

## CHAPTER 4: THERMODYNAMICS OF AIR-VAPOUR MIXTURES

### MODULE A: INTRODUCTION TO MODELLING

#### MODULE OBJECTIVES:

At the end of this module, you will be able to describe:

1. The three types of modelling required for nuclear stations
2. The differences between safety code, training simulator code and engineering code

## **1.0 TYPES OF MODELLING CODE**

In the discussion of mathematical modelling of containment that follows, I will often say that certain approximations are allowable for simple simulations, and that safety analysis require more elaborate calculations. Must therefore understand requirements for different types of simulation.

### **1.1 Simulation for engineering (design and post-construction design changes):**

- **Purpose:** initially confirm system is within design parameters
- **Limited scope** - only parts of plant, few scenarios - and detail;
- **Simplified representation** of overall plant or of a system to design feedback loops

### **1.2 Simulation for safety analysis:**

- **Purpose:** confirm that the nuclear station's design and operation during normal and emergency conditions will not lead to unacceptable excursions in physical parameters leading to equipment failure and risk to the public. Necessary to license plant design and operating mode.
- **Scope:** all situations that may cause unsafe conditions. All systems that may cause such conditions.
- **Very complex representation** of components and physical processes that could lead to public risk
- **Multiple independent programs** for different systems, e.g. radionuclides inside containment, radionuclide dispersal outside containment, hydrogen, peak pressure, seismic qualification.

### 1.3 Simulation for training licensed operating staff

- **Purpose:** ensure that the licensed staff at the nuclear station respond correctly to normal and abnormal operating conditions
- **Scope:** most systems operated from the control room or secondary control area and related to safe and economical operation of plant.
- One integrated model for entire plant, plus elaborate graphical user interface and panels
- Simpler models of components and physical processes, but far more systems and components, including most annunciations and alarms

### 2.0 Differences between training simulator and safety code

- **Why not just use the same code for both?**
- **Time constraint:**
  - Simulator runs in real time, model for entire plant must run in 200-250 ms (milliseconds), on several CPUs in parallel, which leaves maybe 10-20 ms for containment
  - Simulator containment models simplify containment to ~7 rooms with about the same number of interconnecting flows
  - Safety code can run for hours to describe an event taking only seconds.
  - Safety code may describe containment as ~60 control volumes
  - Fixed timestep for training simulator, variable and often very small timestep for safety code.
  - Different mathematical approaches: more abstract for safety code, partial differential equations, possibly 3-dimensional, matrix solution for flow network.

- **Conservative versus best-estimate assumptions**
  - **Safety code underestimates/overestimates parameters for conservatism (make the assumption that leads to the worst outcome, e.g. the highest pressure)**
  - **May assume components do not all function as designed, or response is delayed.**
  - **For example, may assume not all the ACUs are functioning, or that containment isolation is delayed.**
- **Simulator models must reproduce plant response where known - no conservative assumptions**

**Different areas where detailed modelling is required:**

- **Safety code focuses on internal parameters leading to failure, and only those measured quantities leading to safety system initiation, e.g. loads on walls, measured pressure.**
- **Simulator code focuses on what can be seen in the control room that leads operators to make decisions, e.g. rising dewpoint, pattern of beetle alarms.**
- **Simulator may require ad hoc code in training simulator to reproduce observed effects that cannot be modelled, e.g. non-uniform vapour distribution within a room.**
- **Fixed versus variable interactive scenarios:**
  - **For safety code, author controls the inputs, decides when equipment activates, etc.**
  - **For simulators, the trainee operator may do anything, may make a mistake and force code to simulate a situation unforeseen by author, e.g. reverse flow through a heat exchanger. Instructor may also choose arbitrary combination of device failures.**

- **Design basis accident scenarios versus normal plant operation**
  - **Safety code not required to replicate transition in containment response during normal unit startup/shutdown; start from a different set of inputs, possibly with a different selection of correlations, for each case.**
  - **Simulator code must simulate subtle non-accident phenomena, e.g. very small changes in room pressure and flows as heat-generating equipment is switched on.**
  - **Simulator code does not simulate severe accidents**
  - **Safety code only required to simulate events near the envelope of safe operation.**

## CHAPTER 4: THERMODYNAMICS OF AIR-VAPOUR MIXTURES

### MODULE B: CLOSED VESSEL MODEL - PART 1

#### MODULE OBJECTIVES:

At the end of this module, you will be able to describe:

1. The specifications for the simplest possible containment model
2. The equation for the rate of change of enthalpy in an air-vapour mixture in a closed vessel
3. The derivation for this equation from conservation of energy

## 1.0 CLOSED VESSEL MODEL - PART 1

### 1.1 Overview

- Closed vessel model is suitable for use on training simulators, too simple for safety analysis
  - Model is generic and can be used for any closed vessel with separated liquid/vapour phases, e.g. condenser, reheater
  - Simple enough to solve analytically and gain insight into containment thermodynamics
- Air and vapour in thermodynamic equilibrium with each other in a closed vessel (control volume) with liquid in the bottom; vessel's volume may vary with time
- Assume presence of air does not affect vapour thermodynamic properties
- Liquid phase is separated from vapour phase in bottom of vessel; this is not a 2-phase model
- Liquid not necessarily in thermodynamic equilibrium with air/vapour mixture
- Flashing superheated break inflows to gas phase; also air and vapour in/outflows
- Liquid may flow in/out of liquid phase
- All four types of phase changes are modelled, interphase heat transfer, heat loss to exterior
- Significant omissions:
  - bubbling of vapour through liquid,
  - the formation of aerosol droplets
  - kinetic energy associated with fluid velocity,
  - imperfect mixing (nonuniform temperature or vapour distribution)
  - buoyancy effects (hot gases rising)
  - fluid inertia

## 1.2 Formulation in terms of vapour enthalpy

- Advanced models are formulated in terms of internal energy
- Closed vessel model equation for enthalpy is derived from internal energy conservation equation and is equivalent
- Mass Conservation

The mass conservation equations for each phase are as follows, using the conventions defined in the Symbol List in the appendices and the diagram:

### Steam Phase

$$dM_s/dt = W_{si} - W_{so} - W_{con} + W_{evap} \quad (2.1)$$

### Liquid Phase

$$dM_w/dt = W_{wl} - W_{wo} + W_{con} - W_{evap} \quad (2.2)$$

### Air Phase

$$dM_a/dt = W_{al} - W_{ao} \quad (2.3)$$



- **Energy Conservation**

The energy conservation equation may be expressed in words by:

<b>Rate of Rise of Internal Energy</b>	<b>=</b>	<b>Net Rate of Internal Energy Inflow</b>	<b>+</b>	<b>Net Work Done On System</b>	<b>+</b>	<b>Net Heat Inflow Into System</b>
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<b>Term 1</b>	<b>Term 2</b>	<b>Term 3</b>	<b>Term 4</b>
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For the steam phase each term is given by:

Term 1:  $d(M_s u_s)/dt$

Term 2:  $W_{si} u_{si} - W_{so} u_s - W_{con} u_{satl} + W_{evap} u_{satv}$

Term 3:  $W_{si} P_{tot} v_s - W_{so} P_{tot} v_s - W_{con} P_{tot} v_s + W_{evap} P_{tot} v_w$

Term 4:  $Q_s$  (2.4)

The subscripts 'satv' and 'satl' refer to saturated vapour and saturated liquid, respectively.

- Term 2 represents the internal energy flow
- Term 3 represents the flow energy and compression work of the steam against the water upon expansion.

- The ' $Pv_s$ ' terms represent the work is done pushing gas in and out of the control volume
- Further mathematical manipulations:

Substitute the identity  $h = u + Pv$ , where  $h$  is the specific enthalpy, equation (4) for the gas phase may be rewritten as:

$$d(M_s h_s)/dt = W_{si} h_{si} - W_{so} h_s - W_{con} h_{satl} + W_{evap} h_{satv} - P_{tot} d(M_s v_s)/dt + Q_s \quad (2.6)$$

On further simplification by eliminating  $dm_s/dt$  using Equation (2.4)

- Equation (6) can be written in a form suitable for computation, in a form where the unknown  $h_s$  is updated on each iteration of the code:

$$h_s = h_s' + \Delta t [W_{si}(h_{si} - h_s) + W_{ai}(h_{ai} - h_a) - W_{con}(h_{satl} - h_s) + W_{evap}(h_{satv} - h_s) + M_s v_s dP_{tot}/dt + Q_s] / M' \quad (2.7)$$

The superscript  $'$  denotes a value from the previous iteration.

- Practical hint: Be careful about the consistent use of values from the previous iteration during numerical solution of equation (2.7) whenever mass inflows per iteration are significant compared to the mass currently in the vessel.

For example, for the liquid phase when draining a vessel completely, and for the gas phase when

the gas is squeezed into a bubble near the top of the tank by rising liquid.

- Steam and air are in equilibrium (same temperature) at all times, therefore don't need separate equation for air enthalpy update; air included in (2.7) as

$$M' = M_s' + M_a' (C_{ps} / C_{pa}) \quad (2.8)$$

Here  $C_{pa}$  refers to the specific heat capacity of air with units kJ/(kg-C). The correction factor to the mass of steam accounts for the thermal capacity of the air.

For containment, vapour fraction may be negligible (dewpoint <-30C) or it may be >95%; equation (2.8) is valid in entire range.

- Liquid phase equation is similar to that for the steam phase, but note the changes of sign for the evaporation and condensation terms:

$$h_w = h_w' + \Delta t [W_{wi}(h_{wi} - h_w) + W_{con}(h_{satl} - h_w) - W_{evap}(h_{satv} - h_w) + M_w v_w dP_{tot}/dt + Q_w] / M_w' \quad (2.9)$$

- To update the variables defining the contents of the closed vessel, equations (2.7) and (2.9) and the mass equations (2.1)-(2.3) are clearly not sufficient.
- Auxiliary equations defining volumes, pressures, in and outflows for each phase, heat transfers and temperatures will be discussed later

### 1.3 Derivation of enthalpy equation from internal energy equation

- To illustrate the method for the student without complicated algebra, will omit the condensation and evaporation terms and present proof only for superheated steam-air mixture.

If kinetic energy and phase changes are omitted, the fundamental energy conservation formula for a node containing air and vapour is

$$dU/dt = w_{vi}h_{vi} + w_{ai}h_{ai} - w_{ao}h_{ao} - w_{vo}h_{vo} + Q_v - (P_v + P_a)dV/dt. \quad (3.1)$$

Since

$$U = M_v u_v + M_a u_a,$$

$dU/dt$  may also be written as

$$dU/dt = M_v du_v/dt + M_a du_a/dt + w_a u_a + w_v u_v, \quad (3.2)$$

where  $w_a = w_{ai} - w_{ao}$ ,  $w_v = w_{vi} - w_{vo}$ .

Because  $h-u = PV/M$  (by definition), the following equation is true for both air and vapour:

$$PdV/dt = -VdP/dt + (h-u)dM/dt + M (dh/dt-du/dt). \quad (3.3)$$

- After equation (3.1) and (3.2) are equated to each other, and the identity for  $PdV/dt$  is substituted for vapour and air, an expression is obtained from which the internal energy has been eliminated:

$$(M_a dh_a/dt + M_v dh_v/dt) = w_{vi}(h_{vi}-h_v) + w_{ai}(h_{ai}-h_a) + Q_v + V (dP_a/dt + dP_v/dt)$$

If the ratio  $(dh_a/dt)/(dh_v/dt)$  is approximated by a constant  $a$ , then  $dh_a/dt$  may also be eliminated:

$$dh_v/dt = [w_{vi}(h_{vi}-h_v) + w_{ai}(h_{ai}-h_a) + Q_v + V dP_{tot}/dt] / (aM_a + M_v). \quad (3.4)$$

- We now examine the ratio of the derivatives more closely. Since air is a perfect gas within our scope of simulation,  $h_a = C_{pa} T_k$ , where  $T_k$  is temperature in Kelvins, it follows that

$$dh_a/dt = C_{pa} dT/dt.$$

For the vapour, the derivative may be approximated by  $C_{pv} dT/dt$ .

Note that  $C_{pv}$  is very far from being a constant. It depends on both density and temperature, and varies from 1.66 to 1.85 in the range of densities and temperatures used for containment.

Also,  $dh_v/dt$  will depend somewhat on the rate of change of vapour density, but not at containment densities.

- The final result with this approximation is

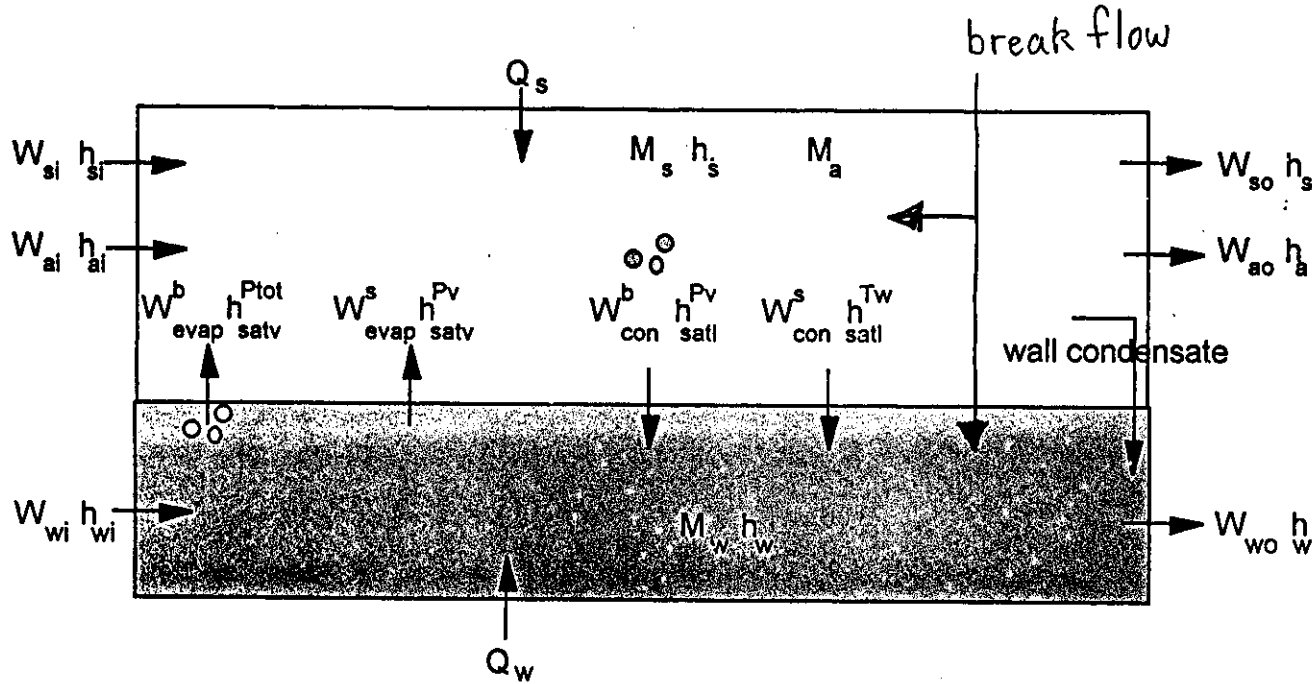
$$dh_v/dt = [w_{vi}(h_{vi}-h_v) + w_{ai}(h_{ai}-h_a) + Q_v + VdP_{tot}/dt] / (C_{pa}M_a/C_{pv} + M_v). \quad (3.5)$$

which is the same as equation (2.7) with no phase changes..

- The physical meaning of the formula can be understood as follows. The quantity in the square brackets is the enthalpy change of the gas mixture. Part of this enthalpy is given to the air, the rest to the vapour.
- To ensure that both gases end up at the same temperature, a fraction inversely proportional its heat capacity must be given to the vapour. This fraction is  $C_{pv}M_v/(C_{pa}M_a + C_{pv}M_v)$
- If an equation for the air enthalpy were ever written, it would mirror (3.5):

$$dh_a/dt = [w_{vi}(h_{vi}-h_v) + w_{ai}(h_{ai}-h_a) + Q_v + VdP_{tot}/dt] / (M_a + M_vC_{pv}/C_{pa}). \quad (3.6)$$

CLOSED VESSEL MODEL



$W_{\text{evap}}^b h_{\text{satv}}^{\text{Ptot}}$  enthalpy carried by flashing of liquid at surface

$W_{\text{evap}}^s h_{\text{satv}}^{\text{Pv}}$  enthalpy carried by evaporation from liquid surface

$W_{\text{con}}^s h_{\text{satl}}^{\text{Tw}}$  enthalpy carried by condensation on liquid surface

$W_{\text{con}}^b h_{\text{satl}}^{\text{Pv}}$  enthalpy carried by rainout (bulk condensation)

## CHAPTER 4: THERMODYNAMICS OF AIR-VAPOUR MIXTURES

### MODULE C: PERFECT GAS IN A CLOSED VESSEL

#### MODULE OBJECTIVES:

At the end of this module, you will be able to describe:

1. Simple formulas for the temperature and pressure change of a perfect gas in a control volume when mass or energy flow in or out
2. Examples of these formulas applied to containment situations



## BEHAVIOUR OF A PERFECT GAS IN A CONTROL VOLUME

### 1.1 Introduction

- Before proceeding with containment modelling it is very useful to understand very thoroughly what happens to a perfect gas in a control volume when mass leaves, mass enters, the volume changes, or heat is transferred.
- Textbooks of thermodynamics rarely consider the first two scenarios, which are critical for our modelling work. Focus is on getting an expanding gas to do work by enlarging the control volume or pushing on turbine blades. Here the control volume is usually fixed.
- The formulas developed below cannot be applied directly to mixtures of gases. However, they can be used to estimate containment responses in many situations where one gas predominates.
- In any scenario, the ideal gas law implies that

$$dP/P = dT/T_k + dM/M$$

which is very useful for back-of-the-envelope estimates, if you remember to use absolute temperature (subscript k), not Centigrade.

- For an ideal monatomic gas,  $C_p/C_v = 5/3$ .
- For any perfect gas,  $C_v + R = C_p$ .
- For water vapour and air, only the second relation is true, and  $C_p/C_v = 1.33$  (vapour) or 1.40 (air).  
N.B. This is for vapour at the low temperature and density characteristic of containment.

- For an ideal gas, the enthalpy  $h$  and the internal energy  $u$  are given by:

$$h = C_p T_k \text{ and } u = C_v T_k$$

## 1.2 Mass leaves the control volume

- Mass leaves a fixed volume;
- no heat transfer;
- ignore kinetic energy contribution to energy carried by flow;
- assume the system undergoes reversible (quasi-static) change of state;
- flow rate is however not assumed to be constant.

- Equation (3.4)

$$dh_v/dt = [w_{vi}(h_{vi}-h_v) + w_{ai}(h_{ai}-h_a) + Q_v + VdP_{tot}/dt] / (C_{pa}M_a/C_{pv} + M_v) \quad (3.4)$$

then reduces to

$$dh/dt = (VdP/dt)/M.$$

Using  $dP/dt = RT_k d\rho/dt + \rho R dT/dt$  and  $T_k = h/C_p$ , one gets

$$(1-R/C_p)(1/T_k)dT/dt = R/C_p dM/dt,$$

hence

$$T/T_0 = (M/M_0)^{R/C_v} \quad (4.1)$$

where the subscript  $T_0$  indicates the initial state of the system.

Since the perfect gas law implies

$$MT/(M_0 T_0) = P/P_0,$$

it follows that

$$P/P_0 = (T/T_0)^{C_p/R} = (M/M_0)^{C_p/C_v}. \quad (4.2)$$

Equation (4.2) can also be written in differential form:

$$dP/P = (C_p/R)dT/T = (C_p/C_v)dM/M. \quad (4.3)$$

**Example:** Pressure equalization between rooms causes a temperature drop

Here is an example taken from the earliest stages of containment response during a loss of coolant accident (LOCA) at PNGSA, when the steam from the break has just started increasing pressure in a room. Normally as the combined air and steam pressure rises within a room, a bursting disk or panel will open and depressurize the room into a neighbouring room. In the example, boiler room pressure has risen enough to burst the panel connecting it to the pressure relief duct. The duct and boiler room have approximately equal volumes, so the final pressure of the two connected volumes is the approximately the average of the two initial pressures:

When the blowout panels open at 15 kPa(d) to equalize pressure at 107 kPa(a) between the boiler room at 115 kPa(a) and the duct at 100 kPa(a), boiler room temperature falls by

$$T/T_0 = (107/115)^{3/1} = .98$$

The resulting drop in temperature from 37C to 31C typically induces condensation even if the steam-air mixture was previously superheated. Equation (4.2) is therefore not appropriate here, later we will do a more exact treatment of the problem of condensation induced by gas leaving a control volume.

Moreover, the mole fraction of vapour is about 10%, since most of the 15% pressure increase was due to the steam partial pressure. Therefore, equation (4.2) would in any case have been only approximate, because it does not apply to a mixture of gases.

### 1.3 Mass enters the control volume

- Mass enters a fixed volume.
- No heat transfer (adiabatic).
- Ignore the kinetic energy contribution to energy carried by flow
- System undergoes a reversible (quasi-static) change of state;
- Inflow rate need not be constant, but incoming enthalpy is constant at  $h_{in}$ .
- You might think that equation (4.2) could be applied here with some change of sign.
- However, the result in this scenario is quite different because the enthalpy carried by the flow was time-varying in the earlier scenario, whereas here the flow carries a constant enthalpy.
- Now equation (3.4) becomes

$$dh/dt = (dM/dt) (h_{in} - h)/M + V(dP/dt)/M$$

Substituting as before for  $dP/dt$  gives

$$(1 - R/C_p)dh/dt = dM/dt ((R/C_p - 1)h + h_{in})/M$$

This equation becomes simpler if  $h' = (1 - R/C_p)h - h_{in}$  is substituted:

$$(1/h')dh'/dt = -(1/M)dM/dt. \quad \text{Hence}$$

$$h'/h'_0 = M/M_0, \text{ or}$$

$$(C_v T_0 - C_p T)/(C_v T - C_p T_{in}) = M/M_0 \quad (4.4)$$

- Multiplying both sides of B(4) by  $T/T$  gives

$$(C_v/C_p - T/T_0)/(C_v/C_p - T_{in}/T) = P/P_0. \quad (4.5)$$

- In differential form, these equations are

$$dP/P = (dT/T)/[1 - (T/T_{in})(C_v/C_p)] = [(T/T_{in})(C_v/C_p)]dM/M. \quad (4.6)$$

**Example:** vacuum building temperature rise before dousing.

During a large steam line break, a mixture of air and steam bursts through into the pressure relief duct, causing the valves between the relief duct and the vacuum building to open at around 105 kPa(a). When this happens, most of the gas in the duct will still be air, not steam, so equation (4.6) will have some validity.

If this air at 27 C then enters the vacuum building at 10 C and raises its pressure from 10 to 60 kPa(a) (when dousing begins and the pressure increase stops), the process can hardly be quasi-static if all the PRV's open at once, and very likely the perfect mixing does not occur either. Nonetheless, (4.5) is used to estimate the resulting temperature increase, assuming the gas is mostly air, and assuming the process is fast enough to be adiabatic (no heat loss to walls):

$$(C_v/C_p - T/T_0)/(C_v/C_p - T_{in}/T) = P/P_0 \quad (4.5)$$

$$(.713 - 300/283)/(.713 - 300/T) = 60/10$$

$$T = 116 \text{ deg C}$$

Much more complex safety analysis code shows temperature peaking at 140 degrees just before dousing starts during the main steam line break . Omitting the kinetic energy term is probably the main reason for the underestimate by equation (4.6).

#### 4.5 Quasi-static volume change.

- The control volume for the gas changes, typically as a result of rising or falling water level in the sumps.

Now equation (3.4) becomes

$$dh/dt = V(dP/dt)/M$$

Taking the derivative of the ideal gas law gives

$$VdP/dt + PdV/dt = (MR/C_p)dh/dt$$

and using the first equation to eliminate dh/dt leads

$$(1/P)dP/dt = -(C_p/C_v)(1/V)dV/dt$$

which is integrated to get

$$P/P_0 = (V/V_0)^{-C_p/C_v}, \quad T/T_0 = (V/V_0)^{-R/C_v} \quad (4.7)$$

**Example: Upper vacuum chamber volume inferred from pressure**

In the upper vacuum chamber, upper chamber pressure is known to increase by a factor of 1.8 at the start of dousing as a result of rising water level. By what factor is the volume reduced at the start of dousing?

The volume must have been reduced by rising water level by a factor of  $1.8^{-.75} = .64$ , not by a factor of  $V/V_0 = 1/1.8 = .556$ , to reproduce this observed result. The difference is due to compression heating.

**4.6 Heat transfer**

- With a variable heat input  $Q$ , equation (3.5) becomes

$$dh/dt = (Q - VdP/dt)/M$$

and  $T - T_0 = \int Qdt/(C_v M)$ , so that (4.8)

$$V(P - P_0) = (R/C_v) \int Qdt \quad (4.9)$$

Equation (4.9) was obtained by substituting  $P\Delta V = MR\Delta T$ .

**Example: loss of air conditioners during full power operation soon causes buttonup**

The air coolers normally remove 740 kW from the 30,000 m<sup>3</sup> boiler room when the unit is at full power. If they fail, and other heat transfers and mass transfers to the boiler room remain unchanged, pressure rises at a rate  $(.3/.7)(740/30,000)$  kPa/s = .01 kPa/s. It will reach the boxup(buttonup) setpoint within minutes.



#### 4.7 Importance of the work term

- It is sometimes tempting to omit the term proportional to  $dP/dt$  from (4.3), the so-called work term. In practice, especially when working in real time with a fixed time step  $\Delta t$ , this derivative often causes numerical problems.
- In trying to eliminate instability, you will be underestimating transient responses by about 33% and you will not be conserving energy during transients.
- If you omit this derivative, there will be no temperature change if mass flows out of the control volume, if the volume changes, or if mass at the same temperature as the node flows into the node. This statement may be verified by repeating derivations 4.3-4.4 without the pressure derivative.
- As a result, the pressure change due to mass transfer will be underestimated by ~33%
  - If there is no temperature change,  $dP/P = dM/M$  instead of (4.3) or (4.6).
  - The pressure change due to volume change is then  $dP/P = dV/V$  instead of (4.7).
- Also, the temperature change due to heat transfer without mass change will be  $dT = dQ/(C_p M)$  instead of  $dQ/(C_v M)$ , i.e. too small by 33%.
- The pressure derivative term in equation (3.4) is sometimes called the work term.
  - Since it is non-zero even in situations where no work is being done by or on the system, in other words when nothing but heat energy is being added, when no mass is entering or leaving the system and the volume is fixed, this nomenclature is highly misleading.

- The volume derivative term  $dV/dt$  in (3.1) truly represents external work done by/on the system due to volume changes.
- However, it does not represent all the external work.
- When mass leaves the system, it is being pushed out; the remaining gas does work to expel it. Similarly, when gas enters the system, it does work compressing the gas already in the control volume.
- To account for this work, we write (3.1) and (3.4) so that the flows carry enthalpy, not internal energy.
- If the work term is omitted from (3.3), the response to mass in/out flows is the same as if the mass flows carried energy  $u$  instead of enthalpy  $h$ . This statement may be verified as follows:

If we replace  $h$  by  $u$  in (3.1) and omit terms unrelated to mass flows:

$$dU/dt = u_{in} w_{in} - u w_{out} \quad (4.10)$$

and then substitute

$$du/dt = d/dt (U/M) = (1/M)dU/dt - (U/M^2)(w_{in} - w_{out})$$

the result is

$$du/dt = w_{in} (u_{in} - u)/M \quad (4.11)$$

which implies no temperature change during mass outflow, and no temperature change when mass flows in at the same temperature as the mass already there. These are the same unphysical responses seen when the work term is dropped from (3.3).

- If several thermodynamic nodes are in series, and the work term is omitted in some nodes but not in others, then energy is not conserved in the system.
- One node sends energy  $h$  into another node, whose temperature and pressure change as if it had received energy  $u$ . It is as if energy were lost in the link. For example, if break flow leaves the RCS with a certain enthalpy, and the work term is omitted in containment, some of the break energy is lost.
- The problem with the pressure derivative can be eliminated by using the total internal energy as the fundamental variable rather than vapour specific enthalpy. No pressure derivatives appear in equation (3.1). The volume derivative does not present a problem because there is rarely feedback; pressure and flow do not cause volume to change.

## CHAPTER 4: THERMODYNAMICS OF AIR-VAPOUR MIXTURES

### MODULE D: STEAM THERMODYNAMICS

#### MODULE OBJECTIVES:

At the end of this module, you will be able to describe:

1. The validity of approximating of superheated steam as a perfect gas
2. How to relate steam table enthalpies to the perfect gas approximation
3. An approximate expression for the saturation vapour pressure
4. An approximate expression for the amount condensed in a control volume with saturated steam
5. How to use steam tables to estimate the amount condensed when vapour flows in or out of a control volume

## 1.0 Perfect gas approximation for superheated and saturated steam

- Textbooks state that you can't use the perfect gas approximation when intermolecular forces are important, i.e. in a gas just about to condense.
- In reality, for the low densities and temperatures typical of containment (usually  $T < 150$ ), steam can be approximated as a perfect gas even on the saturation line
- Error is in fact only a few per cent at  $T \sim 100\text{C}$
- For quantities related to phase changes, such as the latent heat, dewpoint and saturation vapour pressure, simple analytical expressions can also be found that are equally good approximations
- Can be used to get analytical expressions for the way a saturated mixture responds to changes in the control volume.
- Steam tables list the enthalpy and internal energy of vapour relative to liquid water at the triple point, zero Centigrade. In the module 4C, we worked with enthalpies relative to a perfect gas at zero Kelvin. So you will have to shift your perspective and be careful when using the two approaches together.
- If you look at the tables for superheated or saturated steam, you will find that steam enthalpy and energy resemble perfect gas enthalpy and energy with the addition of a constant:

$$u_v \cong u_{v0} + C_{vv}T$$

$$h_v \cong h_{v0} + C_{pv}T$$

where  $u_{v0}$  is the latent heat of vaporization at constant volume at zero C,  $h_{v0}$  is the latent heat of vaporization at constant pressure at zero C, and T is in degrees C. (Values for  $C_{vv}$  and  $C_{pv}$  are listed in the Appendix) The linear approximation is very good up to about 100C, then nonlinearity rapidly becomes noticeable.

- Note that in heavy water steam tables, the enthalpy and internal energy of vapour are quoted relative to liquid heavy water at 3.6 C, which is the freezing point.
- For the pressure of superheated or saturated steam, it is often unnecessary to use steam tables when the perfect gas law holds so well:

$$P_v = R_v \rho_v T_k$$

- Here  $T_k$  must be measured in degrees K.
- The gas constant  $R_v$  varies between .461 and .451 as the temperature of the saturated mixture increases from 10 to 120C, with most of the variation occurring at  $T > 70C$ .

## 2.0 Condensation

- Occurs when the vapour molecules have too little energy to prevent the attractive forces between vapour molecules from causing the molecules to clump together in liquid droplets.
- This condition defines the saturation line separating superheated vapour from the mixed state.
- The condition may be stated mathematically in several equivalent ways, as the vapour pressure or density being too high for the given vapour enthalpy, temperature, or internal energy:

$$P_v > P_{sat}(h_v)$$

$$P_v > P_{sat}(u_v)$$

$$P_v > P_{sat}(T)$$

$$\rho_v > \rho_{\text{satv}}(h_v)$$

$$\rho_v > \rho_{\text{satv}}(u_v)$$

$$\rho_v > \rho_{\text{satv}}(T)$$

$$h_v < h_{\text{satv}}(P_v)$$

$$u_v < u_{\text{satv}}(P_v)$$

$$T < T_{\text{sat}}(P_v)$$

$$h_v < h_{\text{satv}}(\rho_v)$$

$$u_v < u_{\text{satv}}(\rho_v)$$

$$T < T_{\text{sat}}(\rho_v)$$

- The presence of air makes no difference to these saturation conditions.
- Which of these conditions we utilize to check for condensation depends on the details of the algorithms used for the condensing air-vapour mixture.

### 3. Steam Tables

- Saturation steam tables in engineering manuals usually have temperature or pressure as the independent variable given at equal intervals.
- It is also possible to create custom tables with interpolation coefficients having any of the above quantities (internal energy, enthalpy, density) as the independent variable.
- Containment requires tables with unequal intervals because of exponential behaviour of saturation pressure; equal-interval tables would get too large.

- Usually computations of containment response will require tables with enthalpy or internal energy as the independent variable. You will probably want to generate your own.
- More sophisticated containment calculations will also call for derivatives of thermodynamic quantities to help with table-lookup searches and for the partial derivatives used in the matrix solutions. You will also need tables of these partial derivatives.
- Custom tables may be generated from the published sets of virial coefficients, or they may be generated less laboriously from commercial packages.
- If you look at any published set of steam tables, e.g. ASME, you will see the authors simply wrote an expression for the Helmholtz free energy in terms of 6-10 virial (fitting) coefficients, and obtained all the thermodynamic properties from the partial derivatives of the Helmholtz free energy.

#### 4. Saturation line approximations

- The saturation temperature of an air-vapour mixture is sometimes referred to as the dewpoint, since condensation occurs on any surface colder than  $T_{sat}$ .
- Note that dewpoints below the freezing point are physically possible, since the vapour pressure of liquid water at zero Centigrade is not zero.
- For a well-dried room in containment, dewpoints of -25 C are quite achievable despite constant vapour leakage from valve stems, etc.
- Steam tables are not essential for saturation line calculations, if an error of a few per cent is considered acceptable at higher temperatures. The saturation vapour pressure may be approximated very well by



$$P_{\text{satv}}(T_k) = 1.08 \times 10^8 \exp(-5173/T_k) \quad \text{kPa} \quad \text{where } T_k \text{ is the absolute (Kelvin) temperature}$$

which can be combined with the perfect gas law for vapour to give

$$\rho_{\text{satv}}(T_k) = (2.35 \times 10^8 / T_k) \exp(-5173/T_k) \quad \text{kg/m}^3$$

- A table lookup with linear interpolation uses much less execution time than evaluating these exponential expressions or their inverses.
- These relations for vapour pressure and density are not just empirically derived. They follow directly from the Clausius-Clapeyron (or Clapeyron) expression for vapour pressure:

$$(dP_v/dT)_{\text{sat}} = h_{fg} / [T_{\text{sat}} (1/\rho_{\text{satv}} - 1/\rho_{\text{satl}})].$$

If we assume that  $\rho_{\text{satl}} \gg \rho_{\text{satv}}$

and Boyle's law is applied to eliminate  $\rho_{\text{satv}}$  in favour of  $P_{\text{satv}}$ , the Clapeyron equation leads to

$$dP_{\text{satv}}/dT_{\text{sat}} = h_{fg} / (P_{\text{satv}} R_v T_{\text{sat}})$$

which may be integrated, if  $h_{fg}$  is constant, to get

$$P_{\text{satv}} = P_0 \exp(-h_{fg} / (R_v T_{\text{sat}})),$$

- Since  $h_{fg}$  is not constant (it decreases by about 2.6 kJ per degree), one would not expect this expression to be exact. The curve-fitting constant 5173 is however the same as  $h_{fg}/R_v$  if  $h_{fg}$  is evaluated at 51C, about midway in the range of validity of the approximation.

- The expression for  $\rho_{\text{satv}}(T_k)$  in terms of  $T_{\text{sat}}$  leads to a useful expression for

$$(dT_{\text{satv}}/d\rho_{\text{satv}}) = R_v T_{\text{sat}}^2 / (\rho_{\text{satv}} u_{\text{fg}})$$

the derivative along the saturation line, which we will use later in this chapter.

## 5.0 Mixed state of vapour and condensate

- We now turn from superheated steam to a discussion of steam tables in the mixed state.
- “mixed” refers not to a mixture of vapour and air, but to a mixture of phases, which will occur when the vapour is supersaturated and a fraction of it must condense.
- These tables are two-dimensional, having as inputs pairs of independent variables: enthalpy and density, enthalpy and pressure, temperature and pressure, etc. For containment calculations, entropy is not useful.
- As with saturation tables, the user will probably need to create tables specifically for the containment application.
- In elementary texts, only condensation at constant pressure is considered. In that case, there is no change in temperature or pressure in the vessel as vapour condenses; the amounts of water in the two phases simply change.
- The situation with containment is different. The volume, not the pressure, is constant. Hence there is a temperature and pressure drop when condensation occurs.

- Slightly more will be condensed if the phase change occurs at constant volume if the same amount of heat is removed.
- A detailed example is now provided (see workbook) showing numerically how a saturated steam mixture responds to the situations described in the perfect gas lecture.

**Example:**

(1) Start on the saturation line at 70C (vapour density  $\sim .2$  kg/m<sup>3</sup>), reduce specific enthalpy by 10 kJ/kg at constant volume:

About .42% condenses, and the temperature drops by .1 C, pressure by .14 kPa

(2) Starting from saturation at 70C, remove same amount of heat at constant pressure:

About .40% condenses, no temperature or pressure change, but the volume shrinks by same percentage.

(3) Starting from saturation at 70C, let 1% of the vapour flow out of the volume

About 1.2% condenses, temperature drops by .6 C, pressure by .8 kPa

(4) Starting from saturation at 70C, add 1% of saturated vapour at 70C by letting it flow in.

System is now superheated. Temperature rises by 18C, pressure by 2 kPa

- The example of condensation at constant volume shows that the vapour behaves as if its specific heat had increased from  $C_{vv}$  to a very large number.
- When some vapour is allowed to escape from a volume filled with saturated steam, the density decreases, but so does the enthalpy, so it is not clear whether the system ends up superheated or condensing. In fact, in the range of temperatures seen in containment, the escape of vapour causes a significant condensation.

- The converse is also true. If additional vapour flows into a volume full of saturated vapour, the vapour will become superheated, unless the incoming vapour is much colder than the vapour already there.
- Earlier it was stated that condensation at constant volume occurred as if the specific heat was some enormous number compared to  $C_{vv}$ . We will now estimate this effective specific heat.
- Suppose a system consists of saturated vapour at temperature  $T$  and mass  $M_v$  in a volume  $V$ , having internal energy  $U$ . It is initially at a point  $(T, \rho_v)$  on the saturation line. Suppose now the internal energy is reduced by  $dU$ .
- A quantity  $Vd\rho_v$  of liquid must condense as the system moves to a new point  $(T+dT, \rho_v - d\rho_v)$  on the saturation line.

The new total energy must be given, to first order, by

$$U - dU = (M_v - Vd\rho_v)(u_v + C_{vv}dT) + Vd\rho_v u_L$$

Using the expression for  $(dT_{satv}/d\rho_{satv})$  derived earlier, we can eliminate the unknown  $d\rho_v$ , and write

$$dT = dU / [M_v(C_{vv} + u_{fg}^2 / (R_v T^2))] \\ \cong dU R_v T^2 / [M_v u_{fg}^2]$$

- There is some inaccuracy associated with this expression. When the expression for  $U-dU$  is expanded, the  $u_{fg}$  term turns out to be so much bigger than the other contribution that it should really be written to second order.

- The amount condensed can be estimated by substituting  $(dT_{\text{satv}}/d\rho_{\text{satv}})$  in the expression for  $dT$ :

$$Vd\rho_v = dU / [u_{fg}(1 + C_{vw} R_v T^2 / u_{fg}^2)]$$

Note that the term proportional to  $T^2$  is  $\ll 1$ , so that

$$Vd\rho_v \cong dU / u_{fg}$$

## CHAPTER 4: THERMODYNAMICS OF AIR-VAPOUR MIXTURES

### MODULE E: STEAM AND AIR

#### MODULE OBJECTIVES:

At the end of this module, you will be able to describe:

1. A perfect-gas approximation for the temperature and pressure of a superheated steam-air mixture, and the mistake to avoid when doing this.
2. An iterative procedure for finding the temperature and pressure of a superheated steam-air mixture using steam tables.
3. An iterative procedure for finding the temperature and pressure of a supersaturated steam-air mixture using steam tables.
4. Approximate formulas for the temperature change and amount condensed when a saturated air-vapour mixture undergoes various perturbations.
5. What happens to a saturated air-vapour mixture at characteristic containment temperatures and pressures when vapour flows in, the mixture is vented, heat flows out, or the volume decreases.

## 1.0 SUPERHEATED STEAM AND AIR

- To a first approximation, vapour can be treated as a perfect gas.
- Easy therefore to calculate the temperature and pressure of an air-vapour mixture.
- Once the temperature is calculated, check to confirm that the mixture is not supersaturated.
- The temperature of a perfect gas mixture can be calculated using the absolute total internal energy, i.e. the energy relative to a perfect gas at zero K.
- Must use absolute temperatures with this method:

$$\begin{aligned}U_{\text{tot}} &= C_{\text{vv}} M_{\text{v}} T_{\text{kv}} + C_{\text{va}} M_{\text{a}} T_{\text{ka}} \\ &= T_{\text{mixk}} (C_{\text{vv}} M_{\text{v}} + C_{\text{va}} M_{\text{a}})\end{aligned}\tag{1.1}$$

### Example:

A 2000 m<sup>3</sup> volume contains 2000 kg of air at 35C and 600 kg of steam at 250C. What is the temperature and pressure of the mixture?

The total internal energy of the mixture, relative to a perfect gas at absolute zero, is

$$\begin{aligned}U &= 2000 \times (35 + 273) \times 0.7 + 600 \times (250 + 273) \times 1.37 \\ &= 8.61 \times 10^5 \text{ kJ}\end{aligned}$$

hence

$$T = 8.61 \times 10^5 / (2000 \times 0.7 + 600 \times 1.37) = 388 \text{ K} = 115 \text{ C}$$

$$P_{\text{tot}} = 0.46 \times (600/2000) \times 388 + 0.3 \times (2000/2000) \times 388 = 170 \text{ kPa.}$$

Check: vapour density =  $0.3 \text{ kg/m}^3 \ll$  saturation density at 115C =  $0.96 \text{ kg/m}^3$

That was the right way to solve the problem.

Now, this is the wrong way using Centigrade degrees:

$$U = 2000 \times 35 \times 0.7 + 600 \times 273 \times 1.37 = 2.73 \times 10^5 \text{ kJ}$$

$$T = 2.73 \times 10^5 / (2000 \times 0.7 + 600 \times 1.37) = 123 \text{ C.}$$

The total internal energy was calculated relative to vapour at 0C, but the energy difference between vapour at 0C and air at 0C was forgotten, hence the answer is wrong.

This is a very easy mistake to make, especially since the error is not large enough that the engineer will immediately feel the calculation is wrong.

- **WARNING:** Note the wording of the problem was “the volume contains 2000 kg air at 35C and 600 kg steam at 250 C”. If the problem had been “600 kg steam at 250 C flows into a volume with air at 35C...” the answer would have been quite different. We would have had to integrate equation (3.1) from module 4B, which means that the vapour added its enthalpy rather than just its internal energy to the internal energy of the air when the vapour pushed its way in.



- Psychrometric diagrams for air-vapour mixtures can be found in mechanical engineering handbooks in the section on air conditioners.
- Sometimes convenient when doing approximate manual calculations.
- Perfect-gas mixing was only an approximation good to within a few per cent.
  - Can be used as the starting point for an iterative procedure using steam tables.
  - There is no unique method of iterating with the steam tables for an air-vapour mixture.
  - The method depends on what kind of tables are available. Tables with internal energy and density as independent variables make it easiest.
  - The following example shows one possible method. The method I used was somewhat awkward because my on-line steam tables had (enthalpy, density) as independent variables rather than (internal energy, density), which is the more natural choice.

### Example

The initial conditions are  $V=75000 \text{ m}^3$ ,  $T_a=35 \text{ C}$ ,  $M_a=75000$ ,  $M_v=25000$ ,  $h_v=2800$ . Find the exact temperature and pressure. Will any steam condense on mixing with the cooler air?

Using steam tables, we find for steam with  $\rho_v = 0.3333 \text{ kg/m}^3$  and  $h_v=2800$ :

$T_v=160.78$ ,  $P_v=66.4$ ,  $u_v=2600.74$ , quality = 1 (no condensation).

The total initial internal energy  $U_i$ , measured relative to vapour at zero C, is therefore

$$\begin{aligned}U_i &= U_{a0} + M_v (u_v - u_{v0}) + M_a T_a C_{va} \\&= U_{a0} + 25000(2600.74 - 2375.4) + 75000 \times 35 \times 0.7 \\&= U_{a0} + 7.47 \times 10^6 \text{ kJ}\end{aligned}$$

where

$$U_{a0} \equiv T_{273} M_a (C_{va} - C_{vv})$$

represents the difference in internal energy between vapour at zero C and air at zero C. This term is not evaluated numerically since it is subtracted out in the calculation that follows.

**Important:** You *will* have to evaluate this term if your air/vapour masses are changing. For an example, refer to the handout describing a containment model by Hodhod et al.

We make a zeroth order estimate  $T_f^{(0)}$  for the final mixture temperature using:

$$U_i = U_{a0} + T_f^{(0)} (M_v C_{vv} + M_a C_{va})$$

which leads to  $T_f^{(0)} = 86.1$ . The zeroth order approximation to the vapour pressure is

$$P_v^{(0)} = \rho_v R_v (86.1 + 273.2) = 0.3333 \times 0.46 \times (86.1 + 273.2) = 55.1 \text{ kPa.}$$

Before proceeding, we verify using steam tables that steam at  $T = 86.1$  and density =  $0.333 \text{ kg/m}^3$  is superheated. The saturation temperature for this density is about  $83.4 \text{ C}$ , so there is no problem unless the temperature falls several degrees on the next iteration.

The next step is to calculate the total internal energy corresponding to  $T_f^{(0)}$  and a steam density of 0.333. If  $T_f^{(0)}$  were the correct answer, this calculation should return the same energy we started with.

Such a calculation requires steam tables with the internal energy as a function of density and temperature, which the author does not have; what is available is internal energy as a function of enthalpy and density. The density is known, and the vapour enthalpy may be estimated from  $T_f^{(0)}$  using the saturation steam tables:

$$h_v^{(0)} = h_{\text{satv}}(T_f^{(0)}) = 2653.75.$$

We used the fact that the vapour enthalpy is relatively insensitive to density in this temperature range. The next step is to get a new internal energy from  $h_v^{(0)}$  and the vapour density using tables:

$$u_v^{(1)} = u_v(h_v^{(0)}, \rho_v) = u_v(2653.75, 0.33333) = 2489.8.$$

Using the same inputs ( $h^{(0)}$ ,  $\rho_v$ ) to the steam tables, we update our estimates of the temperature and pressure:  $T_f^{(1)} = 85.68$ ,  $P_v^{(1)} = 54.65$ . The pressure is calculated just to see how fast it is converging, but the temperature is needed to get the air contribution to the total energy.

Using the new  $u_v^{(1)}$  and  $T_f^{(1)}$ , we calculate

$$\begin{aligned} U^{(1)} &= U_{a0} + M_v(u_v^{(1)} - u_{v0}) + M_a T_f^{(1)} C_{va} \\ &= U_{a0} + 25000 \times (2489.8 - 2375.4) + 75000 \times 85.68 \times 0.7 \end{aligned}$$

$$= U_{a0} + 7.36 \times 10^6$$

This value is too low. Clearly  $h_v^{(1)}$  should be larger than  $h_v^{(0)}$ . Since  $(U - U_{a0})$  is approximately a linear function of temperature, as is  $h_v$ , a reasonable guess for  $h_v^{(1)}$  is therefore:

$$\begin{aligned} h_v^{(1)} &= h_{v0} + (h_v^{(0)} - h_{v0})[(U_i - U_{a0}) / (U^{(1)} - U_{a0})] \\ &= 2501.4 + (2653.75 - 2501.4)(7.47 \times 10^6 / 7.36 \times 10^6) \\ &= 2565.08 \end{aligned}$$

We now repeat the steam table lookup with inputs  $(h_v^{(1)}, \rho_v)$  and get the following updates:

$$u_v^{(2)} = 2491.6, \quad T_f^{(2)} = 86.9, \quad P_v^{(2)} = 54.8, \text{ and}$$

$$\begin{aligned} U^{(2)} &= U_{a0} + M_v(u_v^{(2)} - u_{v0}) + M_a T_f^{(2)} C_{va} \\ &= U_{a0} + 7.47 \times 10^6 \end{aligned}$$

We see that  $U^{(1)}$  and  $U^{(2)}$  are rapidly approaching  $U_i$  and conclude that the final mixture temperature and pressures are very close to

$$T_f = 86.9, \quad P_{vf} = 54.8, \text{ and air pressure } P_{af} = \rho_a R_a (86.9 + 273.2) = 108.1$$

Note how close these are to the zeroth order approximation:  $T_f^{(0)} = 86.1, P_v^{(0)} = 55.1 \text{ kPa}$

- This calculation points to the strategy to follow for simple containment models when condensation is a possibility:
- Remove (condense) any subcooled vapour, then calculate the temperature and pressure of the remaining superheated vapour-air mixture using a perfect-gas method.

## 2.0 SATURATED STEAM AND AIR

We will first work through an example showing how steam tables are used in the presence of air for a saturated mixture, then look at the effect of small perturbations on a system that is already on the saturation line.

When air is present, steam tables for the mixed state can no longer be used directly, since they are based on conservation of (vapour energy + liquid energy) during the phase change.

When air is present during condensation, part of the latent heat must be given to change the air temperature, if the phase change occurs at constant volume so that there is a temperature change.

Steam tables are therefore used iteratively.

### Example

The initial conditions are: water mass = 125000 kg with enthalpy 1250 kJ/kg, air mass = 75000 kg at 35 C in a volume = 75000 m<sup>3</sup>. What are the temperature and pressure of the saturated mixture? How much condenses?

As in the example for superheated steam, we start by obtaining the specific internal energy of water with  $h_v = 1250$  and  $\rho_v = 125,000/75,000 = 5/3$  kg/m<sup>3</sup>:  $u = u(1250, 1.67) = 1187.6$  kJ/kg

With this specific internal energy we get the total initial internal energy of the air-water mixture relative to liquid water at zero C:

$$\begin{aligned}U_i &= U_{a0} + M(u - u_{v0}) + M_a T_a C_{va} \\&= U_{a0} + 125,000 \times (1187.6 - 2375.4) + 75,000 \times 35 \times 0.7 \\&= U_{a0} - 1.466 \times 10^8 \text{ kJ.}\end{aligned}$$

The final internal total internal energy must be the same after the superheated liquid separates into steam and liquid:

$$U_i = U_{a0} + M_v(u_{fv} - u_{v0}) + M_a T_f C_{va} + (M - M_v) T_f C_w$$

Note that because we assumed there would be some liquid, there is now an additional term in the equation, and there are now two unknowns,  $M_v$  and  $T_f$ , instead of just  $T_f$ . To find a starting point, we could use the approximate relationship between saturation density and saturation density to get a relationship between  $M_v$  and  $T_f$ :

$$M_v/V = P_v/(T_f R_v) \sim (1.08 \times 10^8 / (T_f R_v)) \times \exp(-5173/T_{fk})$$

and substitute the linear approximations for  $u_v$  and  $u_l$ :

$$\begin{aligned}u_v &\sim u_{v0} + C_{vv} T_f \\u_l &\sim u_{v0} - (C_w - C_{vv}) T_f\end{aligned}$$

With these three substitutions,  $U_i$  could be written in terms of only one unknown,  $T_f$ . In principle, some algorithm such as Newton-Raphson would then lead to a solution for the zeroth order approximation to  $T_f$ .

Experience however suggests that for the zeroth order solution, one can ignore the air altogether unless the air mass is far greater than the steam mass.

We therefore use steam tables to get the temperature of water in the mixed state with enthalpy = 2800 and density = 1.67. The steam tables yield: quality = 0.367,  $T_v = 100.79$ ,  $P_v = 104.2$ .

We will use these quantities as zeroth order estimates for the air-vapour mixture:  $T_f^{(0)} = 100.79$ ,  $P_v^{(0)} = 104.2$ .

The first guess at vapour mass is also taken from the zeroth order call to the steam tables:

$M_v^{(0)} = 0.367 \times 125,000 = 4.59 \times 10^4$ , and the liquid mass is:

$M_l^{(0)} = (1 - 0.367) \times 125,000 = 7.91 \times 10^4$ .

We now calculate the total internal energy assuming the air is also at this temperature  $T_f^{(0)}$ , but we are interested in the discrepancy between this value and the initial energy  $U_i$

$$\begin{aligned} U^{(0)} &= U_{a0} + M_l^{(0)}(u_{lv} - u_{v0}) + M_a T_f^{(0)} C_{va} + (M - M_v^{(0)}) T_f^{(0)} C_w \\ &= U_{a0} + M(u - u_{v0}) + M_a (T_f^{(0)} - T_a) C_{va} \\ &= U_i + M_a (T_f^{(0)} - T_a) C_{va} \\ &= U_i + 75,000 \times (101 - 35) \times 0.7 \\ &= U_i + 3.5 \times 10^6. \end{aligned}$$

Not surprisingly, the result is greater than the original value. This signifies that too much water was evaporated, or that the mixture temperature is too high - it amounts to the same thing.

The overestimate occurred because  $3.5 \times 10^6$  kJ of the energy stored in the superheated liquid should have been set aside to heat up the air; instead we used up all of it for latent heat to evaporate the superheated liquid.

If we had set aside  $3.5 \times 10^6$  kJ to heat the air, we would have evaporated less liquid. Because the latent heat is so large, the reduction in the amount evaporated would be only:

$$3.5 \times 10^6 / h_{fg} \sim 3.5 \times 10^6 / 2255 = 1537 \text{ kg.}$$

This suggests a small correction to the vapour and liquid masses for the next iteration:

$$M_v^{(1)} = M_v^{(0)} - 1537 = 44.36 \times 10^4, \text{ and } M_l^{(1)} = M_l^{(0)} + 1537 = 80.64 \times 10^4$$

Using this new saturated vapour density and one-dimensional steam tables, we want to get

$$T_f^{(1)} = T_{\text{sat}}(\rho_{\text{vsat}})$$

but the vapour density should be calculated using the actual volume available to the vapour, which is calculated from the mass and specific volume of liquid at 100C:

$$V_v = V - M_l v_{l\text{sat}}(T_f^{(0)}) = 75000 - 80637 \times 0.001043 = 74916$$

so that

$$T_f^{(1)} = T_{\text{sat}}(\rho_{\text{vsat}}^{(1)}) = T_{\text{sat}}(44.36 \times 10^4 / 74916) = T_{\text{sat}}(0.5922) = 100.34$$



Using the same  $\rho_{vsat}^{(1)}$  as steam table input, we get new estimates for  $u_{vsat}$  and  $u_{lsat} \sim u_{lsat}^{(1)} = 2506.2$ ,  
 $u_{lsat}^{(1)} = 417.75$ ,  $v_{vsat}^{(1)} = 1.6886$ ,  $v_{lsat}^{(1)} = .001043$ . These internal energy values are plugged back into the equation for the total energy to get:

$$\begin{aligned}U^{(1)} &= U_{a0} + M_v^{(1)}(u_v^{(1)} - u_{v0}) + M_a T_f^{(1)} C_{va} + (M - M_v^{(1)})(u_l^{(1)} - u_{v0}) \\&= U_{a0} + 44.363 \times 10^4 \times (2506.18 - 2375.4) + 75,000 \times 99.8 \times 0.7 + 80.637 \times 10^4 \times (4175 - 2375.4) \\&= U_{a0} - 1.467 \times 10^8\end{aligned}$$

and into an equation for the total volume:

$$\begin{aligned}V^{(1)} &= v_{vsat}^{(1)} M_v^{(1)} + v_{lsat}^{(1)} M_l^{(1)} \\&= 1.6886 \times 44.363 \times 10^4 + 0.001043 \times 80.637 \times 10^4 \\&= 74995\end{aligned}$$

$U^{(1)}$  and  $V^{(1)}$  are sufficiently close to the initial total energy and initial volume for us to conclude that the final temperature is  $T_f^{(1)} = 100.34$  C. The corresponding vapour pressure is  $P_{sat}(\rho_v) \sim 102$  and the air pressure is  $\sim 112$  kPa.

Note that the initial estimates differed by only 0.6C and 2 kPa.

## 2. APPROXIMATE EXPRESSIONS FOR SATURATED MIXTURES OF STEAM AND AIR

### 2.1 DERIVATION

- It is useful to have some general expressions for what happens to a saturated air/vapour mixture when gas flows in or out of the volume, or the volume changes, or heat is removed: whether superheating will occur, and how much will condense.
- The result depends very much on the air/vapour ratio and on the temperature.
- We will derive approximate expressions by working with the total internal energy equation.
- Refer to the figure for the conventions. Flow into the volume is defined as positive.
- The volume of the condensate is neglected, since  $\rho_{\text{satv}}/\rho_{\text{satl}} < 0.001$  for  $T < 120$  deg C. The initial and final states are assumed to be saturated.
- Initially there is no liquid present and the system is saturated.:

$$U' = M_a' u_a' + M_v' u_v'. \quad (2.1)$$

- After time  $dt$ , the system is either superheated, or saturated with some condensate  $dM_L$ . If the equation of state indicates superheating, equation (4.1) applies; if there is now liquid present, its energy and mass are separated from the steam energy and mass as follows.
- Assuming some vapour  $dM_L$  has condensed,

$$U = M_a u_a + M_v u_v + dM_L u_L. \quad (2.2)$$

Subtracting (2.2) from (2.1) gives

$$dU = M_a du_a + u_a dM_a + (\sum w_v dt - dM_L) u_v + M_v du_v + dM_L u_L. \quad (2.3)$$

- Vapour and condensate are at the same temperature when the system is in the new state. But this temperature is not the same temperature as before, because the system is at a new point on the saturation line.
- If one defines  $C_{vv}$  as the derivative of  $u$  along the saturation line (note that this not the correct formal definition of constant-volume specific heat, although it is numerically very close in the range of temperatures appropriate for containment)

$$C_{vv} = (du_v/dT)_{sat}$$

so that

$$du_v = C_{vv} dT \text{ and } du_a = C_{pa} dT$$

and recognizes that

$$\begin{aligned} \sum w_v dt - dM_L &= dM_v \\ &= d(r_v V) \\ &= V(d\rho_v dT)_{sat} dT + \rho_v dV \end{aligned} \quad (2.4)$$

and uses the definition

$$u_{fg} = u_v - u_L,$$

then (2.3) becomes

$$\begin{aligned} U - U' = dT [ C_{va} M_a + C_{vv} M_v + u_{fg} V (d\rho_v/dT)_{sat} ] \\ + dt [ u_a \sum w_a + u_v \sum w_v - u_{fg} \sum w_v ] \\ + dV [ u_{fg} \rho_v ]. \end{aligned} \quad (2.5)$$

- Solving for (2.5) for dT yields the temperature change:

$$dT = \{ (U - U') - dt [ u_a \sum w_a + u_v \sum w_v - u_{fg} \sum w_v ] + dV [ u_{fg} \rho_v ] \} / [ C_{va} M_a + C_{vv} M_v + u_{fg} V (d\rho_v/dT)_{sat} ]. \quad (2.6)$$

- The condensate mass  $dM_L$  is obtained from (2.4) once dT is known from (2.6):

$$dM_L = w_v dt - dT V (d\rho_v/dT)_{sat} - \rho_v dV. \quad (2.7)$$

- If  $dM_L$  turns out to be negative, the initial assumption that the final state of the system was on the saturation line was wrong; the system is superheated and previously described methods apply.
- Before studying specific cases, one further simplification based on the Clausius-Clapeyron relation:

$$P_{satv}(T_k) = 1.08 \times 10^8 \exp(-5173/T_k) \quad \text{kPa} \quad \text{where } T_k \text{ is the absolute (Kelvin) temperature}$$

is possible.

- By differentiating the Clausius-Clapeyron relation, combining the result with the ideal gas law, and using  $h - RT = u$ , one obtains an expression useful for estimates:

$$V(d\rho_v/dT)_{sat} = (M_v u_{fg}) / (R_v T_k^2), \quad (2.8)$$

- Note that this derivative is an exponentially increasing function of temperature because of the factor of  $M_v$ .
- So far we have concentrated on what happened inside the control volume. We now use the expression for  $dU$  in terms of mass and energy flows through the control volume boundary to get closure:

$$\begin{aligned} dU &= U - U' \\ &= dt \left( \sum h_{vi} w_{vi} + \sum h_{ai} w_{ai} - h_a \sum w_{ao} - h_v \sum w_{vo} + Q - P_{tot} dV/dt \right) - PdV, \end{aligned} \quad (2.9)$$

- This is what will be plugged into the equation for  $dT$ .
- Now at last we can look at some specific cases.
- In all the numerical examples, typical containment conditions are assumed: saturation with total pressure about 100 kPa and temperatures in the range [10, 120] degrees C. In the algebra, temperatures are absolute (degrees Kelvin).

## 2.2 REMOVE HEAT - Qdt

- In this case the equations (2.6) and (2.9) simplify to

$$\begin{aligned} dT &= -Qdt / [C_{va}M_a + C_{vv}M_{vv} + u_{fg}V(d\rho_v/dT)] \\ &= -Qdt / C_{mix} \end{aligned} \quad (2.10)$$

where equation (2.10) is used to define the effective heat capacity  $C_{mix}$  for a condensing mixture, and

$$dM_L = -dT V(d\rho_v/dT)_{sat}$$

so that the amount condensed is

$$dM_L = Qdt / [u_{fg} + R_v T_k^2 (C_{vv} + C_{va} M_a / M_v) / u_{fg}] \quad (2.11)$$

### Example:

The amount condensed from a saturated air-vapour mixture at 30 deg C and 100 kPa is

$$dM_L = Q dt / (2291 + 25 + 492) \text{ kJ/kg}$$

The denominator shows how the heat is removed from the components of the air-vapour mixture. The 2291 kJ/kg is for condensation, the 25 kJ/kg is for cooling the vapour, and the 492 kJ/kg is for cooling the air.

- Note that the mixture is only ~3% vapour by mass, yet the vapour takes 75% of the available energy for condensation, about 25% goes to the air comprising 97% of the mass.

- If the temperature had been higher, the air:vapour ratio of the saturated mixture would have been lower, and the air would have even less effect.
- Conclusion: the effect of air on the thermodynamics of a condensing a saturated vapour-air mixture is negligible as temperature rises.
- Do not conclude that air can be ignored. It has a very strong effect on the condensing heat transfer coefficient.

### 2.3 ADD VAPOUR TO THE SYSTEM

- This case represents vapour inflow from the break or evaporation from the sumps into an already saturated volume.

$$\text{Now } w_v = w_{vi} \text{ and } dU = h_{vi} w_{vi} dt$$

so that equations (2.6) and (2.7) become

$$dT = (h_{vi} - u_v) w_{vi} / [C_{va} M_a + C_{vv} M_v + u_{fg} V(d\rho_v/dT)_{sat}] \quad (2.12)$$

$$dM_L = w_{vi} dt - dT V(d\rho_v/dT)_{sat} \quad (2.13)$$

Using the fact that  $C_{va} M_a + C_{vv} M_v \ll u_{fg} V(d\rho_v/dT)$ , (2.12) and (2.13) may be combined to give

$$dM_L = w_{vi} dt (u_v - h_{vi}) / u_{fg} \quad (2.14)$$

- There will be condensation only if  $dM_L > 0$ , ie if  $u_v > h_{vi}$ , which requires  $T_{vi}/T < C_{vv}/C_{pv} = 0.75$ , where the temperatures are in degrees K.
- If volume temperature is 40 deg C = 313 deg K, the vapour temperature must be  $< -30$  C to cause immediate condensation.

- If the incoming vapour is hotter, there will not be any condensation accompanying the temperature increase; recall that a negative value for  $dM_L$  indicates superheating.
- Equation (2.14) implies that neither the 250 degree steam from a steam line break nor the 100 degree steam coming from a flashing liquid break can cause bulk condensation in an isolated volume.
- If the system starts on the saturation line, the additional vapour will make it superheated. Temperature and pressure would rise at a rate as if perfect gases were being mixed.
- In reality of course, the volume is not isolated once pressure rises significantly; the outflow of air/vapour through panels/valves will cool the gas and cause condensation. But the initial burst of steam from the break will cause superheating.



## 2.4 AIR/VAPOUR MIXTURE FLOWS OUT OF THE VOLUME

- We assume that what flows out is representative of the mixture in the volume. Let the volumetric outflow be  $F$ . Then

$$w_a = -w_{ao} = -F\rho_a$$

$$w_v = -w_{vo} = -F\rho_v$$

$$dU = -F(\rho_a h_a + \rho_v h_v) dt$$

so that equations (2.6) and (2.7) become

$$dT = dt F \{ (-h_a + u_a)\rho_a + (-h_v + u_v - u_{fg})\rho_v \} / [C_{va}M_a + C_{vv}M_v + u_{fg}V(d\rho_v/dT)]$$

and

$$dM_L = -dt F(\rho_a + \rho_v) - dT V(d\rho_v/dT) \quad (2.15)$$

Clearly  $dT < 0$  since  $h_v > u_v$

- Always some condensation in containment if gas leaves a saturated volume, simply as a result of cooling, and the system travels down the saturation line.
- The sudden opening of rupture disks or continuous venting cools the air/vapour mixture and keeps it on the saturation line.

## 2.5 CHANGE THE VOLUME

Now

$$dU = -PdV$$

$$dT = (-PdV - u_v \rho_v dV) / [C_{vv} M_v + C_{va} M_a + u_v V (d\rho_v/dT)_{sat}] \quad (2.16)$$

$$dM_L = -dT V (d\rho_v/dT) - \rho_v dV .$$

- Clearly  $dT > 0$  for compression.
- To confirm that  $dM_L < 0$  (no condensation) for containment conditions, some numerical substitutions must be made.

### 3.0 EQUIVALENCE OF CONDENSING FORMULATIONS

- In this section, the equation quoted at the beginning of module 4B for  $dh_v/dt$ , when the closed vessel model was introduced, will be derived from first principles and the assumption that vapour specific heat is constant.
- The algebra will not be written out in full, since the approach is almost identical to module 4B.

By using  $h$  and  $H$  instead of  $u$  and  $U$  in equations (2.1) - (2.7), ie by equating

$$\begin{aligned}dH &= d(P_{\text{tot}} V + U) \\ &= d(P_{\text{tot}} V) + dt(w_{vi} h_{vi} + w_{ai} h_{ai} - w_{vo} h_v - w_{ao} h_v + Q) - (P_{\text{tot}})dV\end{aligned}$$

with

$$dH = Mdh + hdM$$

and writing

$$dh_v = C_{vv} dT, dh_a = C_{va} dT$$

we obtain

$$\begin{aligned}dT/dt &= \{ dH/dt - [h_a \sum w_a + h_v \sum w_v - h_{fg} \sum w_v] + Q + h_{fg} \rho_v dV/dt \} / \\ &\quad [C_{pa} M_a + C_{pv} M_v + h_{fg} V(d\rho_v/dT)]\end{aligned} \tag{3.1}$$

where  $C_{vv}$  is defined as

$$C_{vv} = (dh_v/dT)_{sat} \quad (3.2)$$

(This is not the correct formal definition of specific heat !)

Using

$$dH = dU + VdP + PdV,$$

$$dT = dh_v/C_{pv},$$

and expression (2.9) for  $U-U'$ , one obtains from (3.1)

$$\begin{aligned} dh_v/dt = \{ & VdP/dt + [(h_{vi}-h_v)\Sigma w_v + (h_{ai}-h_v)\Sigma w_{ai}] \\ & + h_{fg}[-\Sigma w_v + \rho_v dV/dt] + Q \} / [C_{vv}M_v + C_aM_a + h_{fg}V(d\rho_v/dT)] \end{aligned} \quad (3.3)$$

By writing (2.4) in differential form as follows, with  $w_{con} = dM_L/dt$  being the condensate flow, one gets, solving for  $\Sigma w_v$

$$-\Sigma w_v = -w_{con} - V(d\rho_v/dT) (dh_v/dt)/C_{pv} - \rho_v dV/dt \quad (3.4)$$

which may be substituted inside the square brackets multiplying  $h_{fg}$  in equation (3.3) to yield

$$\begin{aligned} dh_v/dt = \{ & VdP_{tot}/dt + [(h_{vi}-h_v)\sum w_{vi} + (h_{ai}-h_a)\sum w_a + Q] \\ & + h_{fg}[w_{con} - (dh_v/dt)/C_{pv}]V(d\rho_v/dT)\} / \\ & [C_{pv}M_v + C_{va}M_a + h_{fg}V(d\rho_v/dT)] \end{aligned} \quad (3.5)$$

in which the unknown  $dh_v/dt$  appears on both the right and left hand sides. Solving for  $dh_v/dt$  yields

$$\begin{aligned} dh_v/dt = \{ & VdP_{tot}/dt + [(h_{vi}-h_v)\sum w_{vi} + (h_{ai}-h_a)\sum w_a + Q] \\ & + h_{fg}w_{con}\} / [M_a C_{pa}/C_{pv} + M_v] \end{aligned} \quad (3.6)$$

- This is the desired result, except that  $w_{con}$  must be replaced by the value from the previous iteration,  $w'_{con}$ , for numerical solution:

$$\begin{aligned} dh_v/dt = \{ & VdP_{tot}/dt + [(h_{vi}-h_v)\sum w_{vi} + (h_{ai}-h_a)\sum w_a + Q] \\ & + h_{fg}w'_{con}\} / [M_a C_{pa}/C_{pv} + M_v] \end{aligned} \quad (3.7)$$

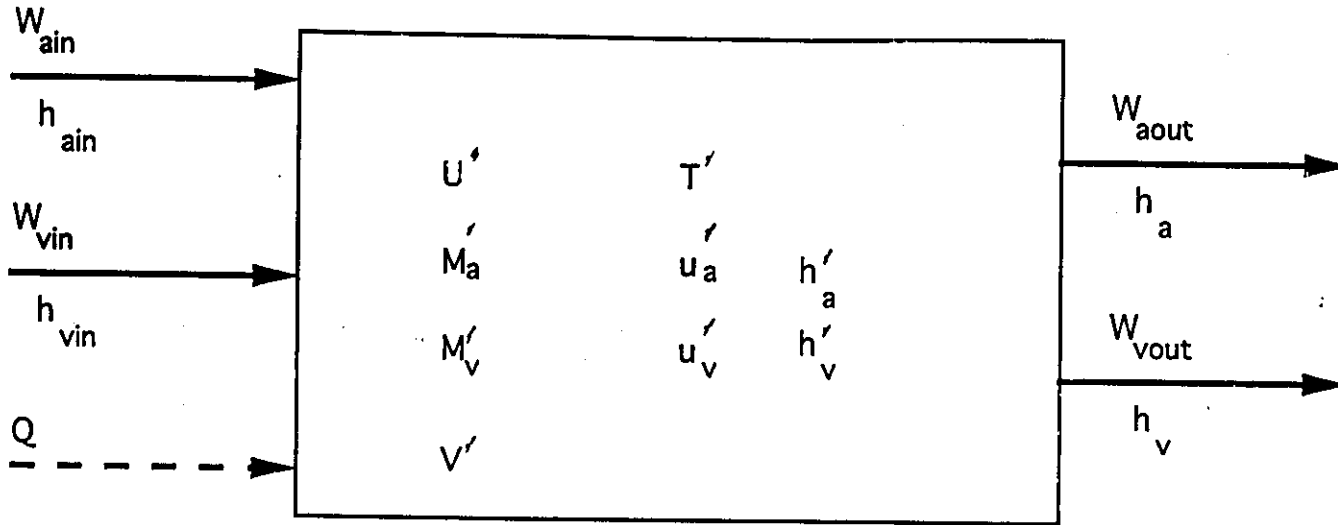
- The condensate flow  $w_{con}$  is still unknown. In the simplest model with no air, the amount condensed is given by steam tables for a saturated mixture:

$$dt w_{con} = M_v (h_{vsat}^{Pv} - h_v) / h_{fg} \quad \text{if } h_v < h_{vsat}^{Pv} \quad (3.8)$$

where the superscript indicates the saturation line quantity is evaluated at vapour pressure.

- Equation (3.8) will not do for an air-vapour mixture what it does in the absence of air, namely condense exactly the right amount necessary to bring the system back to the saturation line in one iteration.
- It will condense too little, so that the system will remain a few degrees on the wrong side of the saturation line.
- However, it can still be used, since the air has little effect once the vapour concentration rises.
- For a simple model, it doesn't matter very much if the condensation rate is not quite right during transients, as long as
  - (a) the system gets back to the saturation line eventually, which guarantees that the integrated condensate flow is correct, and
  - (b) the latent heat is always put back into the total mixture energy, which guarantees energy conservation.
- Note how this formulation in terms of  $dh_v/dt$  gets around the problem described in module 4C, namely having to keep track of the difference between air and vapour absolute internal energies at zero Centigrade.

initial state on saturation line



$$W_a = W_{ain} - W_{aout}$$

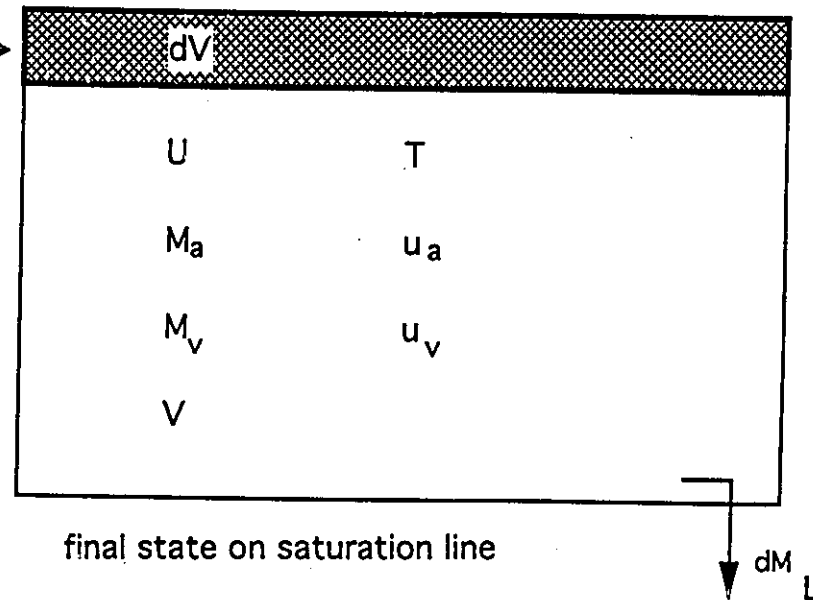
$$W_v = W_{vin} - W_{vout}$$

$$M_a = M'_a + W_a dt$$

$$M_v + dM_L = M'_v + W_v dt$$

$$V = V' + dV$$

volume change →



final state on saturation line

## CHAPTER 4: THERMODYNAMICS OF AIR-VAPOUR MIXTURES

### MODULE F: CLOSED VESSEL MODEL - PART 2

#### MODULE OBJECTIVES:

At the end of this module, you will be able to describe:

1. The equations for a closed vessel containing liquid, air and vapour
2. The conditions for flashing of superheated liquid
3. The conditions for surface evaporation
4. The conditions for rainout (bulk condensation)
5. The conditions for surface condensation
6. Limitations of the closed vessel model



## CLOSED VESSEL MODEL - PART 2

- We now return from that long digression on vapour thermodynamics back to the closed vessel model. Please refer to the closed vessel diagram to refresh your memory.
- The equations for the closed vessel's internal status will now be presented.
- Equations for external flows (heat through walls, mass flow in/out of the vessel) will be presented in Chapter 5.
- Note that the volume now contains the accumulation of condensed liquid, in contrast to the approach of earlier sections .
- The relationship between this liquid and the vapour has to be described. For example, the vapour control volume is now the space left over from the liquid, and evaporation from the liquid must be considered.
- The following equations could also provide a simplified model of any of the tanks on the secondary side, such as the condenser.

### 1.0 VAPOUR AND LIQUID THERMODYNAMICS

- The liquid volume is calculated from the known water mass. Water mass is known because in and outflows were calculated on the previous iteration from pressure.

$$V_w = M_w v_w$$

- The vapour/air volume is then the remaining volume:

$$V_{\text{gas}} = V_{\text{tot}} - V_{\text{w}} \quad (1.1)$$

- The specific volume of vapour is:

$$v_s = M_s / V_{\text{gas}} \quad (1.2)$$

- Either vapour specific volume or density must be calculated in order to calculate the vapour pressure later. It makes little practical difference.
- Through the use of D<sub>2</sub>O or H<sub>2</sub>O steam saturation tables the liquid specific volume is determined as a function of liquid specific enthalpy:

$$v_w = v_{\text{wsat}}(h_w) \quad (1.3)$$

- This is an approximation which is only valid (acceptable) because the vessel contains a separated liquid phase. If the vessel were full of liquid (at the same pressure as the inflowing liquid) this approximation would be inadequate.
- In principle the specific volume of the liquid should be determined from a function of two independent thermodynamic variables, e.g. enthalpy and density.
- Note that for typical containment/sump temperatures, the liquid specific volume varies by only a few per cent over the containment temperature range. It could be treated as constant.
- The vapour pressure is determined via the two dimensional steam lookup table as a function of specific enthalpy and specific volume:

$$P_{\text{vap}} = P_{\text{vap}}(h_s, v_s) \quad (1.4)$$

- Again, for containment conditions, the perfect gas law is accurate to within a few per cent and could be used instead.
- The liquid temperature is determined via a one dimensional steam look-up table as a function of specific enthalpy:

$$T_w = T_{sat}(h_w) \quad (1.5)$$

- In principle, this should also be a 2-D lookup from density and enthalpy. However, since  $T_w$  as a function of enthalpy and density is very insensitive to density at low pressures, it is a very good approximation to use  $h_w$  as the input to a 1-D table of saturation temperature as a function of saturation water enthalpy.
- For containment conditions, one can treat the specific heat of water as a constant without much loss of accuracy, and not bother with the lookup table at all.
- The vapour temperature is determined via a two dimensional steam table as a function of specific enthalpy and specific volume

$$T_s = T_s(h_s, v_s) \quad (1.6)$$

- Again, for containment conditions, one can obtain the approximate temperature directly from the enthalpy by assuming a constant specific heat:  $T_s = h_s / C_{pv}$ .
- If the vapour happens to be supersaturated, because the equation for condensate flow has not removed quite enough vapour, then the approximate equation will return a temperature below the dewpoint instead of the actual temperature; this may or may not be an unacceptable deficiency.

- The air pressure is calculated from the ideal gas law:

$$P_a = R_a T_{ks} M_a / V_g \quad (1.7)$$

where  $R_a$  is the gas constant for air. Since the air phase is in thermodynamic equilibrium with the steam, the air temperature is assumed to be the same as that of the steam.

- Using Dalton's law of Partial Pressures, the total pressure in the vessel is given as:

$$P_{tot} = P_{vap} + P_a \quad (1.8)$$

- The saturated liquid enthalpies at both the total and vapour pressures are determined from one dimensional steam look-up tables, or for a simpler model, using the exponential expressions described in module 4D:

$$h_{satl}^{P_{tot}} = h_{satl}(P_{tot}) \quad (1.9)$$

$$h_{satl}^{P_v} = h_{satl}(P_{vap}) \quad (1.10)$$

- Enthalpy at  $P_{tot}$  is needed to calculate liquid specific volume and to decide whether the liquid will be subject to bulk evaporation (flashing).
- Enthalpy at  $P_{vap}$  is needed later to calculate surface evaporation from the liquid.

- The saturated vapour enthalpies determined similarly to the saturated liquid enthalpy:

$$h_{\text{satv}}^{P_{\text{tot}}} = h_{\text{satv}}(P_{\text{tot}}) \quad (1.11)$$

$$h_{\text{satv}}^{P_{\text{v}}} = h_{\text{satv}}(P_{\text{vap}}) \quad (1.12)$$

- Enthalpy at  $P_{\text{tot}}$  is used to calculate the fraction of any hot liquid entering the vessel that flashes into vapour.
- Enthalpy at  $P_{\text{vap}}$  will be used to calculate bulk condensation (rainout) in the vapour.

## 2.0 Phase changes

- Two types of evaporation are considered in this simple model:
- Bulk evaporation (flashing) in the middle of the liquid volume
- Evaporation from the surface of the liquid in the bottom of the vessel.
- There will also be evaporation from the thin film of liquid condensed on the walls, from the aerosol droplets, and possibly from spray flows, but these effects are not considered here.

## 2.1 Flashing

- Occurs when the liquid has too much energy to remain in the liquid state at the current value of the total gas pressure, i.e. the liquid is superheated. Vapour bubbles form-boils.
- Typically occurs as a result of sudden drop in total pressure, in other words, it does not go on continuously like surface evaporation, at least not for the liquid in the bottom of the vessel - liquid isn't going to stay superheated, it explodes.
- For hot high pressure liquid flowing into a low-pressure vessel, e.g. liquid from a pipe break entering containment, there will however be continuous flashing of liquid into steam.
- The condition for bulk evaporation is therefore mathematically expressed as a function of enthalpy of the liquid and the total pressure. The flashing condition is:

$$h_l > h_{l,sat}^{P_{tot}}$$

- To determine how much of the liquid could be vapourized at constant pressure  $P_{tot}$ , one writes the specific enthalpy  $h_l$  of the superheated liquid  $M_w$  as

$$h_l = m_v h_{v,sat}^{P_{tot}} / (m_l + m_v) + m_l h_{l,sat}^{P_{tot}} / (m_l + m_v) \quad (1.13)$$

where  $m_v$  is the mass to be evaporated and  $m_l$  the condensed subcooled liquid:

$$M_w = m_l + m_v$$

The mass of vapour to be evaporated is found by eliminating  $m_l$ :

$$m_v = M_w (h_l - h_{lsat}^{P_{tot}}) / (h_{vsat}^{P_{tot}} - h_{lsat}^{P_{tot}}) \quad (1.14)$$
$$= M_w (h_l - h_{lsat}^{P_{tot}}) / h_{fg}^{P_{tot}}$$

- This equation is an over-estimate for flashing from sump liquid:
- Only the liquid surface is at pressure  $P_{tot}$ . Since  $h_{lsat}^{P_{tot}}$  is an increasing function of  $P_{tot}$ , the liquid at some distance below the surface certainly won't flash. So (1.14) is an over-estimate.
- The bubbles that form in the superheated liquid certainly do not expand instantaneously to the size predicted from the steam tables
- They cannot make their way instantaneously into the gas volume above the liquid, as they do in this model. They have to travel through the intervening liquid and may collapse or condense before reaching the surface.
- Regard equation (1.14) simply as an theoretical extreme upper limit on the amount to be evaporated from the liquid pool.

- Equation (1.14) leads to an expression for the flashing flow from the liquid:

$$W_{\text{evap}}^b = \max [0, C_{\text{evap}}^b M_w (h_l - h_{\text{lsat}}^{\text{Ptot}}) / (\Delta t h_{\text{fg}}^{\text{Ptot}})] \quad (1.15)$$

where

$$0 < C_{\text{evap}}^b < 1$$

- The complications described in the previous paragraph concerning the amount to be evaporated are hidden in the constant  $C_{\text{evap}}^b$ .
- If the model is being used for safety analysis, some serious attempt must be made evaluate  $C_{\text{evap}}^b$ , based on empirical correlations and the aforementioned depth effect;
- If the model is used for training,  $C_{\text{evap}}^b$  is generally adjusted small enough to prevent instability, but large enough that the liquid does not remain unduly long in the superheated state.
- Small values of  $C_{\text{evap}}^b$  will make the liquid stay above the saturation enthalpy when the pressure drops. It will eventually reach the saturation line.
- Note that  $C_{\text{evap}}^b < 1$  does not violate conservation of the total energy of the gas and liquid. Energy violation is far more serious for modelling than not getting an exact solution to the equation of state immediately after a perturbation.



- Suppose high pressure fluid from the boiler feedwater or RCS bursts out of a pipe into containment.
- If it is superheated at containment pressure, then the reasoning of the previous section holds, only there is no reason not to flash to theoretical maximum.
- In this situation one writes as a simplest expression for the liquid and vapour components of the break flow  $W_{brk}$ :

$$W_{brkv} = \max[0, W_{brk} (h_{brk} - h_{lsat}^{P_{tot}}) / h_{fg}^{P_{tot}}] \quad (1.16)$$

$$W_{brkl} = W_{brk} - W_{brkv}$$

- Assumed the pipe break occurs in the air/vapour space, not below the liquid surface.
- Equation (1.16) should be regarded as a lower limit on the amount of vapour generated from a pipe break, at least for simple models.
- Why a lower limit and not an upper limit as stated for flashing from the liquid pool? In the situation with flashing of a large volume of water, there are many factors tending to reduce the amount of vapour that reaches the surface. With a pipe break, the situation is different, there are factors that tend to increase the amount of vapour generated.
- Because of the high fluid velocity, the emerging jet forms many small droplets that hang suspended in the air or wet the walls. The droplets are initially at  $T_{sat}(P_{tot})$ , but they rapidly cool by evaporation to ambient temperature which is  $T_{sat}(P_{vap})$ .

- If the model does not explicitly include this evaporation from this droplet aerosol or the from the water dribbling down the walls, there will be an underestimate of the amount of vapour generated by the break.
- Consider also what happens when warm (subcooled) rather than superheated water is sprayed out of the break. Equation (1.16) predicts no increase in room vapour concentration as a result (only evaporation once the liquid is on the floor).
- If the model does not include a droplet aerosol, the vapour from a hot break will be underestimated by (1.16).
- Solution: use  $P_v$  rather than  $P_{tot}$  in (1.16), if the simple model does not generate enough vapour in the air to reproduce safety studies or plant data. This choice is equivalent to saying that all the break flow droplets cool by evaporation to room temperature before they hit the floor, usually a reasonable assumption.
- Note that energy conservation is not violated with this choice. You are simply partitioning the incoming energy differently between the gas phase and the sump liquid.
- Note that the enthalpy carried by the flashing vapour will be either  $h_{vsat}^{P_{tot}}$  or  $h_{vsat}^{P_v}$ , depending on the choices discussed above.

## 2.2 Surface evaporation

- Bulk evaporation (flashing) occurs when the total pressure is too low to keep the liquid in the liquid phase and the explosive vapour bubbles form.
- Compare: surface evaporation is a much quieter steadier phenomenon caused by an imbalance in the number of water molecules crossing the water surface. There is a constant two-way traffic across this border.
- The number of vapour molecules per second hitting the liquid surface depends on the density and temperature of the vapour, i.e. the vapour pressure;
- The number of liquid vapour molecules in the tail end of the Boltzmann distribution that have enough energy to escape from the liquid surface depends mainly on the liquid temperature, and this number increases exponentially with temperature.
- The saturation vapour pressure of the liquid is defined as the vapour pressure at which these two rates are equal.
- This concept can be expressed as follows:

$$W_{\text{evap}}^s = C_{\text{evap}}^s A_{\text{evap}} \max (P_{\text{satl}}^{T_W} - P_{\text{vap}}, 0) \quad (1.17)$$

where  $A_{\text{evap}}$  is the surface area of the liquid and  $C_{\text{evap}}^s$  is an empirically determined constant.

- Typically on a training simulator  $C_{\text{evap}}^s$  is chosen so that the system may come to thermodynamic equilibrium in a reasonable length of time.

- The degree of convective mixing of the gas above the liquid will affect the evaporation rate. If saturated vapour is rapidly removed from the liquid surface, by forced convection or buoyancy effects, evaporation will clearly increase. The presence of other gases also affects the evaporation rate. Safety analysis uses elaborate correlations.
- Note that surface evaporation cools the liquid until it reaches  $T_{\text{sat}}(P_{\text{vap}})$ ; it also raises the temperature of the gas above the liquid; hence it tends to bring the two phases into equilibrium.
- Note that the enthalpy carried by the evaporating vapour will be that of vapour at the same temperature as the liquid.

### 2.3 Bulk condensation (rainout)

- Occurs when the vapour molecules have too little energy to prevent the attractive forces between vapour molecules from causing the molecules to clump together in liquid droplets.
- Condition for bulk condensation involves a comparison with saturation enthalpy, but note that  $P_{\text{vap}}$  rather than  $P_{\text{tot}}$  is involved; air does not affect the condition for rainout to occur:

$$h_{\text{satv}}^{\text{Pv}} > h_s.$$

If the condition holds, the bulk condensation rate will be :

$$W_{\text{con}}^{\text{b}} = C_{\text{con}}^{\text{b}} M_s (h_{\text{satv}}^{\text{Pv}} - h_s) / (h_{\text{fg}}^{\text{Pv}} \Delta t) \quad (1.18)$$

- This expression can be derived in the same way as the flashing equation (1.15) - if no air.

- The latent heat of condensation has to be shared with the air, hence the energy conservation equation (1.13) contains another term, and does not correspond to steam tables any more. See module 4E.
- For a simple model, we shall simply state that the presence of air reduces the amount that can be condensed. The empirically chosen constant  $C_{con}^b$  must therefore satisfy

$$1 > C_{con}^b > 0.$$

- One can easily present arguments for  $C_{evap}^b < 1$ , but it is harder to justify  $C_{con}^b < 1$  if not a lot of air is present. Why should supersaturated vapour persist in an environment with many nucleation centres (dust particles)?
- The main reason for reducing  $C_{con}^b$  well below unity is to ensure stable solution of the equations.
- Total energy is still conserved with an incorrect choice of the amount condensed, the only problem may be a vapour phase supersaturated by several degrees during transients.
- For a more elaborate model, the amount condensed is calculated using the iterative method of module 4E.
- Note that the enthalpy carried by the condensing liquid will be  $h_{satl}^{Pv}$

## 2.4 Surface condensation

- Vapour will condense on a surface whose temperature  $T^s$  is less than the vapour dewpoint  $T_{\text{sat}}(P_v)$ .
- In a typical containment problem, there are many surfaces at different temperatures where condensation can occur: the liquid on the floor, the walls, tanks and pipes full of cooling water, etc.
- Condensation on the coils of air conditioners is generally treated as a special case because air passing through the air conditioner is sequestered and no longer reflects average room conditions as it traverses the coils. Air conditioners will be discussed in Module 5A.
- The surface condensation criterion is:

$$T^s < T_{\text{sat}}(P_v)$$

where  $T^s$  is the temperature of the surface, or equivalently:

$$P_v > P_{\text{satv}}(T^s)$$

Given that the process on a molecular scale is similar to surface evaporation, it is justifiable to write for the rate of condensation:

$$W_{\text{con}}^s = C_{\text{con}}^s A_{\text{con}} \max (-P_{\text{satv}}(T^s) + P_{\text{vap}}, 0) \quad (1.19)$$

where  $A_{\text{con}}$  is the area of the condensing surface.

but one can also write the equation in terms of temperatures, and make  $C_{\text{con}}^s$  vary with temperature.

- For training simulators, the constant is empirically chosen to reproduce plant data or safety analysis calculations.
- Why it is necessary to model two separate processes that remove vapour by condensation? Cold walls will cool the average vapour and thus cause bulk condensation anyway, so why bother with equation (1.19)? Two differences:
  - With rainout, vapour density is reduced but all the latent heat is given back to the gas, while with surface condensation, the vapour density is reduced but the latent heat could be given to the surface; we will write the equation as if the latent heat were returned entirely to the gas.
  - With surface condensation, vapour removal starts sooner, since wall temperature is generally below air temperature  $\sim T_{\text{sat}}(P_v)$ .
- Note that the surface condensate flow will be at the same temperature as the surface.
- Often surface condensation flows are omitted altogether:
  - The effect of depositing large amounts of latent heat on the wall is reproduced by making the surface heat transfer coefficient a very rapidly increasing function of vapour pressure. This point will be discussed in module 5B.
  - Thermal equilibrium between pool liquid and gas can be brought about by a heat transfer term proportional to the temperature difference.
- We are now in a position to further specify the equations introduced in module 4B. With explicit expressions for the saturation enthalpies, the steam equation becomes:

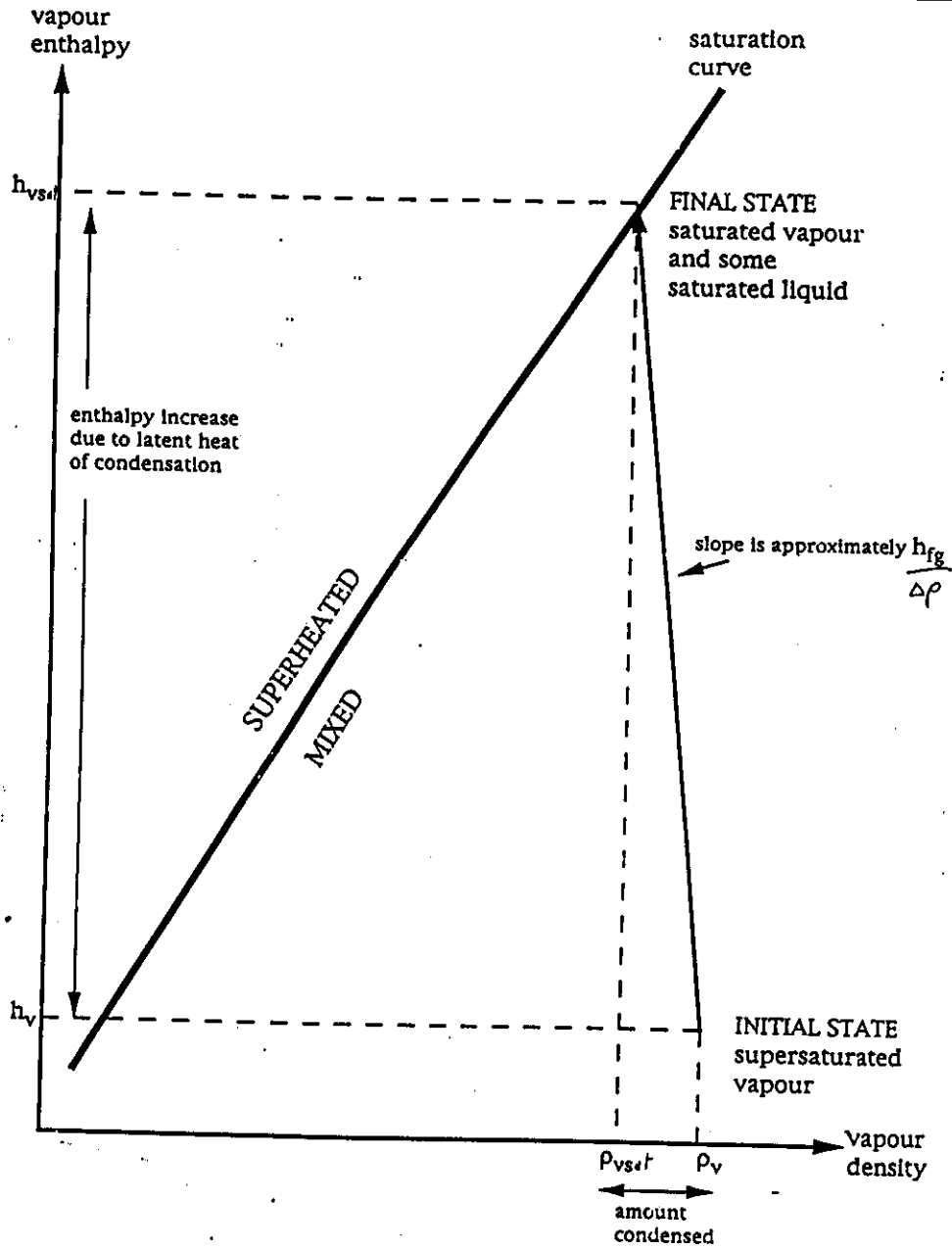
$$\begin{aligned}
 h_s = h_s' + \Delta t [ & \sum W_{si}(h_{si} - h_s') + \sum W_{ai}(h_{ai} - h_a') - W_{con}^b (h_{satl}^{Pv} - h_s') + W_{evap}^b (h_{satv}^{Ptot} - h_s') \\
 & + W_{evap}^s (h_{satv}^{TL} - h_s') - W_{con}^b (h_{satl}^{Pv} - h_s') - W_{con}^w (h_{satl}^{Tw} - h_s') \\
 & + M_s v_s dP_{tot}/dt + Q_s ] / (M_s' + M_a' (C_{ps} / C_{pa})) \quad (1.20)
 \end{aligned}$$

where  $T_L$  is the liquid temperature,  $T_w$  is the wall temperature, and the liquid equation becomes:

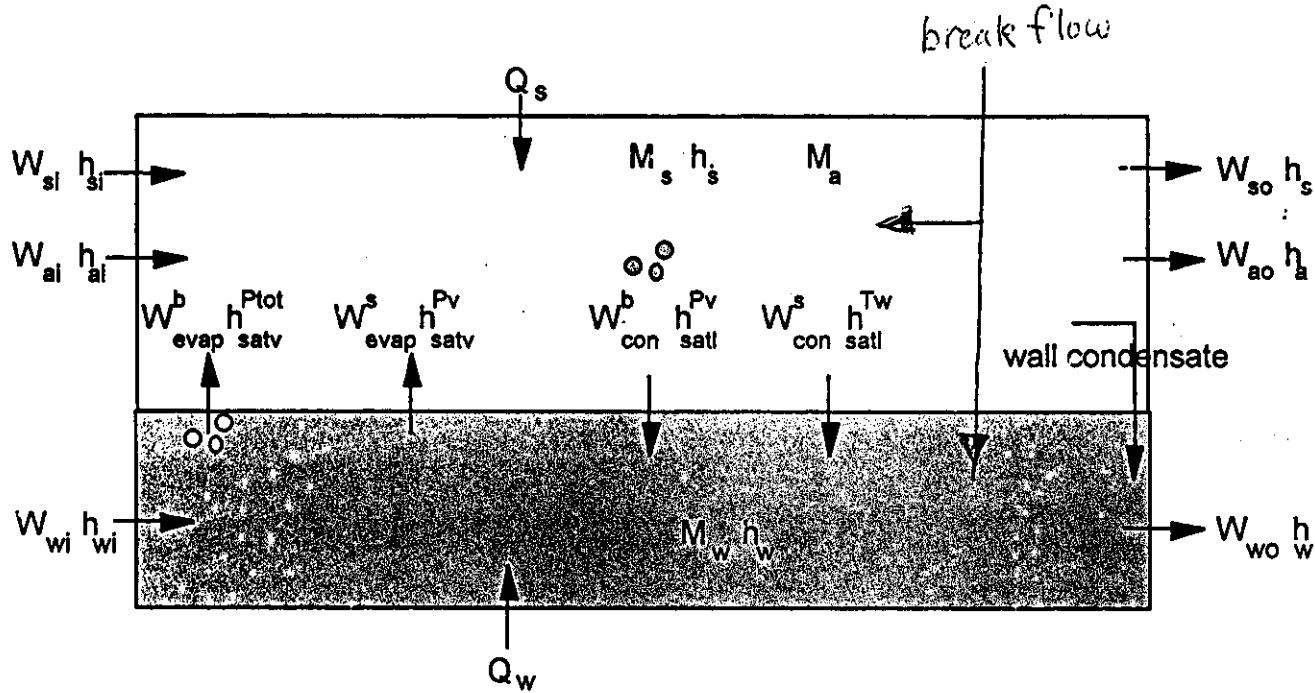
$$\begin{aligned}
 h_w = h_w' + \Delta t [ & \sum W_{wi}(h_{wi} - h_w') + W_{con}^b (h_{satl}^{Pv} - h_w') - W_{evap}^b (h_{satv}^{Ptot} - h_w') \\
 & - W_{evap}^s (h_{satv}^{TL} - h_w') + W_{con}^b (h_{satl}^{Pv} - h_w') + W_{con}^w (h_{satl}^{Tw} - h_w') \\
 & + M_w v_w dP_{tot}/dt + Q_w ] / M_w' \quad (1.21)
 \end{aligned}$$

Break flows do not appear explicitly in these equations. Break vapour is included among the vapour inflows, and break liquid among the liquid inflows.





CLOSED VESSEL MODEL



$W_{\text{evap}}^b h_{\text{satv}}^{\text{Ptot}}$  enthalpy carried by flashing of liquid at surface

$W_{\text{evap}}^s h_{\text{satv}}^{\text{Pv}}$  enthalpy carried by evaporation from liquid surface

$W_{\text{con}}^s h_{\text{satl}}^{\text{Tw}}$  enthalpy carried by condensation on liquid surface

$W_{\text{con}}^b h_{\text{satl}}^{\text{Pv}}$  enthalpy carried by rainout (bulk condensation)