Gas release attenuation within buildings; effects of temperature and stratification

Prepared by
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for the Health and Safety Executive

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Liquefied gas stored under pressure may lose containment through a vessel or pipe rupture, forming a two-phase jet as it expands and vaporises. The release has an associated fall in temperature, which may or may not drop below the local saturation conditions. If the release is confined within a building, temperature gradients are established between the pollutant material and the building walls, causing heat transfer from the walls. The released material will mix with the air in the building before being released to the atmosphere. If the released material is heavy, and has low momentum, the pollutant will stratify within the building due to insufficient turbulence. The pollutant then remains more concentrated in the lower layer, with implications to the release rates from openings at different levels. The consequences of such accidental releases are the subject of the GRAB-T project.

This document describes the development and solution of all sets of model equations, and also sets out all the assumptions made leading to the GRAB-T software package. Details are given on all inputs required to model a postulated scenario, and typical model outputs are outlined. The heat transfer mechanisms, pool formation and ventilation effects employed in the model are explained in detail, and the sensitivity of the model to various key parameters is discussed.

The model has been validated against releases undertaken in a one third linear scale chlorination room, and was found to be in reasonable agreement with the experimental data obtained.

This report and the work it describes were funded by the Health and Safety Executive (HSE). Its contents, including any opinions and/or conclusions expressed, are those of the author alone and do not necessarily reflect HSE policy.
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1. **INTRODUCTION**

1.1 **Background**

On certain industrial sites (such as water treatment plants), chemicals which are gaseous at atmospheric pressure and temperature are stored as a liquid either by refrigeration (at ambient pressure) or pressurisation (at ambient temperature). If such a vessel develops a small rupture, pressurised liquid escapes as a jet into the local environment, or if a large rupture forms, the material may ‘spill’ onto the ground. If the chemical is stored at ambient temperature and at its saturation pressure, and a jet release occurs, it will quickly vaporise upon entering the lower pressure regime of the local environment. This may be justified since a fraction of the pollutant flashes to the vapour phase immediately whilst the remaining liquid constituent vaporises within 2-3 metres [1]. For a release into an enclosed space, the vaporised pollutant mixes with the air in the room, resulting in the reduction of the overall temperature of the room contents, accompanied by a further drop in pressure. This has the effect of producing a small vacuum, which draws in fresh air from outside the building through any available openings.

The effects of such a hazardous vapour release are dependent upon the extent to which the vapour is dispersed into the environment, and the momentum of the release. If the chemical storage vessel is housed within the confines of a room or building, the walls and ceiling will impede the dispersion of any accidental release and, if the pollutant is heavier than air and it is released it will stratify at low momentum. The pollutant vapour will mix with air inside the room (or stratified layer) before exiting (if possible) at a lower concentration and temperature, and at a lower rate than the initial release.

Originally, the isothermal mathematical model, GRAB [2], was developed to simulate the effects of a release of pressure liquefied gas within the confines of a room or building. The GRAB model was then developed into a non-isothermal version named GRAB-T [3], which included the effects of temperature and material flow through up to four openings, but which was based on the assumption of uniform mixing throughout the building. The subject of this study is the further development of the GRAB-T model to include the effects of stratification.

1.2 **Problem Summary**

For small releases, as the pressurised pollutant escapes into the room, it expands, causing much of it to vaporise instantaneously. However, as the pressure within the pollutant jet drops, so does the temperature; hence a temperature gradient is set up between the jet trajectory and the surrounding air, walls, ceiling, floor and the vessel itself. One of two scenarios may then occur:

(i) If there is sufficient heat transfer to the jet, a steady state temperature will be achieved above the pollutant boiling point temperature. This is likely to occur for small releases, where the cooling effect from the release is small. In this instance the pollutant will remain in the vapour phase.
(ii) If there is insufficient heat transfer to the jet, the temperature will continue to drop until the boiling point temperature is achieved. This is likely to occur for larger releases where the cooling would dominate. Here any further pollutant escaping from the vessel will remain in the liquid phase; hence there will be two phases of pollutant in the room.

Similarly, for large releases, the liquid pollutant spills to the ground, where heat transfer from the floor causes evaporation to the vapour phase.

The variations with time of temperature (T), pressure (P), density (ρ), and pollutant mass fractions in both vapour (c_v) and liquid (c_l) phases for a confined (but optionally vented) accidental release are derived in this document. They are then encoded into the software package GRAB-T, which is presented separately.

1.3 Report Outline

This report represents the background technical document detailing the model development and its validation. Two further reports have been produced as part of this project:

Technical Specification

This was developed in conjunction with HSE and sets out the requirements for the software in terms of model capabilities, inputs and outputs.

User Guide

This provides the user with all the information required to load and run the code successfully, and to interpret the output.

A framework for the model is given in Section 2, including an outline of the main assumptions, inputs required and the outputs that will be calculated. The development of the model is described in Section 3, including a summary in Section 3.8. A method of solving the equations is outlined in Section 4 and validation of the model against experimental data is given in Section 5. Some notes on the use of the GRAB-T computer code are given in Section 6, along with examples indicating the model sensitivity to various key parameters.

It should be noted that the nomenclature is given in Appendix A.
2. MODEL FRAMEWORK

2.1 Scope of Model

The scenario considered relates to the effects of a building in mitigating an accidental release that occurs within it. Specifically, it includes the following features:

- 2 phase flashing release;
- Steady or slowly decaying release rate (i.e. non-catastrophic);
- Confined room with openings to the external environment;
- Heavier than air materials;
- Stratified dense gas layer;
- External wind pressure effects;
- Pool formation;
- Optional use of a scrubber unit.

The equations developed in this document are therefore used specifically to model dense (i.e. heavier than air) gas releases within the confines of a room or building, and the subsequent emission to the atmosphere through any openings. The emission rates from the room/building can be used as a source term in dense gas dispersion models, particularly the WS Atkins WEDGE model [4].

2.2 Physical Effects Modelled

Due to the generation of thermal gradients between the pollutant gas/air mixture and the relatively warmer room boundaries (i.e. wall, ground and ceiling) and the storage vessel itself, heat transfer occurs. Based on the findings of a previous Computational Fluid Dynamics (CFD) study [5] of this particular problem, it is assumed that forced heat transfer mechanisms dominate within the room. If this heat transfer is sufficiently large, a steady state temperature can be reached above the saturation conditions of the room. If this is not the case, the room temperature will drop below the saturation temperature and its contents are described as ‘saturated’ – requiring the solution to the second set of equations. Any further liquid pollutant entering the room cannot vaporise and will ‘rain-out’\(^1\) forming a pool. This is subject to heat transfer from the ground, and hence will, in due course, evaporate back into the vapour phase; the third set of equations is used for this part.

All model equations are derived under the assumption of homogeneous mixing, which will be the case for highly turbulent releases. However a low momentum release will not generate sufficient turbulence to mix the room contents fully, resulting in the

---

\(^1\) Throughout the transient, the saturation conditions required for ‘rain-out’ to occur are continuously re-calculated, but it should be noted that this phenomenon does not always occur – especially for low release rates.
dense gas stratifying in a layer initially near the ground. GRAB-T accounts for this by re-distributing the pollutant into the layer whose height and maximum concentration are continually monitored. Due to the re-distribution, the room pressures above and below the layer are also used within the calculation to provide the correct pollutant release rates through any openings.

2.3 Assumptions

In order to develop a mathematical model of the consequences of a release, a series of assumptions are required to simplify otherwise complex mechanics and thermodynamics. These assumptions concerning the release are listed below. Other assumptions concern the development of the three sets of equations and these are also listed below.

a. The room dimensions are that of a cuboid. If a room of complex geometry is to be modelled then a set of regular pseudo-dimensions should be calculated to maintain the correct room surface area and volume.

b. Calculations are performed assuming a homogeneous mixture. The pollutant gas phase is then re-distributed to be below the layer height, thus increasing the concentration in this layer, due to the smaller volume. These modified concentrations are used for the ventilation calculations.

c. Pressurised liquid pollutant enters the room at ambient (storage) temperature.

d. The room may be defined to have any combination of openings to the environment up to a maximum of four (one in each wall, labelled A, B, C and D). For each opening, the dimensions and position within the wall are required, allowing the relevant throughput to be calculated. This throughput is dependent upon the layer height relative to the location of the opening, and hence on whether the material being vented is air, or gas/air mixture.

e. Once the pollutant has entered the room, a fraction flashes off immediately, with the remaining liquid pollutant vaporising within 2-3 metres. This is assumed to occur before the liquid material can fall to the ground or impinge on any obstacles in the room; hence, only vapour phase pollutant will initially be present.

f. If saturation conditions within the room are achieved, any further liquid pollutant released into the room will ‘rain-out’, causing pool formation. Heat transfer from the ground will then cause evaporation.

g. Heat transfer from the walls, ceiling and ground is calculated by the determination of temperature differences between the outer wall/ceiling/ground surfaces and the contents of the room for non-isothermal conditions, and the inner surfaces for boundaries where surfaces are assumed to remain at constant temperature. The walls, ceiling and ground, each have constant thermo-physical properties.

h. All heat transfer coefficients are assumed to be due to forced convection.
i. The ideal gas law applies to the gas / air mixture in the room.

j. Initially the room is full of air under ambient conditions, and is therefore in thermal equilibrium with the environment.

k. If the external pressure at an opening is greater than the room pressure, then fresh air will enter the room at ambient temperature.

l. If the external pressure at an opening is less than the room pressure then, depending upon the position of the dense gas layer relative to that opening, pollutant/air mixture or air at the room temperature will be vented.

m. It is possible for both event (k) and (l) to occur simultaneously through different openings.

n. All physical properties of air and the pollutant (both phases), including the boiling point are assumed to remain constant (see Section 2.5).

2.4 Introduction of Stratification Effects

The original non-isothermal GRAB model included stratification effects, however to simplify modelling upon development at the temperature dependent GRAB-T version; homogeneous mixture was assumed. The current version of the model re-introduced stratification effects by redistributing the gas concentration (calculated assuming a homogeneous mixture) into a layer with an initially predetermined constant height. This height remains constant until a specific layer concentration is achieved. At this point the layer height is calculated maintaining this critical concentration until the layer reaches room height. From here onwards, the concentration is allowed to increase towards a concentration of unity.

2.5 Inputs and Outputs

In order to simulate the non-isothermal events initiated by the accidental release of pollutant stored under pressure, various material physical properties are required. Although most physical properties are functions of temperature and/or pressure, it is assumed that their variation over the likely range of temperatures is not sufficient to warrant the inclusion of physical property modelling. Hence, constant property values measured at or near standard ambient conditions have been used.

Typical release parameters are given in Table 2.1, and a pseudo set of dimensions and thermodynamic data for a test room (constructed with MDF* used to produce data for model validation is displayed in Table 2.2. Example inputs for ventilation and ambient scenarios are illustrated in Tables 2.3 and 2.4 respectively. All tables show a typical value, its units, the representative symbol used throughout this report and a brief description of the variable.

* MDF - Medium Density Fibreboard. It should be noted that this has been used to build a test room and is not a standard building material.
<table>
<thead>
<tr>
<th>Input Data Description</th>
<th>Value</th>
<th>Units</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substance</td>
<td>Chlorine</td>
<td>-</td>
<td>-</td>
<td>Stored material to be released.</td>
</tr>
<tr>
<td>Type</td>
<td>Constant</td>
<td>-</td>
<td>-</td>
<td>Constant or decaying release.</td>
</tr>
<tr>
<td>Rate</td>
<td>0.3</td>
<td>kg/s</td>
<td>$\dot{M}$</td>
<td>Pollutant release rate.</td>
</tr>
<tr>
<td>Duration</td>
<td>300</td>
<td>s</td>
<td>$t_d$</td>
<td>Release duration.</td>
</tr>
<tr>
<td>Decay Time</td>
<td>0</td>
<td>s</td>
<td>$\tau_d$</td>
<td>Time constant for decaying release.</td>
</tr>
<tr>
<td>Height</td>
<td>0.5</td>
<td>m</td>
<td>$h_0$</td>
<td>Height of release from the ground.</td>
</tr>
<tr>
<td>Momentum</td>
<td>High</td>
<td>-</td>
<td>-</td>
<td>Release momentum (high/low/spill)</td>
</tr>
<tr>
<td>Layer Concentration</td>
<td>0.2</td>
<td>kg/kg</td>
<td>$c_m$</td>
<td>Max concentration assumed in layer.</td>
</tr>
</tbody>
</table>

Table 2.1 Release Input Values

<table>
<thead>
<tr>
<th>Input Data Description</th>
<th>Value</th>
<th>Units</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room height</td>
<td>4</td>
<td>m</td>
<td>$H_r$</td>
<td>Height of room.</td>
</tr>
<tr>
<td>Room length</td>
<td>10</td>
<td>m</td>
<td>$L$</td>
<td>Length of room.</td>
</tr>
<tr>
<td>Room width</td>
<td>10</td>
<td>m</td>
<td>$W$</td>
<td>Width of room.</td>
</tr>
<tr>
<td>Pool Constraint</td>
<td>Bund</td>
<td>-</td>
<td>-</td>
<td>Whole area of floor, or bunded pool containment.</td>
</tr>
<tr>
<td>Bund area</td>
<td>40</td>
<td>m$^2$</td>
<td>$A_p$</td>
<td>Area of pool (if bund option is chosen).</td>
</tr>
<tr>
<td>Floor Thermal Conductivity</td>
<td>1.37</td>
<td>W/m/K</td>
<td>$k_f$</td>
<td>Thermal conductivity of floor.</td>
</tr>
<tr>
<td>Wall / Ceiling Thermal Conductivity</td>
<td>0.17</td>
<td>W/m/K</td>
<td>$k_w, k_c$</td>
<td>Thermal conductivity of wall / ceiling.</td>
</tr>
<tr>
<td>Floor thickness</td>
<td>0.3</td>
<td>m</td>
<td>$\delta_f$</td>
<td>-</td>
</tr>
<tr>
<td>Wall / Ceiling thickness</td>
<td>0.013</td>
<td>m</td>
<td>$\delta_w, \delta_c$</td>
<td>-</td>
</tr>
<tr>
<td>Floor Specific Heat</td>
<td>880</td>
<td>J/kg/K</td>
<td>$C_{pf}$</td>
<td>Specific Heat of floor.</td>
</tr>
<tr>
<td>Wall / Ceiling Specific Heat</td>
<td>835</td>
<td>J/kg/K</td>
<td>$C_{pw}, C_{pc}$</td>
<td>Specific Heat of wall / ceiling.</td>
</tr>
<tr>
<td>Scrubber Operation</td>
<td>No</td>
<td>-</td>
<td>-</td>
<td>Availability of scrubber unit.</td>
</tr>
<tr>
<td>Extraction height</td>
<td>0.3</td>
<td>m</td>
<td>$h_{sc}$</td>
<td>Height of extraction from scrubber unit.</td>
</tr>
<tr>
<td>Scrubber Throughput</td>
<td>0.15</td>
<td>m$^3$/m$^3$</td>
<td>$\dot{M}_{sc}$</td>
<td>Volumetric scrubber extraction rate.</td>
</tr>
</tbody>
</table>

Table 2.2 Building Details Input Values
There is the potential for up to four openings, and any combination of these is possible. Table 2.3 only reflects a single opening in A, and hence the width, height and height above the floor refer solely to this opening. Any further openings would also require individual input data for width, height and height above the ground. Figure 2.1 illustrates how the location of an opening is defined making use of the notation referred to in Table 2.3.

![Figure 2.1 Location of Openings A and B](image)

Similarly for wind incidence, this may be incident upon any of the four walls irrespective of whether there is an opening or not.

### Table 2.3 Ventilation Details Input Values

<table>
<thead>
<tr>
<th>Input Data Description</th>
<th>Value</th>
<th>Units</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opening</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>Combinations of openings A,B,C,D.</td>
</tr>
<tr>
<td>Width</td>
<td>0.3 m</td>
<td>m</td>
<td>$W_A$</td>
<td>Width of opening A.</td>
</tr>
<tr>
<td>Height</td>
<td>0.3 m</td>
<td>m</td>
<td>$H_A$</td>
<td>Height of opening A.</td>
</tr>
<tr>
<td>Height above ground</td>
<td>0.3 m</td>
<td>m</td>
<td>$h_A$</td>
<td>Defines height of lower edge of opening A.</td>
</tr>
<tr>
<td>Discharge coefficient</td>
<td>Fixed</td>
<td>-</td>
<td>-</td>
<td>Allows varying or fixed opening area.</td>
</tr>
<tr>
<td>Wind Incidence</td>
<td>C</td>
<td>-</td>
<td>-</td>
<td>The wall that wind is incident.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Input Data Description</th>
<th>Value</th>
<th>Units</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>288 K</td>
<td></td>
<td>$T_a$</td>
<td>Ambient temperature.</td>
</tr>
<tr>
<td>Pressure</td>
<td>101325 N/m$^2$</td>
<td></td>
<td>$P_a$</td>
<td>Ambient pressure.</td>
</tr>
<tr>
<td>Windspeed</td>
<td>5 m/s</td>
<td></td>
<td>$v_w$</td>
<td>Average windspeed.</td>
</tr>
</tbody>
</table>

### Table 2.4 Ambient Conditions Input Values

From the input conditions, a number of intermediate and output conditions are calculated. For a number of properties, such as mass fraction of a component, the
same symbol with different subscripts is used for the different components. The symbols for the intermediate and output conditions are given in Table 2.5 and the subscripts to differentiate between meanings are given in Table 2.6.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>c</td>
<td>kg/kg</td>
<td>Mass fraction</td>
</tr>
<tr>
<td>( F_f )</td>
<td>-</td>
<td>Flash fraction</td>
</tr>
<tr>
<td>m</td>
<td>kg/mol</td>
<td>Molecular mass</td>
</tr>
<tr>
<td>( \dot{M} )</td>
<td>kg/s</td>
<td>Mass flow rate</td>
</tr>
<tr>
<td>P</td>
<td>N/m²</td>
<td>Pressure</td>
</tr>
<tr>
<td>( q )</td>
<td>W</td>
<td>Heat transfer rate</td>
</tr>
<tr>
<td>t</td>
<td>s</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>K</td>
<td>Temperature</td>
</tr>
<tr>
<td>( \chi )</td>
<td>m³/m³</td>
<td>Volume concentration</td>
</tr>
<tr>
<td>( \rho )</td>
<td>kg/m³</td>
<td>Density</td>
</tr>
</tbody>
</table>

Table 2.5 Variables used in Effects of Temperature Calculation

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Air</td>
</tr>
<tr>
<td>e</td>
<td>Evaporation</td>
</tr>
<tr>
<td>g</td>
<td>Gaseous pollutant</td>
</tr>
<tr>
<td>ga</td>
<td>Gaseous pollutant and air mixture</td>
</tr>
<tr>
<td>in</td>
<td>Air ingress</td>
</tr>
<tr>
<td>l</td>
<td>Liquid pollutant</td>
</tr>
<tr>
<td>out</td>
<td>Pollutant/air mixture egress</td>
</tr>
<tr>
<td>ref</td>
<td>Reference</td>
</tr>
<tr>
<td>sc</td>
<td>Scrubber</td>
</tr>
<tr>
<td>t</td>
<td>Total, air, and pollutant liquid and gas phases</td>
</tr>
</tbody>
</table>

Table 2.6 Subscripts used in model equations
3. DEVELOPMENT OF EQUATIONS

3.1 General Relationships

It is known that, during the transient, it is possible that conditions within the room may change from being unsaturated to being saturated. Therefore, as noted in Section 2.1, two sets of equations describing the rate of change of concentration of pollutant are required for jet releases and a separate set for a spill, which evaporates from the floor. However, some equations hold for all three scenarios and are outlined below.

The basis for the formulation of the model equations is that there are three constituent mediums contributing to the room volume; these are the pollutant in gaseous and liquid phases (M_g and M_l) and ambient air (M_a). These are such that the total mass within the room (M_t) is given by:

\[ M_g + M_l + M_a = M_t \]

Or, dividing by M_t

\[ c_g + c_l + c_a = 1 \quad (3.1) \]

where ‘c_a’ is the mass fraction of air, etc.

The pressure in the room is assumed to be related by the ideal gas law to the average molecular mass, the density of the gaseous mixture and the temperature in the room (see assumption (i) Section 2.3). Hence:

\[ P = \frac{\rho_{ga}RT}{m_{ga}} \quad (3.2) \]

The average molecular mass of the gaseous mixture in the room is given by:

\[ m_{ga} = \chi m_g + (1-\chi)m_a = \chi(m_g - m_a) + m_a \quad (3.3) \]

where the volumetric concentration of gas in the gas/air mixture, \( \chi \), is given in terms of the mass fractions \( c_g \) and \( c_l \) as:

\[ \chi = \frac{m_ac_g}{m_g(1-c_l) - c_gm_l - m_a} \quad (3.4) \]

Therefore the average molecular mass of the gaseous mixture in the room is given by:

\[ m_{ga} = \frac{m_am_g(1-c_l)}{m_g(1-c_l) - c_g(m_l - m_a)} \quad (3.5) \]

The average density of the mixture can be obtained by considering the mass of the gaseous pollutant/air mixture. This may be derived by two similar approaches, i.e.
\[ M_{ga} = c_{ga} M_t = (c_g + c_n) M_t = (1 - c_1) \rho_i V_r \]  
\text{(3.6)}

Or,
\[ M_{ga} = \left( V_r - \frac{M_t}{\rho_i} \right) \rho_{ga} = V_r \left( 1 - c_1 \frac{\rho_1}{\rho_1} \right) \rho_{ga} \]  
\text{(3.7)}

Equating (3.6) and (3.7) yields an expression describing the average density of the gaseous pollutant / air mixture, i.e.
\[ \rho_{ga} = \frac{(1 - c_1) \rho_i \rho_1}{\rho_1 - c_1 \rho_i} \]  
\text{(3.8)}

It should be noted that, since the numerical value of the liquid density is much larger than that of the total density (which is primarily gaseous), the denominator of (3.8) tends towards \( \rho_1 \), which means that the average density of the mixture may be simplified to \( \rho_{ga} \approx (1 - c_1) \rho_1 \). However, for modelling purposes the full version as described by (3.8) has been maintained.

The development of the equations that model the variation of the dependent variables with time is described in detail in the following sections. The resulting sets of non-linear simultaneous differential equations are summarised in Section 3.8, and their method of solution is given in Section 4.

3.2 Thermodynamics

3.2.1 Conservation of Mass

Application of the law of conservation of mass, and consideration of assumptions (e) and (f) in Section 2.3, generates an equation for the rate of change of mass of the liquid phase pollutant.
\[ \frac{dM_l}{dt} = (1 - F_f)M - \dot{M}_e \]  
\text{(3.9)}

\( F_f \) describes the flash fraction - the proportion of pollutant that ‘flashes off’ due to sudden expansion when the material experiences a violent change in pressure as it enters the room. Hence the initial term on the right hand side of Equation (3.9) describes the contribution of liquid phase pollutant to the room. The \( \dot{M}_e \) term represents the rate of evaporation to the vapour phase from any pool formed on the floor of the room or contained within the bounds of a bund wall.

The mass of liquid pollutant may be written in terms of the liquid mass fraction and the total density of the room contents, i.e. :
\[ M_l = V_t \rho c_i \]  
\text{(3.10)}

Differentiating (3.10) with respect to time and inserting into (3.9) yields:
The rate of change of pollutant mass in the gas phase is governed by the flash fraction, the amount of material that vaporises or evaporates from the pool, and the fraction discharged through the openings (if any) and/or the scrubber unit.

\[
\frac{dM_g}{dt} = F_t \dot{M} + M_c - c_g \left( M_{\text{out}} + M_{\text{sc}} \right)
\]  

(3.12)

where, \( M_{\text{out}} \) and \( M_{\text{sc}} \) are defined as the total discharge rates of the air/pollutant mixture through all openings, and the scrubber unit respectively.

As in Equation (3.10), the mass of gaseous pollutant may be written in terms of the vapour mass fraction and total room density:

\[
M_g = V_r \rho V c_g
\]  

(3.13)

Differentiating (3.13) with respect to time and inserting into (3.12) gives:

\[
V_r \left[ \rho V \frac{dc_g}{dt} + c_g \frac{d\rho V}{dt} \right] = F_t \dot{M} + M_c - c_g \left( M_{\text{out}} + M_{\text{sc}} \right)
\]  

(3.14)

The rate of change of air is determined by establishing whether fresh air is entering the room or air (as a constituent part of the gas/air mixture) is leaving the room through at least one opening or the scrubber unit, i.e.

\[
\frac{dM_a}{dt} = M_{\text{in}} - c_a \left( M_{\text{out}} + M_{\text{sc}} \right)
\]  

(3.15)

where, ‘ \( M_{\text{in}} \) ’ is defined as the rate of fresh air intake through individual openings A, B, C and D, from the environment (see Section 3.5).

Once again, the mass of air may be written in terms of the pollutant concentrations, via Equation (3.1).

\[
M_a = V_r \rho V c_a = V_r \rho V \left( 1 - c_g - c_i \right)
\]  

(3.16)

Hence, differentiation of (3.16) with respect to time and insertion into (3.15) provides:

\[
V_r \left[ (1 - c_g - c_i) \frac{d\rho V}{dt} - \rho V \frac{dc_g}{dt} - \rho V \frac{dc_i}{dt} \right] = M_{\text{in}} - \left( 1 - c_g - c_i \right) \left( M_{\text{out}} + M_{\text{sc}} \right)
\]  

(3.17)

Addition of (3.11), (3.14) and (3.17) enables an equation to be formulated for the rate of change of total density:
\[
\frac{d\rho_t}{dt} = \frac{1}{V_t} \left[ \dot{M} + \dot{M}_{in} - c_g (\dot{M}_{out_g} + \dot{M}_{sc_g}) - (1 - c_g - c_l) (\dot{M}_{out_l} + \dot{M}_{sc_l}) \right] \tag{3.18}
\]

This may then be substituted back into Equations (3.11) and (3.14) to formulate the rate of change of pollutant mass fractions for a jet release in the two respective phases, yielding:

\[
\frac{dc_l}{dt} = \frac{1}{V_t \rho_t} \left[ (1 - F_f - c_l) \dot{M} - \dot{M}_{e} - c_l \left\{ \dot{M}_{in} - c_g (\dot{M}_{out_g} + \dot{M}_{sc_g}) \right\} - (1 - c_g - c_l) (\dot{M}_{out_l} + \dot{M}_{sc_l}) \right] \tag{3.19}
\]

and,

\[
\frac{dc_g}{dt} = \frac{1}{V_t \rho_t} \left[ (F_f - c_g) \dot{M} + \dot{M}_{e} - c_g \left\{ \dot{M}_{in} + \left( 1 - c_g \right) (\dot{M}_{out_g} + \dot{M}_{sc_g}) \right\} + (c_l + c_g - 1) (\dot{M}_{out_l} + \dot{M}_{sc_l}) \right] \tag{3.20}
\]

where the flash fraction \( F_f \), is given by Equation (3.21), reproduced from [1].

\[
F_f = \frac{C_{pl} (T_e - T_s)}{h_{fg}} \tag{3.21}
\]

**Consideration of saturation conditions.**

The mass fraction equations, (3.19) and (3.20), have been derived for the situation where room conditions are below saturation, i.e. the pollutant within the room is present in both liquid and vapour phases. When the room conditions are above saturation, it is assumed that the pollutant will flash completely giving an \( F_f \) value of unity. As this causes no liquid phase pollutant to be present in the room, the liquid mass fraction \( c_l \) will be zero, resulting in the impossibility of pool formation and hence evaporation; thus \( M_e \) will also be zero. The above saturation versions of Equations (3.19) and (3.20) with \( c_l = M_e = 0 \) and \( F_f = 1 \), are:

\[
\frac{dc_l}{dt} = 0 \tag{3.19b}
\]

\[
\frac{dc_g}{dt} = \frac{1}{V_t \rho_t} \left[ (1 - c_g) \dot{M} - c_g \left\{ \dot{M}_{in} + \left( 1 - c_g \right) (\dot{M}_{out_g} + \dot{M}_{sc_g}) \right\} + (c_g - 1) (\dot{M}_{out_l} + \dot{M}_{sc_l}) \right] \tag{3.20b}
\]

**Consideration of a liquid spill.**

If the rupture aperture is large, a flashing jet will not occur, and the liquid contents will spill onto the ground where subsequent heat transfer will cause rapid evaporation to the vapour phase. For this scenario therefore, a zero flash fraction is experienced. Hence a liquid spill may be modelled by inserting Equation (3.18) into Equations (3.11) and (3.14) with \( F_f = 0 \), resulting in:
\[
\frac{dc_i}{dt} = \frac{1}{V_r \rho_i} \left[ (1 - c_i)\dot{M} - \dot{M}_c - c_i \left( \frac{M_{\text{in}} - c_g \left( M_{\text{out}} + M_{\text{sc}} \right)}{\left( 1 - c_g - c_i \right) \left( M_{\text{out}} + M_{\text{sc}} \right)} \right) \right]
\]  
(3.19c)

\[
\frac{dc_g}{dt} = \frac{1}{V_r \rho_i} \left[ \dot{M}_c - c_g \left\{ \dot{M} + \dot{M}_{\text{in}} + \left( 1 - c_g \right) \left( M_{\text{out}} + M_{\text{sc}} \right) \right\} \right]
\]  
(3.20c)

### 3.2.2 Conservation of Energy

The room is subject to energy changes as a result of the:

(i) ingress of pollutant due to the release,
(ii) heat transfer from the walls, ceiling, ground and storage vessel,
(iii) discharge of gas/air mixture and/or the ingress of fresh air through one or more of the available openings and/or the scrubber unit.

An energy balance applied to the system taking the above inputs and outputs into consideration results in an equation describing the rate of change of internal energy. However this equation will be different for each of the three scenarios experienced by the room, each of which is considered separately below.

**Above Saturation.**

Both liquid and vapour phase pollutant enter the room as part of a two-phase jet at the rupture orifice. The room contents supply energy vaporising any remaining liquid phase. Energy also enters the room due to the ingress of fresh air and heat transfer from the various surfaces. Energy is however lost through any material escaping via the scrubber unit and/or any openings.

\[
\frac{dE}{dt} = \dot{M} \left[ F_c h_g (T_s) + \left( 1 - F_c \right) \left\{ h_l (T_s) - h_{f_g} \right\} \right] + \dot{M}_{\text{in}} h_a (T_s) + \sum \dot{q} - c_g \left( M_{\text{out}} + M_{\text{sc}} \right) h_g (T) - c_a \left( M_{\text{out}} + M_{\text{sc}} \right) h_a (T)
\]  
(3.22a)

where, \( \sum \dot{q} = \dot{q}_{\text{wall}} + \dot{q}_{\text{ceiling}} + \dot{q}_{\text{ground}} + \dot{q}_{\text{vessel}} \)

and,

\[
\dot{q}_{\text{wall}} = \beta_{\text{wall}} A_{\text{wall}} (T_a - T)
\]

\[
\dot{q}_{\text{ceiling}} = \beta_{\text{ceiling}} A_{\text{ceiling}} (T_a - T)
\]

\[
\dot{q}_{\text{ground}} = \beta_{\text{ground}} A_{\text{ground}} (T_a - T)
\]

\[
\dot{q}_{\text{vessel}} = \beta_{\text{vessel}} A_{\text{vessel}} (T_a - T)
\]

**Below Saturation.**

As above, liquid and vapour phase pollutant enters the room as part of a two-phase jet. However, under these conditions the liquid phase immediately undergoes ‘rain-out’ falling directly to the ground forming a pool. From the pool, a heat transfer
gradient will be established causing evaporation to commence and providing an additional gaseous component to the vapour phase. To do this, the ground will lose an amount of energy equivalent to that required causing the evaporation. All other energy gains and losses due to openings and the scrubber unit will be as in Equation (3.22a).

\[
\frac{dE}{dt} = M_t \left[ F_{r} h_{v} (T_v) + (1 - F_r) h_{l} (T_l) \right] + M_g \left[ h_{g} (T_b) - h_{ig} \right] + M_{in} h_{a} (T_a) + \sum q - c_{g} \left( M_{out_{g}} + M_{sc_{g}} \right) h_{a} (T) - c_{a} \left( M_{out_{a}} + M_{sc_{a}} \right) h_{a} (T) \tag{3.22b}
\]

**Liquid spill**

For this scenario the release is non-flashing, and the pollutant is therefore assumed to be entirely in the liquid phase when entering the room. The only other forms of energy input to the room are from the evaporating pool, heat transfer from various surfaces and fresh air ingress. Energy is removed via the scrubber unit and/or ventilation effects.

\[
\frac{dE}{dt} = M_{h} (T_r) + M_{v} h_{v} (T_v) + M_{g} h_{g} (T_b) + \sum q - c_{g} \left( M_{out_{g}} + M_{sc_{g}} \right) h_{a} (T) \tag{3.22c}
\]

The internal energy may also be written in terms of enthalpy and room pressure via the following standard correlation:

\[
E = M_t \left( h - P v \right) = \rho_t V_t \left( h - P v \right) = V_t \left( \rho, h - P \right) \tag{3.23}
\]

Using the chain rule to differentiate (3.23) with respect to time gives:

\[
\frac{dE}{dt} = V_t \left[ h \frac{d\rho}{dt} + \rho \frac{dh}{dt} - \frac{dP}{dt} \right] \tag{3.24}
\]

Hence Equation (3.22a, b and c) may be used in conjunction with (3.24) to represent the rate of change of internal energy of the system for each scenario considered, giving:

\[
V_t \left[ h \frac{d\rho}{dt} + \rho \frac{dh}{dt} - \frac{dP}{dt} \right] = C \tag{3.25}
\]

Where ‘C’ is the RHS of Equations (3.22a), (3.22b) and (3.22c). Equation (3.25) can be written more simply as:

\[
\rho_t \frac{dh}{dt} = C' - h \frac{d\rho}{dt} + \frac{dP}{dt} \tag{3.26}
\]

where,
Hence (3.26) may be used to model the enthalpy change of the system, in relation to the density and pressure transients, the surface temperatures of the wall, ceiling, ground and storage vessel, where C is given by $C_1$, $C_2$ or $C_3$.

Above the saturation point
When the temperature is above the saturation point, it is assumed that the pollutant is entirely in the gaseous phase (i.e. $c_l = 0$). Thus, from equations (3.5) and (3.8), the average molecular mass and density are given respectively as:

$$m_{ga} = \frac{m_a m_g}{m_g - c_g (m_g - m_a)} \quad (3.27)$$
$$\rho_{ga} = \rho_1 \quad (3.28)$$

Differentiation of Equation (3.27) with respect to time generates a term expressing the rate of change of molecular mass in terms of the gaseous mass fraction:

$$\frac{dm_{ga}}{dt} = \frac{m^2_a (m_g - m_a)}{m_a m_g} \frac{dc_g}{dt} \quad (3.29)$$

Using (3.28), the rate of change of average density can be given by a modified version of Equation (3.18) in which $c_1$ is set to zero, i.e:

$$\frac{d\rho_{ga}}{dt} = \frac{d\rho_1}{dt} = \frac{1}{V_r} \left[ \dot{M} + \dot{M}_{in} - c_g (\dot{M}_{out_g} + \dot{M}_{sc_g}) - (1 - c_g) (\dot{M}_{out_a} + \dot{M}_{sc_a}) \right] \quad (3.18b)$$

The total enthalpy of the room contents above saturation conditions is provided by the specific heats of the two constituent components, namely air and vapour phase pollutant.

$$h = (c_g C_{pg} + c_a C_{pa}) (T - T_{ref}) \quad (3.30)$$
This may be rewritten in terms of the pollutant gas mass fraction, by considering Equation (3.1), and setting \(c_i = 0\).

\[
h = [c_g \left(C_{pg} - C_{pa}\right) + C_{pa}] (T - T_{ref})
\]

(3.31)

The rate of change of enthalpy under these conditions is determined by establishing the differential of (3.31) with respect to time, i.e.

\[
\frac{dh}{dt} = \frac{\partial h}{\partial c_g} \frac{dc_g}{dt} + \frac{\partial h}{\partial T} \frac{dT}{dt}
\]

Or,

\[
\frac{dh}{dt} = G_1 \frac{dc_g}{dt} + G_2 \frac{dT}{dt}
\]

(3.32)

where \(G_1\) and \(G_2\) are the partial derivatives of \(h\):

\[
G_1 = \left(C_{pg} - C_{pa}\right) (T - T_{ref}) ; \quad G_2 = c_g \left(C_{pg} - C_{pa}\right) + C_{pa}
\]

Equation (3.32) may be rearranged to generate an equation describing the rate of change of temperature for the ‘above saturation’ conditions, i.e.

\[
\frac{dT}{dt} = \frac{1}{G_2} \left(\frac{dh}{dt} - G_1 \frac{dc_g}{dt}\right)
\]

(3.33)

Differentiating the pressure equation (3.2) yields:

\[
\frac{dP}{dt} = P \left[\frac{1}{T} \frac{dT}{dt} + \frac{1}{\rho_t} \frac{d\rho_t}{dt} - \frac{1}{m_{ga}} \frac{dm_{ga}}{dt}\right]
\]

(3.34)

and substitution of (3.29) and (3.33) into (3.34) produces:

\[
\frac{dP}{dt} = \lambda_1 \frac{dh}{dt} + \lambda_2 \frac{dc_g}{dt} + \lambda_3 \frac{dP_t}{dt}
\]

(3.35)

where,

\[
\lambda_1 = \frac{1}{G_2 T} ; \quad \lambda_2 = \left[\frac{G_1}{G_2 T} + \frac{m_{ga}}{m_a m_{ga}} \left(m_g - m_a\right)\right] ; \quad \lambda_3 = \frac{1}{\rho_t
\]

Thus, substitution of (3.35) into (3.26) provides a rate of change of enthalpy equation, which may be simplified to give:

\[
\frac{dh}{dt} = \left(\frac{1}{\rho_t - P\lambda_1}\right) \left[C_1 + (P\lambda_3 - h) \frac{dP_t}{dt} + P\lambda_2 \frac{dc_g}{dt}\right]
\]

(3.36)
where \( \frac{dc_g}{dt} \) is given by Equation (3.20b) and \( \frac{d\rho}{dt} \) is given by Equation (3.18b).

Below the saturation point, and a liquid spill
When the temperature is below the saturation point, both pollutant phases are considered possible (i.e. \( c_l \neq 0 \)). Also for the spill scenario, a liquid mass is available to form and subsequently evaporate from the pool, hence \( c_l \neq 0 \). In these instances the rate of change of molecular mass and density are found by differentiating (3.5) and (3.8) with respect to time.

The enthalpy of the room conditions is given by Equation (3.31) assuming the liquid phase is not airborne, but is in the pool. Evaporative terms are accounted for within the rate of change of vapour phase pollutant. Hence the rate of change of enthalpy may be given by Equation (3.32).

Inserting Equations (3.37) and (3.33) into Equation (3.34) gives:

\[
\frac{dP}{dt} = \frac{\lambda_1}{\lambda_1} \frac{dh}{dt} + \lambda_2 \frac{d\rho}{dt} + \lambda_3 \frac{dc_l}{dt} + \lambda_4 \frac{dc_g}{dt}
\]

where:

\[
\lambda_4 = -\frac{c_g m_g (m_g - m_s)}{m_a m_g (1 - c_l)^2}; \quad \lambda_5 = \frac{G_{1L} + m_g (m_g - m_s)}{G_a T + m_a m_g (1 - c_l)}
\]

Thus, as in the previous case, substitution into Equation (3.26) provides the a rate of change of enthalpy, which may be simplified to:

\[
\frac{dh}{dt} = \left( \frac{1}{\rho_l - P \lambda_1} \right) \left[ C_2 + (P \lambda_3 - h) \frac{d\rho}{dt} + P \lambda_4 \frac{dc_l}{dt} + \lambda_5 \frac{dc_g}{dt} \right]
\]

In this equation, \( \frac{dc_g}{dt} \), \( \frac{dc_l}{dt} \) and \( \frac{d\rho}{dt} \) are given by Equations (3.20), (3.19) and (3.18) respectively for a jet release below saturation conditions and Equations (3.19c), (3.20c) and (3.18) respectively for a liquid spill.
3.3 Heat Transfer.

All four walls surrounding the test-room are assumed to be of the same thickness and constructed from the same, constant property, material. The floor and ceiling are assumed to have constant thickness and properties (although not necessarily the same). Corners and edges are ignored and the temperature within a boundary is assumed to vary only with distance from the surface of the boundary. Therefore the constant property, one dimensional, transient heat equation with no internal generation applies to the temperature through a boundary. Hence for the vertical walls of temperature, $T_w$, the spatial temperature transient may be given by:

$$\frac{\partial^2 T_w}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T_w}{\partial t}$$  (3.46)

where $x$ is the distance from the outside surface of the wall and $\alpha$ is the thermal diffusivity of the solid ($\alpha = k_w/\rho_w C_p$). The wall surface in contact with the outside air is at $x = 0$ and the surface in contact with the room contents is at $x = \delta_w$ where $\delta_w$ is the wall thickness. Therefore the boundary conditions required for Equation (3.46) are $x = 0$ and $x = \delta_w$.

If the walls are assumed to have surface temperatures of $T_a$ at $x = 0$ and $T_w$ at $x = \delta_w$, where throughout the release $T_a$ remains constant and the room temperature $T$ varies due to the pollutant release, an effective heat transfer coefficient ($h_{eff}$) may be obtained. This effective coefficient combines the effects from thermal conduction through the wall, and convection from the wall to the room. This is done by performing a heat balance over the inner wall surface, where one-dimensional conduction occurs to this surface (through the wall) and convection occurs from this surface to the room, as illustrated schematically in Figure 3.1.

![Figure 3.1 Wall cross section](image)

Therefore, assuming there is no internal heat generation, the rate of heat transfer due to conduction ($\dot{q}_{\text{cond}}$) must equal the rate of heat transfer due to convection ($\dot{q}_{\text{conv}}$), i.e.

$$\frac{k_w}{\delta_w} (T_a - T_w) = h_{cv} (T_w - T)$$  (3.47)
where \( k_w \) is the thermal conductivity of the wall and \( h_{cv} \) is the heat transfer coefficient between the room contents and the wall surface at temperature \( T_w \).

Due to air/mixture movement within the room, it is assumed that forced convection occurs from the wall surface, requiring an appropriate heat transfer coefficient. This may be determined via correlations involving dimensionless groups such as the Nusselt (Nu), Reynolds (Re) and Prandtl (Pr) numbers, i.e.:

\[
\psi = \frac{Nu \cdot k_{ga}}{\psi}
\]  

(3.48)

where \( \psi \) is a characteristic length (normal to the direction of heat transfer, e.g. wall height) and \( k_{ga} \) is the thermal conductivity of the air/gas mixture respectively. The Nusselt number may be written in terms of Re and Pr [1] such that:

\[
Nu = 0.648 \cdot Re^{0.3} \cdot Pr^{0.3}
\]  

(3.49)

where,

\[
Re = \frac{\mu_{ga} \cdot u \cdot \psi}{\mu_{ga}}, \quad Pr = \frac{C_{pga} \cdot \mu_{ga}}{k_{ga}}
\]  

(3.50)

and,

\[
\mu_{ga} = c_g (\mu_g - \mu_a) + \mu_a (1 - \Delta)
\]  

(3.51)

\[
C_{pga} = c_g (C_{pg} - C_{pa}) + C_{pa} (1 - \Delta)
\]  

(3.52)

\[
k_{ga} = c_g (k_g - k_a) + k_a (1 - \Delta)
\]  

(3.53)

(Note that \( u \) is taken as 0.2 m/s, as discussed after Equation (3.70).)

Hence, considering Equation (3.47), this may be re-arranged to give an expression for \( T_w \):

\[
T_w = \frac{k_w \cdot T_a + \delta_w \cdot h_{cv} \cdot T}{\delta_w \cdot h_{cv} + k_w}
\]  

(3.54)

Substitution of this into the convection equation gives an equation for the effective heat transfer rate from the walls, i.e.

\[
\dot{q}_{wall} = h_{eff,w} \cdot A_{wall} \cdot (T_a - T)
\]  

(3.55)

where,

\[
h_{eff,w} = \frac{h_w \cdot k_w}{\delta_w \cdot h_{cv} + k_w}
\]  

(3.56)

By adopting the same approach, the effective heat transfer from the ceiling and ground may be formulated.
\[ \dot{q}_{\text{ceiling}} = h_{\text{eff},c} A_{\text{ceiling}} (T_a - T) \] (3.57)
\[ \dot{q}_{\text{ground}} = h_{\text{eff},g} A_{\text{ground}} (T_a - T) \] (3.58)

Equation (3.59) is a general form of the effective forced convection heat transfer coefficient for each surface where \( i = \text{wall, ceiling, and ground} \):

\[ h_{\text{eff},i} = \frac{h_{\text{cv},i} k_i}{\delta_i (h_{\text{cv},i} + k_i)} \] (3.59)

However, although the same Nusselt number equation (3.49) is employed in determining \( h_{\text{cv}} \), \( \psi \) may be defined to be the ratio of the surface area to the perimeter [6]. Thus, if the room has a width \( W \) and a length \( L \), the characteristic length is given by:

\[ \psi_c = \psi_g = \frac{WL}{2(W + L)} \] (3.60)

This is generally used for surfaces with non-uniform geometry, but, for simplicity in modelling, the room is assumed to have regular walls, i.e., forming a cuboid. In these instances, the characteristic length to be used for \( h_{\text{cv},c} \) and \( h_{\text{cv},g} \) may be taken as the square root of the ceiling or floor area.

\[ \psi_c = \psi_g = \sqrt{W.L} \] (3.60b)

Also, for simplicity in modelling, the heat transfer characteristics from the vessel and other objects within the room are assumed to be the same as that for the walls. The only exception is that of the heat transfer area, which is assumed to be 25% of the wall area (\( A_{\text{wall}} \)), giving:

\[ \dot{q}_{\text{vessel}} = 0.25 \dot{q}_{\text{wall}} \] (3.61)

Heat transfer areas should be calculated according to the actual room dimensions, accounting for any area not available for heat transfer. For example, the wall area should account for any openings (e.g. windows), and the ground should account for the pool area, i.e., if \( L = \text{room length} \), \( H = \text{room height} \) and \( W = \text{room width} \):

\[ A_{\text{wall}} = 2H(L + W) - \sum_{x=A}^{D} A_{A_x} \] (3.62)

\[ A_{\text{ground}} = LW - A_p \] (3.63)

\[ A_{\text{ceiling}} = LW \] (3.64)

Care should also be taken if an individual room boundary is to be modelled as an isothermal surface. In this case the effective heat transfer coefficient should not replace the original heat transfer coefficient described by Equation (3.48).
3.4 Pool formation and evaporation

When the pollutant escapes from the pressurised vessel into the room, it expands due to the sudden drop in pressure. A fraction of the release immediately ‘flashes off’ to the vapour phase, leaving a liquid phase that is assumed either to vaporise within 2-3 metres or to fall directly to the ground, forming a pool, depending upon the saturation conditions within the room.

For the latter case, as the pool forms, it is subject to heat transfer from the ground, which will be at a higher temperature than the pool contents. This heat transfer results in evaporation from the pool into the vapour phase, and may be modelled by the following correlation [7]:

\[
\dot{M}_v = k_{mt} A_p p_p \frac{m_v}{RT}
\] (3.65)

\(p_p\) is the partial pressure of the pollutant, modelled by the application of a polynomial regression analysis over data obtained from Perry and Green [1]. For chlorine and Freon-22, the regression equation obtained is found to be a fourth order polynomial function of temperature, i.e.

\[
p_p = aT^4 + bT^3 + cT^2 +dT + e
\] (3.66)

where the coefficients are defined in Table 3.1.

<table>
<thead>
<tr>
<th>Regression Coefficients</th>
<th>Chlorine</th>
<th>Freon-22</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (x 10^3)</td>
<td>1.5174</td>
<td>2.0441</td>
<td>N/m²/K⁴</td>
</tr>
<tr>
<td>b</td>
<td>-0.87754</td>
<td>-1.1923</td>
<td>N/m²/K³</td>
</tr>
<tr>
<td>c (x 10²)</td>
<td>1.8573</td>
<td>2.574</td>
<td>N/m²/K²</td>
</tr>
<tr>
<td>d (x 10⁴)</td>
<td>-1.6767</td>
<td>-2.4201</td>
<td>N/m²/K</td>
</tr>
<tr>
<td>e (x 10⁵)</td>
<td>5.2824</td>
<td>8.2736</td>
<td>N/m²</td>
</tr>
</tbody>
</table>

Table 3.1 Chlorine and Freon-22 partial pressure coefficients

\(k_{mt}\) is defined as the mass transfer coefficient established either by considering the log-mean-concentration-difference, or via an approach involving the Sherwood (Sh) and hence Schmidt (Sc) and Reynolds (Re) dimensionless groups, i.e.

\[
Sh = k_{mt} \frac{d_p}{D_m} = f(Re,Sc)
\] (3.67)

where \(D_m\) is the diffusion coefficient, and \(d_p\) is the ‘effective’ pool diameter; hence if \(A_p\) is the pool area, then \(d_p\) is given by:
\[ d_p = 2\sqrt{\frac{A_p}{\pi}} \]  

(3.68)

The Sherwood number may also be given by:

\[ Sh = \begin{cases} 0.664Sc^{1/3}Re^{1/2} & : \text{Re} < 3.2 \times 10^5 \\ 0.037Sc^{1/3}(Re^{4/3} - 15200) & : \text{Re} > 3.2 \times 10^5 \end{cases} \]  

(3.69)

where the Reynolds and Schmidt numbers are defined to be:

\[ \text{Re} = \frac{up_{ga}d_p}{\mu_{ga}} \quad \text{Sc} = \frac{\mu_{ga}}{\rho_{ga}D_m} \]  

(3.70)

In the Reynolds number, a constant value of 0.2 m/s has been assumed for the velocity term, \( u \), representing a convection current within the building. This value is expected to be relatively high for an internal air velocity and thus represents a worst case scenario. The effective pool diameter, \( d_p \), should be defined by the total floor area unless a bund wall around the vessel is considered to contain the pool, as would normally be the case. Hence, by employing the critical value of the Reynolds number (\( \text{Re} = 3.2 \times 10^5 \)), a velocity of 0.2 m/s and the properties of air, a critical value for the pool diameter is calculated to be \( \approx 22 \) m, which is likely to exceed the size of containment in most buildings. Hence it is likely that the appropriate Sherwood number is defined by the \( \text{Re} < 3.2 \times 10^5 \) condition, giving a mass transfer coefficient of:

\[ k_{ml} = 0.664\frac{D_mSc^{1/3}Re^{1/2}}{d_p} \]  

(3.71)

The diffusion coefficient \( (D_m) \) may then be calculated via the Fuller, Schettler and Giddings equations \([8],[1]\) incorporating the sum of the atomic diffusion volumes of both the pollutant and air (see Equation 3.72).

\[ D_m = \frac{\left(101325 \times 10^{-7}\right)T^{1.75}\left[\left(m_a + m_p\right)\right]^{1/2}}{\left[\sum \nu_a^{1/2} + \left(\sum \nu_p^{1/2}\right)^2\right]} \]  

(3.72)

The sum of the atomic diffusion volumes are tabulated in references \([8]\) and \([1]\), and are 37.7 for chlorine, 20.1 for air and an estimate of 35.04 is taken for Freon 22. Equation (3.72) shows that the diffusion coefficient is a function of both system temperature and pressure, and hence will require re-calculation at each iteration of the release transient; however typical values in the order \( 10^{-5} \) m\(^2\)/s may be expected. Once the diffusion coefficient is known, the Schmidt number, and hence the mass transfer
coefficient, is determined, which in turn allows for the calculation of the rate of evaporation $M_e$.

### 3.5 Ventilation

The natural ventilation of a building due to ambient wind can be calculated from the British Standard on wind loading (BS 6399) [9]. This defines pressure coefficients on the external surfaces of a building for wind acting normal to the surface, but does not cover oblique incidence. Further information is available from a variety of sources, most of which relate to wind loading calculations (e.g. Cook, [10]). Solution of the various sets of differential equations is currently independent of the location of any openings within a wall. This is because the equations have been derived with the assumption of homogeneous mixing. However due to stratification, the position of each opening affects the outflow as discussed in detail in Section 3.6. It should be noted that openings in the ceiling are not considered in this model.

In this study, wind may be incident normally on any building wall (see Figure 3.2), and a maximum of four openings (one in each of the four walls, A through D) in any combination may be considered.

![Figure 3.2 Plan of four sided building with incident wind](image)

The pressure on an external wall surface ($P_b$) due to incident wind is determined via Equation (3.73), [11]:

$$P_b = P_w + P_a$$  \hspace{1cm} (3.73)

where $P_w$ is wind pressure and $P_a$ is the background atmospheric pressure at the same location. The wind pressure is calculated by considering the dynamic head per unit area generated by incident wind with a velocity, $v_w$, on the wall surface [12], i.e.

$$P_w = \frac{1}{2} \rho_w v_w^2 C_{pwd}$$  \hspace{1cm} (3.74)

Pressure coefficients, $C_{pwd}$, for a particular wall are dependent upon which wall the wind is incident upon and the aspect ratio, $\tau$, of the wall (defined as the wall width divided by height). BS 6399 [9] gives $C_{pwd}$ for specific aspect ratios, and suggests
interpolation for intermediate values. Table 3.2 illustrates $C_{pwd}$ values for windward, leeward and side walls.

<table>
<thead>
<tr>
<th>Face</th>
<th>Pressure Coefficient $C_{pwd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau \leq 1$</td>
</tr>
<tr>
<td>Windward</td>
<td>0.8</td>
</tr>
<tr>
<td>Leeward</td>
<td>-0.3</td>
</tr>
<tr>
<td>Sides</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

Table 3.2 Wind Pressure Coefficients from BS 6399

For simplicity in modelling, it is assumed that buildings have an aspect ratio of approximately unity, resulting in constant pressure coefficients for a wall surface, i.e.

<table>
<thead>
<tr>
<th>$C_{pwd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windward face</td>
</tr>
<tr>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 3.3 Wind Pressure Coefficients for Modelling

It may be seen from this table that there are possibilities for the generation of both positive and negative pressures on different walls. The implications of this will depend upon the pressure difference between $P_b$ and the room pressure, which varies throughout a release. If the pressure difference is positive (i.e. the external pressure is greater than the internal pressure) then fresh air will flow in through the opening under consideration. However, if the pressure difference is negative then consideration of the layer height (after stratification effects have been accounted for) will determine whether air at room temperature or the pollutant/air mixture will flow out from the room. It should be noted that certain scenarios will allow both positive and negative pressure differences to occur simultaneously at different openings, in such a way that a through-flow can be established.

**Discharge Rates**

If there is flow of fresh air into the room through an opening, $x$, the density of this flow will always be $\rho_d(T_a)$ and the flow rate is given by:

$$M_{in,x} = v_d \rho_d(T_a)C_dA_d$$  \hspace{1cm} (3.75)

where the velocity into the room, $v_d$, is given by Bernoulli’s equation:

$$\Delta P = \frac{1}{2}\rho_a v_d^2 \Rightarrow v_d = \sqrt{\frac{2}{\rho_a}\Delta P}$$  \hspace{1cm} (3.76)
When the internal room pressure is greater than the pressure at the opening, and the layer height is above the opening height, gas/air mixture leaves the room, with a flow rate determined via:

\[
\dot{M}_{\text{out},x} = v_d \rho_{ga} C_d A_d
\]  \hfill (3.77)

Or, if the layer is below the opening height, then air at room temperature will escape according to:

\[
\dot{M}_{\text{out},x} = v_d \rho_a(T) C_d A_d
\]  \hfill (3.77a)

where the velocity out of the room, \(v_d\), is given by Bernoulli’s equation:

\[
\Delta P = \frac{1}{2} \rho_{ga} v_d^2 \Rightarrow v_d = \sqrt{\frac{2}{\rho_{ga}} \Delta P} \]  \hfill (3.78)

\[
\Delta P = \frac{1}{2} \rho_a(T) v_d^2 \Rightarrow v_d = \sqrt{\frac{2}{\rho_a(T)} \Delta P} \]  \hfill (3.78a)

Therefore the total discharge and ingress rates are given by:

**Discharge with layer height above openings**

\[
\dot{M}_{\text{out}} = c_g \sum_{x:P>P_b} \rho_{ga} C_d A_d x \sqrt{\frac{2}{\rho_{ga}} (P - P_b)}
\]  \hfill (3.79)

\[
\dot{M}_{\text{out}} = (1 - c_g - c_l) \sum_{x:P>P_b} \rho_{ga} C_d A_d x \sqrt{\frac{2}{\rho_{ga}} (P - P_b)}
\]

**Discharge with layer height below openings**

\[
\dot{M}_{\text{out},x} = 0
\]  \hfill (3.80)

**Ingress of fresh air**

\[
\dot{M}_{\text{in}} = \sum_{x:P<P_b} \rho_a(T_x) C_d A_d x \sqrt{\frac{2}{\rho_a(T_x)} (P_b - P)}
\]  \hfill (3.81)

Where each opening is assessed individually.

### 3.6 Stratification

The technique used to obtain the solution to the required set of equations is described in detail in Section 4, but is essentially a time marching technique performed at small time increments. As the sets of model equations are derived under the assumption of...
homogeneous mixing, modification at each time step is required to account for stratification.

Each set of equations produces a value for the concentration of the gaseous phase pollutant averaged over the entire room volume. If the pollutant release is of low momentum, little turbulence will be generated, allowing the heavy gaseous pollutant to settle on or near the ground. In this situation, the same mass of pollutant is confined to a much smaller volume, giving a concentration in the layer which is higher than the average in the room. The increases in pollutant and air concentrations are dependent upon the ratio of the layer height \((h_o)\) to the room height \((H_R)\), and are given by:

\[
c'_g = \frac{H_R m_g c_g}{c_g (m_g - m_a) (H_R - h_o) + h_o m_g}
\]  
(3.82)

\[
c'_a = \frac{c_g m_a (h_o - H_R) + (1 - c_g) m_g h_o}{c_g m_a (h_o - H_R) + (1 - c_g) m_g h_o + m_g c_g H_R}
\]  
(3.83)

\[
c'_i = 1 - c'_g - c'_a
\]  
(3.84)

Initial layer height:

The layer height initially remains constant at a predetermined value ascertained from the momentum of the jet release. For a high momentum jet it is assumed that sufficient turbulence is generated within the room allowing complete mixing to result in an initial layer height at the room height, i.e. \(h_o = H_R\). For a low momentum jet, it is assumed that turbulence will only cause mixing to the height of release, which is therefore used as the initial layer height setting. For a liquid spill, the gaseous content only arises due to pool evaporation; hence the initial layer height will be very small i.e. \(h_o = 0.01\)m.
Layer restrictions:
The layer will start with a zero initial concentration that should steadily increase throughout the release duration to a predetermined value \( c_m \), which can be set arbitrarily at some value <1 to reflect the fact that some mixing is likely to take place, however quiescent the developing lower layer appears. Once the layer has attained this concentration, the height will increase towards (if it is not already at) the room height, maintaining the concentration at \( c_m \). If the layer does not reach the room height, the concentration will then be allowed to increase towards unity. This is summarised in Figure 3.3.

3.7 Scrubber unit

The scrubber unit is employed to remove trace levels of pollutant that may be present in the room due to minor leaks from low-pressure pipework etc. For simplicity this is modelled with a constant volumetric throughput, which can be converted to a mass throughput via density relations.

The density value used is dependent upon the layer height relative to the height of extraction area of the unit. Again for simplicity, this area is assumed to lie in a horizontal plane. If the layer is above this extraction height then the gas/air mixture will be extracted whereas if it is below this height only air will be extracted. The relevant density is therefore chosen according to the layer position.

3.8 Summary of equations

The model comprises a set of five, first order, ordinary differential equations, which are to be solved simultaneously at various time steps. These equations have been developed to simulate the transient behaviour of the conditions within a room with a
continuous pressurised release of a pollutant stored at an ambient temperature and saturation pressure. Conditions within the room are described by the:

(i) mass fraction of the pollutant in the liquid phase,
(ii) mass fraction of the pollutant in the vapour phase,
(iii) overall density of the pollutant / air mixture,
(iv) temperature (found indirectly from an enthalpy evaluation) and,
(v) pressure.

As mentioned, the temperature is determined from the enthalpy transient. The total enthalpy equation (3.41) may be used to establish this new temperature, by rearranging to make temperature the subject.

\[ T = T_{ref} + \frac{h + c_{lg} \cdot h}{c_{lg} (C_{pg} - C_{pa}) + c_{l} (C_{pl} - C_{pa}) + C_{pa}} \]  

(3.81)

Hence, when new (time stepped) values of enthalpy and the pollutant mass fractions are inserted into Equation (3.81), a new temperature is obtained.

The values for insertion into the temperature equation are determined by the thermodynamics of the room, which in turn define the differential equations that model the various transients. As two possible situations may arise depending upon the heat transfer rate from the walls, ceiling and floor, the set of equations must be altered accordingly. For the initial scenario, where the conditions in the room are above the saturation point, the set of five rate equations to be solved is:

\[ \frac{dc_{lg}}{dt} = \frac{1}{V_{r} \cdot \rho_{l}} \left[ \left( 1 - c_{lg} \right) M_{in} - c_{lg} \left( M_{out_{lg}} + M_{sc_{lg}} \right) \right] \]  

(3.20b)

\[ \frac{dc_{l}}{dt} = 0 \]  

(3.19b)

\[ \frac{d\rho_{l}}{dt} = \frac{1}{V_{r}} \left[ M + M_{in} - c_{lg} \left( M_{out_{lg}} + M_{sc_{lg}} \right) \right] \]  

(3.18b)

\[ \frac{dh}{dt} = \left( \frac{1}{\rho_{l} - P \cdot \lambda_{l}} \right) \left[ C_{g} + \left( P \cdot \lambda_{g} - h \right) \frac{d\rho_{l}}{dt} + P \cdot \lambda_{2} \frac{dc_{lg}}{dt} \right] \]  

(3.36)

\[ \frac{dP}{dt} = P \left[ \lambda_{l} \frac{dh}{dt} + \lambda_{2} \frac{dc_{lg}}{dt} + \lambda_{3} \frac{d\rho_{l}}{dt} \right] \]  

(3.35)

where,
\[ \lambda_1 = \frac{1}{G_2 T}; \quad \lambda_2 = \left[ \frac{G_1}{G_2 T} + \frac{m_g (m_g - m_a)}{m_a m_g} \right]; \quad \lambda_3 = \frac{1}{\rho_t} \]

\[ G_1 = (C_{pg} - C_{pa}) (T - T_{ref}); \quad G_2 = c_g (C_{pg} - C_{pa}) + C_{pa}; \]

\[ m_{ga} = \frac{m_a m_g}{m_g - c_g (m_g - m_a)} \]

and

\[ C'_i = \frac{1}{V_i} \left[ M + \left( \frac{1 - c_g}{c_g} \right) M + \dot{M}_i - \dot{M}_s - c_i \left( \dot{M}_{out_g} + \dot{M}_{sc_f} \right) \right] \]

If there is insufficient heat transfer from the walls, ceiling, floor, and storage vessel to the room contents, the temperature will continue to drop below the saturation point. Once this regime has been reached, the assumption that the liquid content of the pollutant remains suspended in droplet form in the gas phase will no longer be valid. It is thus assumed that the liquid falls to the floor forming a pool either within the bounds of a bund wall or over the entire floor area. As heat transfer from the ground causes pool evaporation, the set of differential equations to be solved is now:

\[ \frac{d c_g}{dt} = \frac{1}{V_i \rho_t} \left[ \left( F_i - c_g \right) M + \dot{M}_i - c_g \left( \dot{M}_{out_g} + \dot{M}_{sc_f} \right) \right] \]

\[ \frac{d c_i}{dt} = \frac{1}{V_i \rho_t} \left[ \left( 1 - F_i - c_i \right) M - \dot{M}_i - c_i \left( \dot{M}_{out_g} + \dot{M}_{sc_f} \right) \right] \]

\[ \frac{d \rho_i}{dt} = \frac{1}{V_i} \left[ M + \dot{M}_{in} - c_g \left( \dot{M}_{out_g} + \dot{M}_{sc_f} \right) - \left( 1 - c_g - c_i \right) \left( \dot{M}_{out_g} + \dot{M}_{sc_f} \right) \right] \]

\[ \frac{dh}{dt} = \left( \frac{1}{\rho_i - \rho L} \right) \left[ C'_2 + (P \lambda_3 - h) \frac{d \rho_i}{dt} + \lambda_4 \frac{d c_i}{dt} + \lambda_5 \frac{d c_g}{dt} \right] \]

\[ \frac{d P}{dt} = P \left[ \lambda_1 \frac{dh}{dt} + \lambda_3 \frac{d \rho_i}{dt} + \lambda_4 \frac{d c_i}{dt} + \lambda_5 \frac{d c_g}{dt} \right] \]

where,

\[ F_i = \frac{C_{ps} (T_s - T_h)}{H_{vap}}; \quad m_{ga} = \frac{m_a m_g (1 - c_i)}{m_g (1 - c_i) - c_g (m_g - m_a)} \]
\[ \lambda_4 = -\frac{c_m m_g (m_g - m_a)}{m_a m_g (1-c)} \]
\[ \lambda_5 = \left[ \frac{G_t + m_g (m_g - m_a)}{G_t m_a (1-c)} \right] \]

and
\[ C_2' = \frac{1}{V_p} \left[ \hat{M}_f h_g (T_s) + (1 - \hat{F}_f) h_1 (T_s) + \hat{M}_m h_m (T_s) + \right] \]
\[ \sum q - c_g \left( \hat{M}_{out_s} + \hat{M}_{sc} \right) h - c_d \left( \hat{M}_{out_s} + \hat{M}_{sc} \right) h_a (T) \]

The heat transfer from the walls, ceiling, floor and storage vessel, \( \dot{q}_{wall} \), \( \dot{q}_{ceiling} \), \( \dot{q}_{ground} \) and \( \dot{q}_{vessel} \) respectively are all defined by effective forced convection heat transfer mechanisms using the Nusselt, and hence Prandtl, and Reynolds dimensionless groups to determine effective heat transfer coefficients (see Equation (3.59)), i.e.

\[ \dot{q}_{wall} = h_{eff,w} A_{wall} (T_a - T) \quad (3.55) \]
\[ \dot{q}_{ceiling} = h_{eff,c} A_{ceiling} (T_a - T) \quad (3.57) \]
\[ \dot{q}_{ground} = h_{eff,g} A_{ground} (T_a - T) \quad (3.58) \]
\[ \dot{q}_{vessel} = 0.25 \dot{q}_{wall} \quad (3.61) \]

Ventilation effects are considered by determining the pressure difference across all available openings. The pressure at an opening may be influenced by wind effects, causing one of two situations to arise. Either fresh air will be drawn into the room (if opening pressure > room pressure), or the air/pollutant mixture will be forced out (if opening pressure < room pressure). It is possible for both situations to occur simultaneously over different openings or depending upon the layer height. So the flow rate through an opening may be determined by:

**Discharge with layer height above openings**

\[ \hat{M}_{out_s} = c_g \sum_{x>P} \rho_{gs} C_d A_{dx} \sqrt{\frac{2}{\rho_{ga}} (P - P_b)} \quad (3.79) \]
\[ \hat{M}_{out_s} = (1 - c_g - c_i) \sum_{x>P} \rho_{ga} C_d A_{dx} \sqrt{\frac{2}{\rho_{ga}} (P - P_b)} \]

**Discharge with layer height below openings**

\[ \hat{M}_{out_s} = 0 \]
\[ \hat{M}_{out_s} = \sum_{x>P} \rho_a (T) C_d A_{dx} \sqrt{\frac{2}{\rho_a (T)} (P - P_b)} \quad (3.80) \]
The set of differential equations to be solved is determined by the calculation of saturation parameters and a comparison is made with room conditions. This determines whether the room is above or below saturation. The saturation conditions are defined by the following pressure, temperature (derived from the Antoine equation) and enthalpy expressions:

\[
P_{\text{sat}} = \frac{P_m c_g}{m_a c_g + m_g (1 - c_1 - c_g)} \quad (3.81)
\]

\[
T_{\text{sat}} = \frac{A_b}{A_a - \ln \left( \frac{P_{\text{sat}}}{133.32} \right)} - A_c \quad (3.82)
\]

\[
h_{\text{sat}} = \left[ c_g (C_{pg} - C_{pa}) + C_{pa} \right] (T_{\text{sat}} - T_{\text{ref}}) \quad (3.83)
\]

where the constants for the Antoine equation [8] are tabulated below:

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>(A_a)</th>
<th>(A_b)</th>
<th>(A_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorine</td>
<td>15.961</td>
<td>1978.32</td>
<td>-27.01</td>
</tr>
<tr>
<td>Freon 22</td>
<td>15.5602</td>
<td>1704.8</td>
<td>-41.3</td>
</tr>
</tbody>
</table>

Table 3.4 Constants for the Antoine equation

Hence, by knowing the room pressure and concentrations of the pollutant in both phases, the saturation enthalpy (\(h_{\text{sat}}\)) may be calculated, which may be compared with the enthalpy of the room contents (\(h\)). If \(h > h_{\text{sat}}\) then the room is above the saturation point and Equations (3.20b), (3.19b), (3.18b), (3.36) and (3.35) are solved, or if \(h < h_{\text{sat}}\) then the room contents are below the saturation point and Equations (3.20), (3.19), (3.18), (3.45) and (3.44) are solved.
4. SOLUTION TECHNIQUE

4.1 Programming approach

A computer program “GRAB-T” has been written in C++ to solve the mathematical model described in Section 3. The code uses an input form (developed in Visual Basic version 5) to read in the inputs described in Section 2.3. In addition it reads in the release duration and maximum simulation time. The User may also decide whether to simulate a constant or exponentially decaying release rate. This latter option decays as a function of pressure, simulating the loss of head as the material leaves the storage vessel.

A second Visual Basic screen is then used to display various model results. Options included on this screen are time histories of temperature (T), total density ($\rho$), gas mass fraction ($c_g$), liquid mass fraction ($c_l$), ingress and egress rates ($\dot{M}_{in}$ and $\dot{M}_{out}$), room pressure (P), pollutant release rate ($M$) and layer height ($h_o$). The methods employed to obtain the relevant data for each of these plots are detailed below.

4.2 Integration techniques

Either set of five differential equations described in Section 3.5 may be solved by a numerical integration technique. The fourth order Runge-Kutta technique has been adopted, chosen mainly due to its simplicity and accuracy when compared to other appropriate methods. The technique facilitates programming, is self-starting, economical on computer storage space and presents no convergence problems [13]. To employ the technique, four auxiliary quantities are computed for each differential equation, which are then used to calculate the solution for each step.

The Runge-Kutta method requires the calculation of four auxiliary quantities (e.g. $\sigma_1$, $\sigma_4$) per differential equation which are then used in a time stepping approach to produce the various transients. For the five differential equations, the following functional statements may be written, where the terms in the brackets are the input terms for the particular function, and $\Delta t$ is the time step.

$$
\begin{align*}
\sigma_1 &= \Delta t \cdot f_{\rho t}(c_l, \rho_l, P) \\
\omega_1 &= \Delta t \cdot f_{\rho g}(c_g, c_l, \rho_l, P, T) \\
\eta_1 &= \Delta t \cdot f_{cl}(c_l, \rho_l, P, T) \\
\varepsilon_1 &= \Delta t \cdot f_{h}(c_g, c_l, \rho_l, h, P, T) \\
\phi_1 &= \Delta t \cdot f_{P}(c_g, c_l, \rho_l, h, P, T) \\
\sigma_2 &= \Delta t \cdot f_{\rho t}(c_l + \eta_1/2, \rho_l + \sigma_1/2, P + \phi_1/2) \\
\omega_2 &= \Delta t \cdot f_{\rho g}(c_g + \omega_1/2, c_l + \eta_1/2, \rho_l + \sigma_1/2, P + \phi_1/2, T) \\
\eta_2 &= \Delta t \cdot f_{cl}(c_l + \eta_1/2, \rho_l + \sigma_1/2, P + \phi_1/2, T) \\
\varepsilon_2 &= \Delta t \cdot f_{h}(c_g + \omega_1/2, c_l + \eta_1/2, \rho_l + \sigma_1/2, h + \varepsilon_1/2, P + \phi_1/2, T) \\
\phi_2 &= \Delta t \cdot f_{P}(c_g + \omega_1/2, c_l + \eta_1/2, \rho_l + \sigma_1/2, h + \varepsilon_1/2, P + \phi_1/2, T) \\
\sigma_3 &= \Delta t \cdot f_{\rho t}(c_l + \eta_2/2, \rho_l + \sigma_2/2, P + \phi_2/2) \\
\omega_3 &= \Delta t \cdot f_{\rho g}(c_g + \omega_2/2, c_l + \eta_2/2, \rho_l + \sigma_2/2, P + \phi_2/2, T)
\end{align*}
$$
The time stepped solution for each quantity may then be written as a weighted average of these auxiliary terms, i.e.

\[
\begin{align*}
\eta_3 &= \Delta t \cdot f_0(c_1 + \eta_2/2, \rho_1 + \sigma_2/2, P + \phi_2/2, T) \\
\epsilon_3 &= \Delta t \cdot f_0(c_1 + \omega_2/2, c_1 + \eta_2/2, \rho_1 + \sigma_2/2, h + \epsilon_2/2, P + \phi_2/2, T) \\
\phi_3 &= \Delta t \cdot f_0(c_1 + \omega_2/2, c_1 + \eta_2/2, \rho_1 + \sigma_2/2, h + \epsilon_2/2, P + \phi_2/2, T) \\
\sigma_4 &= \Delta t \cdot f_{pl}(c_1 + \eta_3, \rho_1 + \sigma_3, P + \phi_3) \\
\omega_4 &= \Delta t \cdot f_{pl}(c_1 + \omega_3, c_1 + \eta_3, \rho_1 + \sigma_3, P + \phi_3, T) \\
\eta_4 &= \Delta t \cdot f_{pl}(c_1 + \eta_3, \rho_1 + \sigma_3, P + \phi_3, T) \\
\epsilon_4 &= \Delta t \cdot f_{pl}(c_1 + \omega_3, c_1 + \eta_3, \rho_1 + \sigma_3, h + \epsilon_3, P + \phi_3, T) \\
\phi_4 &= \Delta t \cdot f_{pl}(c_1 + \omega_3, c_1 + \eta_3, \rho_1 + \sigma_3, h + \epsilon_3, P + \phi_3, T)
\end{align*}
\]

These calculated values for the various parameters are then set to be the initial conditions for the next time step, and the routine is performed once more. Hence, by continually repeating the procedure, and recording the values of the parameters of interest, the various transients may be generated.

As previously mentioned, it may be noted that the room enthalpy is one of the transiently calculated variables. In order to obtain the corresponding temperature from a particular value of enthalpy, Equation 3.81 is used. This is the rearranged version of the equation describing the overall enthalpy of the room contents, i.e.

\[
T = T_{ref} + \frac{h + c_i h_{fg}}{c_g (C_{pg} - C_{pa}) + c_i (C_{pi} - C_{pa}) + C_{pa}}
\] (3.81)

Hence, as values of \(c_g, c_i\) and \(h\) are updated in the model, \(T\) is continuously updated via the above equation, producing the temperature transient.

4.3 Stability of solution

The integration technique is a time marching method; that is, starting from an initial condition, a value of the solution is obtained at a desired time step. The value of the chosen time step does however affect the stability of the solution transient. If the time step is too small the number of steps required and the round-off errors become increasingly large; similarly, if the time step is too big, a large truncation error per step is induced.

The stability criterion proposed by Kreyszig [13] has been applied to ensure stable solutions. This method bounds a ratio, \(\kappa\), of the auxiliary equations mentioned above,
between two values. For the total density function (as defined above), the ratio \( \kappa \) is defined by:

\[
\kappa = 2 \frac{\sigma_3 - \sigma_2}{\sigma_2 - \sigma_1}
\]  

(4.1)

It is advised that, if \( 0.01 \leq \kappa \leq 0.05 \) then the time step should remain unchanged, however, if \( \kappa > 0.05 \), the time step should be halved, and if \( \kappa < 0.01 \), the time step should be doubled.

A problem arises however in that the solutions for some variables require smaller time steps than those for others. Although stable, accurate solutions may be obtained using the smallest applicable time steps, the penalty is an extended execution time for the model. A series of computational experiments have been performed to optimise the time step for both stability and execution time, and the resulting value has been set as the fixed initial value within the code.

4.4 Efficiency

The time efficiency of the model is dependent upon the step size used in the numerical integration. The smaller the step size the more iterations are required. A pre-set time step has been chosen (see Section 4.3) to compromise between speed and stability of solution.

The GRAB-T program is constructed as two linked modules; a User Interface module and a Computational module. The former module is written in Visual Basic (VB) version 5, providing a user friendly input screen. Although VB may be employed for the numerical integration algorithm (computational module) it is not considered suitable in terms of runtime efficiency. The solution algorithm is hence performed using C++ to optimise and maintain runtime efficiency.
5. MODEL VALIDATION

5.1 Test Data

Results from GRAB-T have been compared with experimental data provided by the Health & Safety Laboratory (HSL). Experimental data were obtained by measuring temperature and concentration at numerous positions in a purpose built test room. Chlorodifluoromethane (Freon-22) was the chosen pollutant, and was released at various constant mass flow rates as described in Table 5.1 below. Results from the model are compared with these data in this section.

<table>
<thead>
<tr>
<th>Jet Type</th>
<th>Flow rate (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>0.0117</td>
</tr>
<tr>
<td>Medium</td>
<td>0.032</td>
</tr>
<tr>
<td>Large</td>
<td>0.139</td>
</tr>
<tr>
<td>Extra Large</td>
<td>0.236</td>
</tr>
</tbody>
</table>

Table 5.1 Mass flow rates used for validation runs

5.2 Inputs Used

Although the test room has a uniform height of 2.44 metres, it does not have a simple regular geometry. By considering a scaled diagram of the test room [14], a total surface area (walls, ceiling and floor) of 144.26 m² has been calculated, and a free air volume of 52.7 m³ is also quoted in this literature. By maintaining the constant room height, it can be shown that a room of length and width 19.61 m and 1.1 m respectively produce this volume and surface area and these values have been used in this assessment.

The external and internal walls of the test room are constructed from 13 mm hardwood stage panel (thermal conductivity of 0.17 W/m/K) and 12 mm medium density fibreboard (thermal conductivity of 0.16 W/m/K) respectively. The ceiling material was also constructed from MDF and, although the floor was made from concrete (thermal conductivity of 1.4 W/m/K), it was maintained as an isothermal surface. Due to the similarities between the wall properties, a constant thickness of 13 mm with thermal conductivity of 0.17 W/m/K has been used for both walls and ceiling.

The test room contains a 9.71 m² bund beneath the tanks. If saturation conditions are met and rain-out commences, it is assumed that a liquid pool will form in this bund.

The test room was unventilated with the exception of a vertical bifurcating extraction duct. The main cross section of this duct had an area of 0.09 m², and the two openings were located 0.1 m above the ground [14]. For validation purposes, all openings in the GRAB-T model are assumed closed, and the scrubber unit is assumed to be representative of the extraction duct. Volumetric scrubber throughputs for the four release flow rates are assumed by considering graphical test data, provided by HSL [15], on the velocities produced within the duct during testing. By considering the HSL Test 3 data (release rate of 0.139 kg/s), after 30 seconds a constant velocity of
1.0 m/s was recorded through the duct. By assuming a linear relation between release rate and duct velocity, and by considering the duct area, volumetric scrubber throughputs have been calculated and are given in Table 5.2.

<table>
<thead>
<tr>
<th>Flow rate (kg/s)</th>
<th>Duct velocity (m/s)</th>
<th>Area (m²)</th>
<th>Throughput (m³/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0117</td>
<td>0.084</td>
<td>0.09</td>
<td>0.00756</td>
</tr>
<tr>
<td>0.032</td>
<td>0.23</td>
<td>0.09</td>
<td>0.0207</td>
</tr>
<tr>
<td>0.139</td>
<td>1.00</td>
<td>0.09</td>
<td>0.0900</td>
</tr>
<tr>
<td>0.236</td>
<td>1.70</td>
<td>0.09</td>
<td>0.1530</td>
</tr>
</tbody>
</table>

**Table 5.2 Scrubber throughputs**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Openings A,B,C,D</td>
<td>False</td>
<td>-</td>
</tr>
<tr>
<td>Wind Incident on face</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Substance released</td>
<td>Freon-22</td>
<td>-</td>
</tr>
<tr>
<td>Release type</td>
<td>Constant</td>
<td>-</td>
</tr>
<tr>
<td>Release momentum</td>
<td>High</td>
<td>-</td>
</tr>
<tr>
<td>Release height</td>
<td>2</td>
<td>m</td>
</tr>
<tr>
<td>Room Height</td>
<td>2.44</td>
<td>m</td>
</tr>
<tr>
<td>Room Length</td>
<td>19.61</td>
<td>m</td>
</tr>
<tr>
<td>Room Width</td>
<td>1.1</td>
<td>m</td>
</tr>
<tr>
<td>Pool type</td>
<td>Bund</td>
<td>-</td>
</tr>
<tr>
<td>Bund Area</td>
<td>9.71</td>
<td>m²</td>
</tr>
<tr>
<td>Scrubber operation</td>
<td>On</td>
<td>-</td>
</tr>
<tr>
<td>Scrubber extraction height</td>
<td>0.1</td>
<td>m</td>
</tr>
<tr>
<td>Air Temperature</td>
<td>284.25</td>
<td>K</td>
</tr>
<tr>
<td>Air Pressure</td>
<td>101325</td>
<td>N/m²</td>
</tr>
<tr>
<td>Wind speed</td>
<td>N/A</td>
<td>m/s</td>
</tr>
</tbody>
</table>

**Table 5.3 Input data for validation runs**

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat of gas phase</td>
<td>(C_{pg})</td>
<td>657</td>
<td>J/kg/K</td>
</tr>
<tr>
<td>Specific heat of liquid phase</td>
<td>(C_{pl})</td>
<td>1193</td>
<td>J/kg/K</td>
</tr>
<tr>
<td>Heat of vaporisation</td>
<td>(h_{fg})</td>
<td>233517</td>
<td>J/kg</td>
</tr>
<tr>
<td>Molecular mass</td>
<td>(m)</td>
<td>86.5 \times 10^{-1}</td>
<td>kg/mol</td>
</tr>
<tr>
<td>Viscosity of gas phase</td>
<td>(\mu_g)</td>
<td>1.3 \times 10^5</td>
<td>N.s/m²</td>
</tr>
<tr>
<td>Viscosity of liquid phase</td>
<td>(\mu_l)</td>
<td>2.25 \times 10^{-5}</td>
<td>N.s/m²</td>
</tr>
<tr>
<td>Density of liquid phase</td>
<td>(\rho)</td>
<td>1262</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Liquid enthalpy</td>
<td>(h_l)</td>
<td>408200</td>
<td>J/kg</td>
</tr>
<tr>
<td>Boiling point</td>
<td>(T_b)</td>
<td>232</td>
<td>K</td>
</tr>
<tr>
<td>Thermal conductivity of liquid</td>
<td>(k_l)</td>
<td>0.09</td>
<td>W/m/K</td>
</tr>
<tr>
<td>Thermal conductivity of gas</td>
<td>(k_g)</td>
<td>0.0117</td>
<td>W/m/K</td>
</tr>
</tbody>
</table>

**Table 5.4 Physical properties of Freon-22**
Validation input data is tabulated in Table 5.3, all relevant physical properties of Freon-22 are given in Table 5.4 and thermal properties of the test room construction materials are given in Table 5.5.

<table>
<thead>
<tr>
<th>Boundary</th>
<th>Property</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceiling</td>
<td>Specific heat</td>
<td>1255</td>
<td>J/kg/K</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity</td>
<td>0.17</td>
<td>W/m/K</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td>0.013</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Isothermal</td>
<td>False</td>
<td></td>
</tr>
<tr>
<td>Walls</td>
<td>Specific heat</td>
<td>1255</td>
<td>J/kg/K</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity</td>
<td>0.17</td>
<td>W/m/K</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td>0.013</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Isothermal</td>
<td>False</td>
<td></td>
</tr>
<tr>
<td>Ground</td>
<td>Specific heat</td>
<td>880</td>
<td>J/kg/K</td>
</tr>
<tr>
<td></td>
<td>Thermal conductivity</td>
<td>1.4</td>
<td>W/m/K</td>
</tr>
<tr>
<td></td>
<td>Thickness</td>
<td>0.013</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Isothermal</td>
<td>True</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.5 Thermal properties of test room construction materials

5.3 Comparison of Results

Once the above information was entered into the input form, the only change necessary to simulate each of the four test cases was to alter the pollutant release rate and scrubber throughput in accordance with the first and last columns of Table 5.2.

Results from GRAB-T are compared with the HSL data for each release rate below. The HSL experiments produced temperature and gas concentration profiles at forty-four and twenty-one different locations respectively [15]. As GRAB-T is a simple, lumped parameter model, HSL results taken from sensors in the middle of the test room (i.e. sensor location K) were considered to be the most appropriate for comparison. At this location, four sensors are arranged vertically, and for the same reason as the choice of location, the two central sensors (K2 and K3) are taken for comparison.

It should be noted that the gas concentration calculated in GRAB-T is a mass concentration ($c_{\text{mass}}$), which is to be compared against the experimental concentration by volume ($c_{\text{vol}}$). In order for a comparison to be made, Equation 5.1 below should be employed:

$$c_{\text{vol}} = \frac{c_{\text{mass}} M_a}{c_{\text{mass}} M_a + M_g (1 - c_{\text{mass}})}$$  \hspace{1cm} (5.1)

Predictions from GRAB-T of temperature and concentration at the end of the release period are compared with results from both the previous version of GRAB-T and the HSL experiments. The main difference between the previous and current version of
GRAB-T is the inclusion of stratification, although the details of the thermodynamic calculations have also been improved. The predictions are illustrated graphically in Figures 5.1 (temperature drop) and 5.2 (concentration) and a brief description of the results is also given below.

Figure 5.1  Comparison between HSL and GRAB-T temperatures

**Small Jet**

The two HSL temperature sensors initially had a mean temperature of 284.25 K. Data for a 550 s (9 min 10 sec) release of Freon-22 into the test room indicate a mean temperature drop of ~3.25 K. This is compared with a predicted drop of 1.06 K by GRAB-T.

Similarly the volumetric gas concentrations at the sensors had an average value of 4.0% after 550 seconds, compared with a predicted volumetric concentration of 3.38%.

**Medium Jet**

For the medium jet, the mean temperature drop was recorded as 6.9 K, compared with 2.85 K from GRAB-T.

A recorded concentration by volume of 10.5% is compared against a calculated volumetric concentration of 9.54 %.

**Large Jet**

Here the recorded fall in room temperature at the two sensors is ~12.5 K, compared with a prediction of 11.43 K from GRAB-T.

There is no HSL information available for concentration comparison.
Figure 5.2  Comparison between HSL and GRAB-T concentration

Extra Large Jet

As in the Large Jet validation run, only a temperature profile is available. The HSL data give a temperature drop of ~21K whereas GRAB-T predicts a reduction of 18.34K.

There is no HSL information available for concentration comparison.

As can be observed from Figure 5.1, the new version of GRAB-T provides an improved temperature drop trend compared with the previous version. It is also noticeable that the closest match between HSL data and GRAB-T predictions are produced for the large release rate, where the duct velocity is known with a greater level of confidence. It is possible that the validation cases for the other release rates would provide a closer agreement with the test data if the duct velocity (and hence scrubber throughput) were known with a greater level of confidence.

Figure 5.2 shows that, for the two HSL concentration data points, the predictions of the new version of GRAB-T are closer than those of the previous version.

By comparing data in Figure 5.2, it can be seen that the GRAB-T model provides concentration predictions that are in close agreement with the HSL experimental data. The predictions are more accurate than the previous version of the model; knowledge of the correct duct velocities would possibly make these results closer still.

A comparison of the predicted temperature and concentration transients for the small and medium jets, with the corresponding HSL sensor K2 and K3 data, is given in Figures 5.3 – 5.6. The generally more rapid predicted temperature drop at the beginning of the transient probably reflects the delay time in material being detected at the sensors. The temperature discrepancies in the latter part of the transient are
probably due to the use of the fully mixed assumption in the model, which may not have been the case in the experiment.

![Figure 5.3 Small Jet – Temperature comparison plot](image)

**Figure 5.3** Small Jet – Temperature comparison plot

![Figure 5.4 Small Jet – concentration comparison plot](image)

**Figure 5.4** Small Jet – concentration comparison plot
Figure 5.5 Medium jet – temperature comparison plot

Figure 5.6 Medium jet – concentration comparison plot
6. MODEL SENSITIVITY

6.1 Base Case Definition

In order to assess the effects of key model parameter variation, a base case scenario was defined. This is the case from which the test parameters were varied.

For the purpose of this sensitivity study, the base case is based upon the extra large release scenario from the HSL test series (see Section 5). This was a 0.236 kg/s, constant, high momentum release of Freon-22, into a room with equivalent dimensions of 19.61m x 1.1m x 2.44m. The room is unventilated (i.e. no openings), and the scrubber unit is set to operate with a 0.153m³/s throughput at a height of 0.1m from the ground. The vessel is contained within a bund of area 9.71m². All walls and the ceiling are constructed of materials in accordance with Table 5.5. Ambient temperature, pressure and windspeed are set to be 284.25K, 101325 N/m² and 0.5m/s respectively, although the windspeed value in the base case is not used in any calculation.

6.2 Time Step Variation

By setting the simulation time to be greater than the release duration, the effects of heat transfer from the ceiling, walls, ground and vessel can be monitored. This heat transfer energy should eventually restore the temperature of the room contents back to its pre-release value.

An investigation into the effects of different initial time steps was performed using the base case scenario and employing various time steps (as tabulated below). Upon comparing the output files produced in each case, the maximum temperature drop and the final room temperatures (for a 650 second simulation) are as tabulated below:

<table>
<thead>
<tr>
<th>Time step (seconds)</th>
<th>Temperature drop (Kelvin)</th>
<th>Final temperature (Kelvin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>18.336</td>
<td>265.914</td>
</tr>
<tr>
<td>0.001</td>
<td>18.336</td>
<td>265.914</td>
</tr>
<tr>
<td>0.0025</td>
<td>18.335</td>
<td>265.915</td>
</tr>
<tr>
<td>0.005</td>
<td>18.335</td>
<td>265.915</td>
</tr>
<tr>
<td>0.01</td>
<td>18.336</td>
<td>265.914</td>
</tr>
</tbody>
</table>

Table 6.1 Time step variation

It may be observed that all results are in good agreement with each other, but it should also be noted that the smaller the time step the more iterations are required for the simulation time. This in turn increases the required computing time and resultant output file.

Although the end results of the case with a time step of 0.01s are close to the smaller time step results, they increase the potential of introducing numerical instability. It was also found that larger time steps (i.e. 0.5s and 0.1s) produced unstable solutions, and hence have not been presented here. Therefore in order to generate accurate
results in a short space of time, and in an attempt to reduce the risk of introducing numerical instability to the solution technique, an initial time step of 0.0025s has been chosen as default.

6.3 Release Rate variation

The validation above was performed using the default constant pollutant release rate. However, in reality as the pollutant escapes, the pressure inside the vessel falls, tending towards equilibrium with the room pressure. As a consequence of this, the release rate, which is dependent upon the pressure difference between the vessel and the room, will decay exponentially, as shown in Figure 6.1.

![Exponential decay release rate](image)

**Figure 6.1** Exponential decay release rate

Hence, if the ‘Variable’ option is selected in the ‘Release Details’ section, the constant release rate ‘$\dot{M}$’, is replaced by:

$$\dot{M} = \dot{M}_{\text{init}} e^{-\frac{t}{\tau_d}}$$

where ‘$\tau_d$’ is the decay constant which governs how rapidly the release rate falls towards zero (see Figure 6.1). The lower the decay constant, the steeper the gradient, giving shorter duration releases. Three sensitivity runs have been performed to illustrate the consequences of three different decay constants (i.e. $\tau_d = 50$ s, 100 s and 150 s).
The main output from these test runs is illustrated in Figures 6.2 (temperature) and 6.3 (concentration):

![Graph](image)

**Figure 6.2  Exponential decay temperature profile**

\( \tau_d = 50 \text{ s} \) : The release becomes negligible after \( \sim 300 \text{ seconds} \) (5 min), and the room temperature drops to a minimum of 271.7 Kelvin at \( \sim 30 \text{ seconds} \). The heat transfer effects from the room then begin to dominate, forcing the temperature to return to the original room temperature.

\( \tau_d = 100 \text{ s} \) : A negligible release rate is noticed at approximately 9 minutes, and the minimum room temperature of 269.9 K is achieved at \( \sim 48 \text{ seconds} \). This then tends towards steady state.

\( \tau_d = 150 \text{ s} \) : This decaying release does not quite achieve a zero mass flow rate before the end of the release duration period. The release duration (550 seconds) is long enough to maintain non-zero pollutant ingress before the decay asymptotes to the zero flow rate axis. Here the temperature drops to its minimum (269 K) after 50 seconds, and then increases towards steady state as in the other cases.

In all three cases the gas mass fraction rises at a similar rate before tending towards an individual steady state.
6.4 Ventilation effects

6.4.1 Single opening

In order to assess the sensitivity of the model to openings, the base case has been compared with a room ventilated by a single opening with a fixed discharge coefficient. The opening is defined to have both a width and height of 0.3m, giving an area of 0.09m² (i.e. that of the scrubber), and is 0.1m above the ground. Runs have been performed over 550 seconds with a wind speed of 2m/s incident on various room faces (relative to the opening) with the scrubber unit not in operation.

Maximum temperature drop and mass flow rate results from these runs are given in Table 6.2.

<table>
<thead>
<tr>
<th>Opening position (relative to wind incidence)</th>
<th>Max temperature drop (K)</th>
<th>Max mass flow rate (kg/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident</td>
<td>16.534</td>
<td>0.30985</td>
</tr>
<tr>
<td>Opposite</td>
<td>16.534</td>
<td>0.309851</td>
</tr>
<tr>
<td>Side</td>
<td>16.534</td>
<td>0.309851</td>
</tr>
</tbody>
</table>

Table 6.2 Single opening position

It may be observed that for a single opening, its position does not have a significant effect on the results. It is however interesting to observe that the temperature drop results obtained for these runs are close to that for the base case (i.e. 18.34K) which
employed the scrubber unit instead of an opening. A plot of the air and gas flow rates through the opening for the ‘Incident’ case is given in Figure 6.4.

![Flow rates through single opening for incident wind case](image)

**Figure 6.4** Flow rates through single opening for incident wind case

It may be observed that, as the temperature (and pressure) in the room fall in the initial stages of the transient, air is drawn in through the opening, but as the pressure increases, material is expelled at an increasing rate until equilibrium is established.

### 6.4.2 Multiple openings

To investigate the effects of more than one opening, a series of model runs are performed with combinations of multiple openings each with the same properties. All other model settings are as in the single opening cases.

**Two openings – straight through:** Two openings on opposite sides of the room, with wind incident upon one of them. Initially air is drawn in through the incident opening, whilst gas/air is expelled through the other; however, as the pressure builds, gas/air is expelled through both openings, until equilibrium is attained.

**Two openings – sides:** Two openings on opposite sides of the room with wind incident upon a third side. Initially, air is drawn in through both openings and, as expected, the flow pattern through both openings is identical (they both have the same wind pressure coefficient). As in the previous case, the pressure inside the room soon dominates the direction of flow, with the gas/air mixture exiting the room at the same rate through each opening.

**Three openings – straight through and side:** In this case, air is drawn in through the incident opening throughout the entire time history. Whilst the gas/air mixture is
expelled through the other two openings. (The side opening has a greater flow rate compared with the opening opposite to wind incidence).

Four openings: Here, all openings are active. Air is drawn in through the incident opening throughout the entire transient, and through the opposite opening only during the initial stages. As the pressure differences across the openings change, gas/air mixture is then forced out through the opposite opening. The mixture is expelled through the two side openings throughout the transient. A plot of this scenario is given in Figure 6.5. (As the flow rates through both of the side openings are identical, they appear as a single line on the plot.)

![Figure 6.5 Mass flow rate through four openings](image)

It is observed that, as the direction of flow through the incident opening changes (~20 seconds), an element of numerical instability arises. This is quickly damped to produce a smooth profile.

6.4.3 Vent area

Two ventilation areas have been investigated to examine the effects of the various flows. Plots of outflow through the opening(s) are given in Figure 6.6 and 6.7 for the two sensitivity cases tested with different ventilation areas, and an incident windspeed of 2m/s. The areas chosen are defined as (0.3m x 0.3m =) 0.09m², and (2.5m x 0.3m =) 0.75m², both 0.1m above the ground.

It was found that larger ventilation areas do not produce larger flow rates through them for single openings. At the end of the transient, the mass flow rates and mixture density in both cases are approximately 0.31 kg/s and 2.42 kg/m³ respectively, giving a volumetric flow rate through the opening of 0.128 m³/s. Subsequently, the velocity
of the flow through each opening is calculated as 1.42m/s and 0.17m/s respectively for the 0.09m² and 0.75m² opening areas.

**Figure 6.6** Mass flow rate through single opening of area 0.09m²

**Figure 6.7** Mass flow rate through two openings; two cases with different ventilation areas
This is also true for the double opening scenario, and as expected in this case, the outflow from the opening at the rear of the room is greater than that through the opening facing the incident wind.

Once more a slight fluctuation in results may be observed as the flow direction changes.

6.5 Wind effects

6.5.1 Windspeed

Since the base case validation run was performed assuming no openings, with material being vented via the scrubber unit, the effects of windspeed have not been assessed. To observe these effects, various windspeeds were introduced to otherwise identical cases describing a 550s release and a 650s simulation time (to observe the post-release warming effects).

A 2 m/s wind was introduced to face A, with the 0.09 m\(^2\) opening in the same face. This low windspeed did not appear to have an effect on any results. Hence, 10 m/s and 27 m/s windspeeds were tried; also appearing to have no significant affect on any results. The windspeed thus has no affect on these results which are only for a single opening and therefore do not allow any flow of air through the building.

The same set of windspeeds was used for a building with two opposite openings allowing both ingress and egress to be established. These results are somewhat different. Here, the higher windspeeds produced higher minimum room temperatures due to more air at ambient temperature purging the system of the colder gas/air mixture. Thus concluding that windspeed is influential on the results, provided there are multiple openings (see Table 6.3).

<table>
<thead>
<tr>
<th>No of openings</th>
<th>Windspeed (m/s)</th>
<th>Minimum room temperature (K)</th>
<th>Final room temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>267.716</td>
<td>282.875</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>267.718</td>
<td>282.875</td>
</tr>
<tr>
<td>1</td>
<td>27</td>
<td>267.729</td>
<td>282.869</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>267.708</td>
<td>282.897</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>269.070</td>
<td>283.578</td>
</tr>
<tr>
<td>2</td>
<td>27</td>
<td>272.155</td>
<td>284.054</td>
</tr>
</tbody>
</table>

Table 6.3 Windspeed sensitivity results
6.6  Momentum effects

6.6.1  Low momentum

To investigate the effects of stratification, a variation on the base case has been taken with a low momentum release at a height of 1m. The maximum layer concentration is set at 0.4 kg/kg. This redistributes the gas in the room such that it remains below the layer height (set to the release height), until the concentration within this layer reaches the pre-set maximum. The layer height then increases up to the room height so as to maintain this concentration within the layer. As in the base case, the scrubber unit is employed with no openings.

![Figure 6.8 Low momentum stratification](image)

As can be seen from Figure 6.8 the concentration rises until it reaches 0.4 kg/kg (right hand axis) at which point the layer height increases (maintaining a constant layer concentration) until the room height is attained. At this point the concentration begins to increase once more. Hence the stratification option of the model predicts the correct behaviour.

6.6.2  High momentum

The other extreme is the assumption that a high momentum release will give complete mixing throughout the room. This feature has already been demonstrated in the validation and sensitivity cases presented in Sections 5 and 6.
7. CONCLUSIONS

7.1 Model Features

GRAB-T has been developed to allow the transient simulation of the release of a liquefied gas stored within a building. The release is considered to be a flashing, two-phase release, which initially results in the reduction of room temperature and pressure. This drop in temperature is caused by the vaporisation of the pollutant as it expands on entering the much lower pressure regime of the room.

If any ventilation openings are present, the initial reduction in pressure may be at least partially compensated by air from outside the building being drawn into the room. The rate of air intake is dependent upon a number of parameters including vent size, vent position and number of vents. These parameters also influence the rate at which the pollutant gas/air mixture escapes from the room in different scenarios.

GRAB-T also includes heat transfer effects from the various room surfaces (wall, ceiling and ground), including heat transfer from the storage vessel. The heat transfer works to restore thermal equilibrium to the room contents, and is more noticeable if a simulation time longer that the release duration is modelled. In this case, the temperature of the room contents begins to return towards the original room temperature in the period after the release has stopped.

The formation of a pool is also considered. When the room contents achieve saturation conditions, the liquid pollutant droplets previously suspended in the gas/air mixture ‘rainout’ to form a pool. This pool is either contained in a bund, or is allowed to cover the entire floor area. Once a pool begins to form, it is subject to heat transfer from the ground, and hence will evaporate into the mixture.

A further feature is that of stratification. By setting the release to be of low momentum, the pollutant is redistributed into a layer contained between the ground and the release height. The pollutant concentration within this layer increases to a preset maximum value. When this concentration is reached, it is maintained and the layer height increases until the room height is achieved. As the layer cannot rise any further the concentration is then allowed to increase towards unity.

7.2 Model development

In order to model the features outlined above, mass and enthalpy balances were performed for above and below saturation condition scenarios and for a liquid spill. The conservation of mass equations were based upon three constituent mediums present in the room, i.e. liquid and gas phase pollutant, and air. This allowed rate equations to be developed for the total mixture density ($\rho_t$) and the mass fractions of the two pollutant phases ($c_g$ and $c_l$). Along with the enthalpy ($h$) balance, and an equation describing the rate of change of pressure ($P$), this produced five first order ordinary differential equations which were solved simultaneously.

The solution for $c_g$, $c_l$, $\rho_t$, $P$ and $h$ was obtained via a time-wise integration using a fourth order Runge-Kutta algorithm, with automatic time step control, in an attempt to
maintain solution stability. A solution for temperature is then calculated via a rearranged enthalpy equation.

The model equations have been encoded into the GRAB-T software package using C++ for the high-level solution algorithms, and Visual Basic (version 5) for the low-level user interface.

On the user interface, the user can initialise all relevant parameters, such as the number and area of ventilation openings, windspeed, wind incidence, building geometry (including materials, dimensions and relevant thermo-physical data). Other options include an exponentially decaying release rate, release momentum and stratification.

7.3 Model validation

The model has been validated against test data obtained from tests performed by the Health and Safety Laboratory (HSL). The tests were carried out using a one third linear scale replica of a chlorination room at a water treatment plant. Because of the toxicity of chlorine, Freon-22 was used, and released at various mass flow rates. Temperature and concentration profiles obtained from a series of sensors were used for comparison against results predicted from GRAB-T.

The GRAB-T results are in close agreement with the data produced by the HSL experiments. Temperature drops within the room are underpredicted by GRAB-T by approximately 3K. For the limited HSL data, volumetric concentration predictions are within 1%. In general, the validation results obtained from this version of GRAB-T are in closer agreement with the HSL data than the results obtained from the previous version.

7.4 Model application

A limitation on the GRAB-T model described above is the assumption that the pollutant vaporises completely within the first 2-3m of exiting the pressurised vessel. This is based on the assumption that the jet does not impinge on any obstacles in its path before being vaporised, which is always a possibility.

Another restriction is the assumed regular building geometry. This means that a pseudo-room should be designed if the test room does not already have a rectangular plan view and constant wall height. The dimensions of this pseudo-room should be such that the current room volume and surface area are maintained (an example of this situation is presented in Section 5.2).

Various parameters used in the development of the model are varied from a base case value to observe their influence on model results. In these sensitivity studies, it was found that:

- The time step used in the numerical integration could be increased from the default 0.0025s; however in doing so there is an increased risk of introducing numerical instability to the general solution technique.
- GRAB-T facilitates the modelling of exponentially decaying release rates. The exact nature of the release profile may be determined by specifying a ‘decay time constant’; where the smaller the constant, the quicker the rate of decay.

- Windspeed is only influential when multiple openings are present.

- Flow characteristics through an opening are affected by the location of the face upon which the wind is incident, the number, position and area (defined by the width and height) of other openings.

- Stratification may be modelled by opting for a low momentum release, setting the release height (hence the initial layer height) and the maximum concentration in the layer. This influences the material flowing out of the building, as it is dependent upon the layer height relative to any opening dimensions.

7.5 Uses of model

GRAB-T has the potential to be applied as part of a risk assessment to determine the effects of pollutant containment of a building. This has been documented, using both GRAB [2] and an early version of GRAB-T [3], in a study for HSE [16].

It could also be used to provide the input parameters to the WEDGE dispersion model [4], which assesses the effects of building wakes on dense gas dispersion.
## APPENDIX A

### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{ceiling}}$</td>
<td>Ceiling heat transfer area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$A_{dx}$</td>
<td>Discharge area of opening ‘x’</td>
<td>m$^2$</td>
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<tr>
<td>$A_{\text{ground}}$</td>
<td>Ground heat transfer area</td>
<td>m$^2$</td>
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<tr>
<td>$A_{\text{vessel}}$</td>
<td>Vessel heat transfer area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$A_{\text{wall}}$</td>
<td>Wall heat transfer area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$A_p$</td>
<td>Pool / bund area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$c_a$</td>
<td>Air mass fraction</td>
<td></td>
</tr>
<tr>
<td>$c_g$</td>
<td>Gaseous pollutant mass fraction</td>
<td></td>
</tr>
<tr>
<td>$c_{ga}$</td>
<td>Pollutant gas/air mixture mass fraction</td>
<td></td>
</tr>
<tr>
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<td>Liquid pollutant mass fraction</td>
<td></td>
</tr>
<tr>
<td>$c_m$</td>
<td>Maximum layer concentration</td>
<td>kg/kg</td>
</tr>
<tr>
<td>mass</td>
<td>Concentration by mass</td>
<td>kg/kg</td>
</tr>
<tr>
<td>$c_{\text{vol}}$</td>
<td>concentration by volume</td>
<td>m$^3$/m$^3$</td>
</tr>
<tr>
<td>$C_d$</td>
<td>Discharge coefficient</td>
<td></td>
</tr>
<tr>
<td>$C_{pa}$</td>
<td>Specific heat of air</td>
<td>J/kg/K</td>
</tr>
<tr>
<td>$C_{pc}$</td>
<td>Specific heat of ceiling material</td>
<td>J/kg/K</td>
</tr>
<tr>
<td>$C_{pf}$</td>
<td>Specific heat of floor material</td>
<td>J/kg/K</td>
</tr>
<tr>
<td>$C_{pg}$</td>
<td>Specific heat of gaseous pollutant</td>
<td>J/kg/K</td>
</tr>
<tr>
<td>$C_{pga}$</td>
<td>Specific heat of gaseous pollutant/air mixture</td>
<td>J/kg/K</td>
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<tr>
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<td>Specific heat of liquid pollutant</td>
<td>J/kg/K</td>
</tr>
<tr>
<td>$C_{pw}$</td>
<td>Specific heat of wall material</td>
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<td>-</td>
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<td>$h$</td>
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<td>J/kg</td>
</tr>
<tr>
<td>$h_a(T)$</td>
<td>Enthalpy of air at room temperature</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h_a(T_a)$</td>
<td>Enthalpy of air at ambient temperature</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h_{cv}$</td>
<td>Heat transfer coefficient</td>
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</tr>
<tr>
<td>$h_{\text{eff},c}$</td>
<td>Effective ceiling heat transfer coefficient</td>
<td>W/m$^2$/K</td>
</tr>
<tr>
<td>$h_{\text{eff},g}$</td>
<td>Effective ground heat transfer coefficient</td>
<td>W/m$^2$/K</td>
</tr>
<tr>
<td>$h_{\text{eff},w}$</td>
<td>Effective wall heat transfer coefficient</td>
<td>W/m$^2$/K</td>
</tr>
<tr>
<td>$h_{fg}$</td>
<td>Heat of vaporisation of pollutant</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h_g(T_b)$</td>
<td>Enthalpy of gaseous pollutant at boiling point</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h_g(T_s)$</td>
<td>Enthalpy of gaseous pollutant at storage temperature</td>
<td>J/kg</td>
</tr>
<tr>
<td>$h_l(T_s)$</td>
<td>Enthalpy of liquid pollutant at storage temperature</td>
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<tr>
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<td>Scrubber extraction height</td>
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</tr>
<tr>
<td>$h_o$</td>
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<td>J/kg</td>
</tr>
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<td>$h_{\text{sat}}$</td>
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<td>Height above ground of opening ‘x’</td>
<td>m</td>
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<tr>
<td>$H_r$</td>
<td>Room height</td>
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</tr>
<tr>
<td>$H_x$</td>
<td>Height of opening ‘x’</td>
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<tr>
<td>$k_a$</td>
<td>Thermal conductivity of air</td>
<td>W/m/K</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Thermal conductivity of ceiling material</td>
<td>W/m/K</td>
</tr>
</tbody>
</table>
kg Thermal conductivity of gaseous pollutant $\text{W/m/K}$

$k_f$ Thermal conductivity of floor material $\text{W/m/K}$

$k_{ga}$ Thermal conductivity of gas / air mixture $\text{W/m/K}$

$k_{mt}$ Mass transfer coefficient $\text{m/s}$

$k_w$ Thermal conductivity of wall material $\text{W/m/K}$

$L$ Room Length $\text{m}$

$m_a$ Molecular mass of air $\text{kg/mol}$

$m_g$ Molecular mass of pollutant $\text{kg/mol}$

$m_{ga}$ Average molecular mass of gaseous mixture $\text{kg/mol}$

$M$ Pollutant release rate $\text{kg/s}$

$M_e$ Evaporation rate $\text{kg/s}$

$M_{in}$ Ingress rate of fresh air into room $\text{kg/s}$

$M_{out_a}$ Discharge rate of air through openings $\text{kg/s}$

$M_{out_p}$ Discharge rate of pollutant through openings $\text{kg/s}$

$M_{sc}$ Volumetric extraction rate through scrubber $\text{m}^3/\text{s}$

$M_{sc_a}$ Discharge rate of air through the scrubber $\text{kg/s}$

$M_{sc_p}$ Discharge rate of pollutant through scrubber $\text{kg/s}$

$M_a$ Mass of air $\text{kg}$

$M_g$ Mass of gaseous pollutant $\text{kg}$

$M_{ga}$ Mass of pollutant gas/air mixture $\text{kg}$

$M_l$ Mass of liquid pollutant $\text{kg}$

$M_t$ Mass of pollutant/air mixture $\text{kg}$

$Nu$ Nusselt number -

$p_p$ Partial pressure of liquid pollutant $\text{N/m}^2$

$P$ Pressure of room contents $\text{N/m}^2$

$P_a$ Ambient pressure $\text{N/m}^2$

$P_b$ Pressure of building surface $\text{N/m}^2$

$Pr$ Prandtl number -

$P_{sat}$ Saturation pressure $\text{N/m}^2$

$P_w$ Pressure due to wind effect $\text{N/m}^2$

$\dot{q}$ Total heat transfer rate $\text{J/s}$

$\dot{q}_{cond}$ Rate of heat transfer due to conduction $\text{J/s}$

$\dot{q}_{conv}$ Rate of heat transfer due to convection $\text{J/s}$

$\dot{q}_{ceiling}$ Rate of heat transfer from ceiling $\text{J/s}$

$\dot{q}_{ground}$ Rate of heat transfer from ground $\text{J/s}$

$\dot{q}_{vessel}$ Rate of heat transfer from storage vessel $\text{J/s}$

$\dot{q}_{wall}$ Rate of heat transfer from walls $\text{J/s}$

$Re$ Reynolds number -

$R$ Universal gas constant $\text{J/mol/K}$

$Sc$ Schmidt number -

$Sh$ Sherwood number -

$t$ Time $\text{s}$

$t_d$ Release duration $\text{s}$

$T$ Temperature of room contents $\text{K}$
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<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<td>$T_b$</td>
<td>Pollutant normal boiling point temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Storage temperature</td>
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<td>Reference temperature</td>
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<td>Temperature of inner wall surface</td>
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<td>$u$</td>
<td>Velocity of air in test room</td>
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<td>Flow velocity through openings</td>
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<td>$x$</td>
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<table>
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<td>Heat transfer coefficient for ceiling</td>
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<td>Heat transfer coefficient for storage vessel</td>
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<td>$\beta_{wall}$</td>
<td>Heat transfer coefficient for walls</td>
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<tr>
<td>$\chi$</td>
<td>Volumetric concentration of gas in gas/air mixture</td>
<td>-</td>
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<tr>
<td>$\delta_c$</td>
<td>Ceiling thickness</td>
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<td>Floor thickness</td>
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<td>$\delta_w$</td>
<td>Wall thickness</td>
<td>m</td>
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<td>Viscosity of air</td>
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<td>Viscosity of pollutant gas</td>
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<td>Viscosity of pollutant gas / air mixture</td>
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<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_a(T_a)$</td>
<td>Density of air at ambient temperature</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{ga}$</td>
<td>Density of pollutant gas/air mixture</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>Density of liquid pollutant</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_t$</td>
<td>Density of pollutant liquid/pollutant gas/air mixture</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>Density of wall material</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Aspect ratio</td>
<td>-</td>
</tr>
<tr>
<td>$\tau_d$</td>
<td>Decay constant for pollutant release</td>
<td>s</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Characteristic length</td>
<td>m</td>
</tr>
</tbody>
</table>
8. REFERENCES


9. British Standard 6399


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