	2.38	1.56	1.03	0.79	0.77
4	1.023	0.78	4.07	2.69	1.76	1.36	1.31

## A. Instrumented Spray Orifices

## **B.** Plastic Spray Orifices

	<u> </u>		Orifice discharge Ratio				
Orifice Number	Valve	Orifice D <sub>v</sub>	1	2	3	4	5
Spray	Diameter (mm)		0.251	0.393	0.632	0.866	0.955
Orifice D <sub>s</sub>		Discharge Coeff.	0.78	0.74	0.66	0.59	0.52
А	0.425	0.78	1.69	1.07	0.77	0.56	0.55
В	0.565	0.78	2.25	1.48	0.97	0.75	0.72
С	0.725	0.78	2.89	1.89	1.25	0.96	0.93
D	0.975	0.78	3.88	2.55	1.68	1.29	1.25
E	1.147	0.78	4.57	3.00	1.97	1.52	1.47

Note.

Orifice Discharge Ratio = 
$$\sqrt{\frac{Cqs}{Cqv}} \times \frac{Ds}{Dv}$$

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#### **APPENDIX VII**

## THE USE OF THE PHASE DOPPLER ANALYSER FOR THE ANALYSIS OF THE CLOUDS GENERATED FROM METERED DOSE INHALERS

#### **INTRODUCTION**

In Section 6.3 it was stated that an investigation into the dynamics of the plumes generated from metered dose inhalers would be valuable in understanding the interactions between this form of delivery system and the human airways. However, attempts to use a conventional diffraction analyser to carry out this type of study were hampered by a lack of sensitivity and a lack of both sizing and time resolution. Attention therefore turned to the use of the Phase Doppler Particle Analyser (PDPA) as described by Bachalo (1980). The phase Doppler technique is reported to have excellent spatial, temporal and size resolution and, with the correct signal processing, is capable of 'viewing' in particularly noisy signal environments. It also has the capability of simultaneous measurement of both the size and velocity of the individual droplets within the spray plume.

Unfortunately, due to the limited availability of phase Doppler instrumentation, it only proved possible to carry out a very preliminary study using this technique. It is the purpose of this Appendix to describe the methods, results and conclusions from this preliminary investigation. The results are presented here in direct support of the data presented in the preceding sections of this thesis.

#### **EXPERIMENTAL**

#### **Instrument Description**

The optical principles upon which the phase Doppler technique is based have been described by a large number of authors (Bachalo, 1980, Bachalo, 1984 Sanker, 1990). An optical system similar to that used in a conventional laser

receiver is located at a 'preferred' angle to the beams and is used to detect the light scattered by the particle, or droplet, as it passes through the beam intersection. Light scattered from each of the beams interferes in the plane of the detector to form a temporal and spatially varying interference pattern.

The temporal variation of the pattern produces a 'Doppler burst' signal whose frequency is proportion to the particle velocity as it passes through the beam intersection. The signal from a single detector is sufficient to determine the frequency and hence the droplet velocity.

The spatial frequency of the interference fringe pattern, on the other hand, has been shown to be proportional to the size of the spherical particle, or droplet, passing though the beam. (Accurate results, for droplet size, are only obtained from the PDPA system when the droplets, or particles, are truly spherical. However, in the context of the present investigations this is not a limitation since, on the whole, the propellant or surfactant droplets will be essentially spherical). Measurement of the spatial frequency of the interference fringes requires the use of at least 2 spatially separated detectors. Due to the apparent motion of the interference fringe pattern the spatial separation of the detectors results in the 2 doppler signals received by the detectors having the same frequency but having a relative phase shift. The phase shift can then be related droplet size.

Light scattering interferometry theory is used to generate the response relationships between the measured phase angle and droplet diameter and to determine the 'preferred' angle for the detectors. The calculation of droplet size from the theory requires a knowledge of the beam intersection angle, the detection angle, receiver aperture geometry and particle refractive index. (The refractive index of the propellant formulations and surfactant used in the experiments reported below are broadly similar, ranging from 1.4 - 1.45. Without much loss of accuracy a mean value of 1.425 was used for all the droplet size calculations. A forward scattering angle of 70 deg was also used in order to minimise the effect of refractive index (Bachalo, 1984).)

In the practical instrument 3 detectors are usually used. The use of the third detector, at a larger spatial separation than the second detector, allows the instrument to be used over a much larger phase shift and droplet size range. It also facilitates a method of confirming particle sphericity. The magnitude of the disagreement in computed droplet diameter between each pair of detectors is a measure of how non-spherical the measured droplet is. An additional refinement in the commercial instruments is the use of a Bragg cell or diffraction grating to phase shift one of the laser beams. This results in the fringe pattern exhibiting a constant motion in the detector plane and allows the determination of the sign of the velocity as well as its magnitude.

The instrument used in the current study was a Dantec Particle Dynamics Analyser. The Dantec PDA uses a 5 watt Ar-ion laser with 3 detectors positioned in near forward scatter. The signal processor uses a covariance technique which allows processing of low signal to noise 'Doppler bursts' at an average sustainable data rate of approximately 120,000 particles per second. The resolution of the instrument is better than 0.1  $\mu$ m in droplet diameter, 1  $\mu$ s in terms of arrival time at the beam intersection and 0.1 ms<sup>-1</sup> in velocity determination. The particular optical configuration used in the experiments reported below is summarised in **Table AVII.1**. Figure AVII.1 presents a photograph of the system.

#### **Experimental Program**

As stated above the experimental program was, by necessity, limited in extent. The experiments covered the effect of propellant vapour pressure, distance from the spray orifice and the metering volume. Table AVII.2 summarises the experimental program and measurement conditions.

#### **Experimental Results**

The variation of droplet velocity and particle diameter during the pulse from a 100  $\mu$ l metered volume of propellant 12, 5 cm down-stream of the spray orifice, is shown in **figure AVII.2**. **Figure AVII.2A** presents the velocity profile **figure AVII.2B** presents the droplet size profile. Each dot on the size and velocity plots represents a determination of size and velocity for an individual

## TABLE AVII.1 Optical Configuration of Dantec PDA used for Metered Spray Experiments

## **Transmitting Optics**

Laser power	1 Watt
Laser wavelength	0.5145 µm
Gaussian beam diameter	2.2 mm
Beam Separation	39.0 mm
Lens focal length	310 mm
Polarization orientation	parallel to fringes
Fringe spacing	4.09 µm

## **Recieving Optics**

Scattering angle	70 deg
Lens focal length	310 mm
Polarisation angle	0 deg
Direction of fringe motion	Negative
Particle/medium refractive index	1.425

## FIGURE AVII.1 Photograph of Dantec Phase Doppler Analyser



# TABLE AVII.2 Experimental Test Program Using the Dantec ParticleDynamics Analyser.

Formulation (propellant 12:114)	Metering volume (µL)	Distance from spray Origin (cm)
100:00	100	5, 10, 20
60:40	100	5
	50	5
40:60	100	5

1. Discharge diameter ratio for all experiments was approximately 1.1

2. All formulations contained 0.25 %w/w sorbitan trioleate.

## FIGURE AVII.2 Velocity and Droplet Diameter Profiles for a 100µl metered Discharge of Propellant 12



A) Velocity Profile



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droplet with in the spray pulse. As would be expected the individual droplet velocities show a marked scatter around a mean value. Also, as would be expected, the mean value shows a sharp rise at the start of the pulse, a maximum value (approximately  $35 \text{ ms}^{-1}$ ) and a subsequent decay. The droplet diameter, expressed as number, shows no marked change over the pulse width although there does appear to be a tendency for a number of large droplets to be detected in the centre portion of the pulse. The pulse width, of 150-175 ms, is in agreement with the estimates reported in sections 4 and 6 above.

Figure AVII.3 presents droplet velocity data for 100  $\mu$ l discharges of propellant 12 as a function of distance from the spray orifice. It can be seen that the pulse seems to spread slightly and the velocities are lower as distance from the spray orifice increases. This will be discussed further below.

Figure AVII.4 presents droplet velocity data for 100  $\mu$ l discharges from canisters containing propellants of differing vapour pressures. All the measurements were made 5 cm downstream of the spray orifice. It can be seen that lower vapour pressures result in lower droplet velocities. The average peak velocities of 35 ms<sup>-1</sup>, 22 ms<sup>-1</sup> and 18 ms<sup>-1</sup> for each respective formulation is in good agreement with the peak velocity determination reported in section 6.

Figure AVII.5 compares the velocity profiles from 100  $\mu$ l and 50  $\mu$ l discharges of 60:40 propellant 12:114; both measurements were made 5 cm down-stream of the spray orifice. It can be seen that peak velocities are broadly similar and that the pulse width is approximately proportional to metering volume.

Table AVII.3 summarises the number median droplet diameter for each experimental configuration. The data has been left in number form because conversion to a weight median on the basis of only 1,000 to 2,000 particles actually measured was considered to be inaccurate. As would be expected from the data presented in sections 5 and 6, the PDA data shows that the spray plume gets finer as it travels away from the spray orifice and that lower vapour pressures generate coarser sprays. Also as would be expected from section 6, at a discharge diameter ratio of 1.1, the data shows that there is very little difference in the droplet diameter produced from either a 100  $\mu$ l or a 50  $\mu$ l discharge.

## FIGURE AVII.3 Velocity Profiles for a 100 $\mu$ l metered Discharge of Propellant 12 at Increasing Distance from the Spray Orifice

(0.25 %w/w Span)



## FIGURE AVII.4 Velocity Profiles for 100 µl metered Discharges of Propellants of Various Vapour Pressures

(5 cm from Spray Orifice, 0.25 %w/w Span)



## FIGURE AVII.5 Velocity Profiles for a 100 µl and a 50 µl metered Discharge of Propellant 12

(5 cm from Spray Orifice, 0.25 %w/w Span)





B) 50µl Discharge

## Table AVII.3 Summary of the Number Median Droplet Diameters of MeteredPropellant Sprays as Determined by the Dantec PDA

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Formulation (propellant 12:114)	Metering volume (μL)	Distance from Spray Orifice (cm)	Number Median Diameter (µm)
100:00	100	5	1.20
		10	0.92
		20	0.65
60:40	100	5	1.29
	50	5	1.29
40:60	100	5	1.75

- 1. Discharge diameter ratio for all experiments was approximately 1.1
- 2. All formulations contained 0.25 %w/w sorbitan trioleate.

In general it can be seen that the trends observed in the PDPA data are consistant with the data presented in earlier section of this thesis.

Figure AVII.6 presented the peak velocity and droplet size data summarised in Figure AVII.3 and Table AVII.3 in graphical form. The abscissa is distance from the spray orifice the ordinates are velocity and droplet size. Also shown on the figure are residual and calculated initial droplet diameter, determined using the APS33, and a velocity theoretical curve calculated from Eq 5.33. It can be seen that agreement between the methods and the theoretical expression is very good.

#### CONCLUSIONS

The peak velocities determined from the velocity profiles of the individual spray pulses are consistent with the orifice exit velocities determined in section 6. The velocity decay with distance also confirms Fletcher's (1975) equation which states that the axial velocity of the cloud should be inversely proportional to distance from the spray origin (Eq 5.33).

The pulse widths determined from the PDPA data are also in good agreement with those determined by high speed filming, section 4, or by the thermodynamic experiments reported in section 5.

Finally the droplet size and decrease in median diameter with distance from the spray orifice shows good agreement with the Malvern diffraction data for continuous sprays reported in section 5 and the APS33 residual diameter data for metered sprays reported in section 6.

Overall the data obtained from the PDPA system supports the data presented in earlier sections of this thesis. The PDPA system seems an ideal instrument for carrying out further investigations into the development of metered spray plumes both in free space or in more restrictive environments such as oropharyngeal casts. The instrument's ability to measure large numbers of droplets within individual metered sprays means that it can fully characterise velocity profiles and droplet evaporation kinetics.



#### Figure AVII.6 Peak Exit Velocity and Number Median Droplet Diameter Vs. Distance (100ul, Propellant 12)

(NMDD = number median Diameter)
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