HydDown

User guide and technical reference

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1 Introduction

HydDown is an open source python tool for calculation of Hydrogen (or other pure gas phase species) vessel/container depressurization and filling. The HydDown logo shown in Fig. 1.1 visualizes the key parameters and transport phenomena during gas vessel filling or discharging. The thermodynamic state inside the vessel changes over time as seen from immediately observable variables temperature (T) and pressure (P). This is caused by change in fluid inventory (density) due to flow of gas either in- or out of the vessel. Further, heat is transfered from or to the surroundings via convective heat transfer on the in- and outside of the vessel - with heat being conducted thorugh the vessel wall.

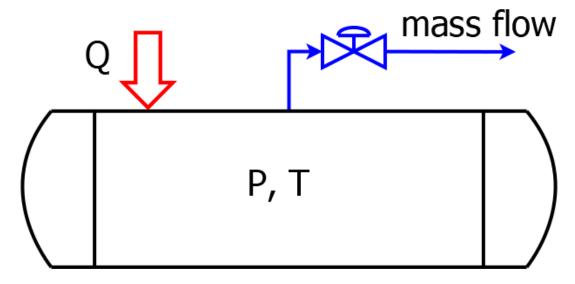


Figure 1.1: HydDown logo

Run the code as simple as:

```
1 python main.py input.yml
```

where main.py is the main script and input.yml is the input file in Yaml syntax.

1.1 Background

This is a small spare time project for calculation of vessel filling and depressurisation behaviour. This is mainly to demonstrate, that although perceived as a very tedious/difficult task to write your own code for such an apparent complex problem, actually a fairly limited amount of code is necessary if you have a good thermodynamic backend.

A few choices is made to keep things simple to begin with:

- Coolprop is used as thermodynamic backend
- · Only pure substances are considered
- · Gas phase only
- No temperture stratification in the gas phase
- No temperture gradient through vessel wall
- Heat transfer is modelled as simple as possible

These choices makes the problem a lot more simple to solve, First of all the the pure substance Helmholtz energy based equation of state (HEOS) in coolprop offers a lot of convenience in terms of the property pairs/state variables that can be set independently. Using only a single gas phase species also means that component balances is redundant and 2 or 3-phase flash calculations are not required. That being said the principle used for a single component is more or less the same, even for multicomponent mixtures with potentially more than one phase.

1.2 Requirements

- Python (3.8 at least python3)
- Numpy
- matplotlib
- Coolprop (6.4.1)
- cerberus
- PyYaml
- pandas

The script is running on Windows 10 x64, with stock python installation from python.org and packages installed using pip. Should run om linux (it does on an Ubuntu image on GitHub) or in any conda environment as well, but I haven't checked.

1.3 Units of measure

The SI units are adapted for this project. The following common units are used in the present project and this also applies to the units used in the input files:

Table 1.1: Unit system

Property	Unit	Comment
Temperature	K	° C is used in plots
Pressure	Pa	bar is used in plots
Mass	kg	
Volume	m^3	
Time	S	minutes used in plots
Energy	J	
Duty/power	W	
Length	m	
Area	m^2	
Heat flux	${ m W/m^2}$	
Heat transfer coefficient	$\mathrm{W/(m^2\ K)}$	
Density	${\sf kg/m^3}$	
Heat capacity	J/(kg K)	

As will be noted when presentaing the equations implemented in the code, some of the equations utilise different units than the ones listed in tbl. 1.1. However, it is important to note that the unit conversions are built in to the methods implemented, so the user shall not worry about unit conversion.

1.4 Credit

In the making of this document I have sourced a great deal of material (and modified it) from a good collegues M.Sc. thesis (Eriksen and Bjerre 2015), co-published papers (Bjerre et al. 2017) (Andreasen et al. 2018) and from on-line material published under permissive licenses (with proper citation). Further, the making of this project would not have possible without the awesome CoolProp library (Bell et al.

2014). I am thankful for enlightning discussions with colleague Jacob Gram Iskov Eriksen (Ramboll Energy, Denmark) and former Ramboll Energy colleague Carsten Stegelmann (ORS Consulting) in relation to vessel depressurisation, nozzle flow and heat transfer considerations.

The present document is typeset using Markdown + pandoc with the Eisvogel template.

1.5 License

MIT License

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2 Usage

2.1 Basic usage

Run the code as simple as:

```
1 python main.py input.yml
```

where main.py is the main script and input.yml is the input file in Yaml syntax.

The Yaml input file is edited to reflect the system of interest.

2.2 Calculation methods

The following methods are implemented:

- Isothermal i.e. constant temperature of the fluid during depressurisation (for a very slow process with a large heat reservoir)
- Isenthalpic/Adiabatic (no heat transfer with surroundings, no work performed by the expanding fluid)
- Isentropic (no heat transfer with surroundings, PV work performed by the expanding fluid)
- Isenergetic i.e. constant internal energy
- Energy balance. This is the most general case and is based on the first law of thermodynamics applied to a flow process.

For isothermal/isenthalpic/isentropic/isenergetic calculations the minimal input required are:

- Initial conditions (pressure, temperature)
- vessel dimensions (ID/length)
- valve parameters (Cd, diameter, backpressure)
- Calculation setup (time step, end time)
- · Type of gas

If heat transfer is to be considered the calculation type energybalance is required. A few options are possible:

- Fixed U (U-value required, and ambient temperature)
- Fixed Q (Q to be applied to the fluid is requried)
- Specified h, the external heat transfer coefficient is provided and either the internal is provided or calculated from assumption of natural convection from a vertical cylinder at high Gr number. Ambient temperature is required.
- Fire (Stefan-Boltzmann equation heat duty)

2.3 Script

HydDown comes with a script which can be used as a command-line tool to start calculations. If an input filename (path) is given as the first argument, this input file will be used. If no arguments are passed the script will look for an input file with the name input.yml. The content of the main script is shown below.

```
1 import yaml
   import sys
3 from hyddown import HydDown
4
5 if __name__ == "__main__":
6
       if len(sys.argv) > 1:
7
           input_filename = sys.argv[1]
       else:
8
           input_filename = "input.yml"
9
10
       with open(input_filename) as infile:
           input = yaml.load(infile, Loader=yaml.FullLoader)
13
14
15
       hdown=HydDown(input)
16
       hdown.run()
       hdown.verbose=1
17
18
       hdown.plot()
```

2.4 Module import

To use HydDown simple import the main calculation class HydDown.

```
1 from hyddown import HydDown
```

2.5 Input file examples

When using HydDown a dictionary holding all relevant input in order for HydDown to do vessel calculations shall be provide when the class is initialized. One way is to read an input file. For HydDown a Yaml format is chosen, but if JSON is a preference this should also work with the Yaml parser being substitued with a JSON parser.

An example of a minimal file for an isentropic vessel depressurisation (no heat transfer) is shown below

```
1 vessel:
    length: 1.524
3 diameter: 0.273
4 initial:
   temperature: 388.0
5
    pressure: 15000000.
6
7
    fluid: "N2"
8 calculation:
9 type: "isentropic"
10 time_step: 0.05
11 end_time: 100.
12 valve:
13 flow: "discharge"
14 type: "orifice"
15 diameter: 0.00635
16 discharge_coef: 0.8
17
     back_pressure: 101300.
```

A more elaborate example which includes heat transfer and with validation data (some data points dropped for simplicity) included:

```
1 vessel:
2 length: 1.524
3 diameter: 0.273
4 thickness: 0.025
5 heat_capacity: 500
6 density: 7800.
    orientation: "vertical"
8 initial:
9 temperature: 288.0
10 pressure: 15000000.
11
   fluid: "N2"
12 calculation:
13 type: "energybalance"
  time_step: 0.05
14
  end_time: 100.
15
16 valve:
17 flow: "discharge"
18 type: "orifice"
```

```
19 diameter: 0.00635
20
    discharge_coef: 0.8
21
     back_pressure: 101300.
22 heat_transfer:
23 type: "specified_h"
    temp_ambient: 288.
24
25 h_outer: 5
26 h_inner: 'calc'
27 validation:
28
    temperature:
29
     gas_high:
       time: [0.050285, ..., 99.994]
31
        temp: [288.93, ...,241.29]
32
       gas_low:
33
        time: [0.32393, ..., 100.11]
        temp: [288.67, ...,215.28]
34
       wall_low:
       time: [0.32276, ..., 100.08]
37
         temp: [288.93, ...,281.72]
       wall_high:
38
        time: [0.049115, ...,100.06]
39
40
         temp: [289.18, ...,286.09]
41
    pressure:
42
      time: [0.28869, ..., 98.367]
43
       pres: [150.02, ..., 1.7204]
```

2.6 Input fields and hierachy

In the following the full hierarchy of input for the different calculation types is summarised.

At the top level the following fields are accepted, with the last being optional and the second last dependant on calculation type:

```
initial: mandatory
vessel: mandatory
calculation: mandatory
valve: mandatory
heat_transfer: depends on calculation type
validation: optional
```

2.6.1 Calculation

The subfields under calculation, with value formats and options are:

```
1 calculation:
```

The simulation end time is specified as well as the fixed time step used in the integration of the differential equations to be solved. The four main calculation types are shown as well.

2.6.2 Vessel

```
vessel:
length: number, mandatory
diameter: number, mandatory
thickness: number, required when heat transfer is calculated
heat_capacity: number, required when heat transfer is calculated
density: number, required when heat transfer is calculated
orientation: string, required when heat transfer is calculated
```

2.6.3 Initial

```
1 initial:
2 temperature: number, mandatory
3 pressure: number, mandatory
4 fluid: string, mandatory , e.g. "N2", "H2"
```

2.6.4 Valve

The valve field determines the mode of the process is it for depressurisation/discharge from the vessel using the value discharge or if mass flow is entering the vessel, filling it up/increasign pressure with the value filling.

Different types of mass flow devices can be specified:

- Restriction orifice
- Relief valve/pressure safety valve (only for discharge not filling)
- Control valve (controlvalve)
- A specified mass flow (mdot)

For the physical devices a back_pressure is required for the flow calculations. The value of the back_pressure is also used to specify the reservoir pressure when the vessel is filled. See also Sec. 3.2 for details about the calculation of flow rates.

2.6.5 Heat transfer

For more information about the actual estimation of heat transfer see also Sec. 3.3. For the case of fire heat input predetermined parameters for the Stefan-Boltzmann fire equation are used to calculate different background heat loads cf. Tbl. 2.1

Table 2.1: Fire heat loads

Source	Fire type	Heat load (kW/m^2)
API521	Pool	60
API521	Jet	100
Scandpower	Pool	100
Scandpower	Jet	100

2.6.6 Validation

In order to plot measured data against simulated data the field validation is incldued.

The following arrays (one or more) are supported in the sub-field temperature:

- gas_high: highest measured values of the bulk gas
- gas_low: lowest measured values of the bulk gas
- gas_mean: average measured values of the bulk gas
- wall_mean: average measured values of the vessel (inner) wall
- wall_high i.e. highest measured values of the vessel (inner) wall
- wall_low i.e. lowest measured values of the vessel (inner) wall

For each of the above fields arrays for timeand tempshall be supplied with matching length.

A field for measured vessel pressure is also possible, wheer timeand pres shall be identical length arrays. See also example below.

```
1 validation:
    temperature:
2
3
     gas_high:
        time: [0.050285, ..., 99.994]
4
5
        temp: [288.93, ...,241.29]
       gas_low:
6
        time: [0.32393, ..., 100.11]
7
8
        temp: [288.67, ...,215.28]
9
       wall_low:
        time: [0.32276, ..., 100.08]
10
11
         temp: [288.93, ...,281.72]
       wall_high:
12
         time: [0.049115, ..., 100.06]
13
14
         temp: [289.18, ...,286.09]
15
     pressure:
       time: [0.28869, ..., 98.367]
16
17
       pres: [150.02, ..., 1.7204]
```

3 Theory

In this chapter the basic theory and governing equations for the model implementation in HydDown is presented. The following main topics are covered:

- thermodynamics
- mass transfer
- heat transfer

3.1 Thermodynamics

3.1.1 Equation of state

The equation of state used by HydDown is the Helmholtz energy formulation as implemented in CoolProp (Bell et al. 2014). Most of the text in the present section has been sourced from the CoolProp documentation to be as accurate and true to the source as possible. The Helmholtz energy formulation is a convenient construction of the equation of state because all the thermodynamic properties of interest can be obtained directly from partial derivatives of the Helmholtz energy.

It should be noted that the EOS are typically valid over the entire range of the fluid, from subcooled liquid to superheated vapor, to supercritical fluid. In general, the EOS are based on non-dimensional terms δ and τ , where these terms are defined by

$$\delta = \rho/\rho_c$$

$$\tau = T_c/T$$

where ρ_c and T_c are the critical density of the fluid if it is a pure fluid. For pseudo-pure mixtures, the critical point is typically not used as the reducing state point, and often the maximum condensing temperature on the saturation curve is used instead.

The non-dimensional Helmholtz energy of the fluid is given by

$$\alpha = \alpha^0 + \alpha^r$$

where α^0 is the ideal-gas contribution to the Helmholtz energy, and α^r is the residual Helmholtz energy contribution which accounts for non-ideal behavior. For a given set of δ and τ , each of the terms α^0 and α^r are known. The exact form of the Helmholtz energy terms is fluid dependent, but a relatively simple example is that of Nitrogen, which has the ideal-gas Helmholtz energy of

$$\alpha^{0} = \ln \delta + a_{1} \ln \tau + a_{2} + a_{3}\tau + a_{4}\tau^{-1} + a_{5}\tau^{-2} + a_{6}\tau^{-3} + a_{7} \ln[1 - \exp(-a_{8}\tau)]$$

and the non-dimensional residual Helmholtz energy of

$$\alpha^{r} = \sum_{k=1}^{6} N_{k} \delta^{i_{k}} \tau^{j_{k}} + \sum_{k=7}^{32} N_{k} \delta^{i_{k}} \tau^{j_{k}} \exp(-\delta^{l_{k}}) + \sum_{k=33}^{36} N_{k} \delta^{i_{k}} \tau^{j_{k}} \exp(-\phi_{k} (\delta - 1)^{2} - \beta_{k} (\tau - \gamma_{k})^{2})$$

and all the terms other than δ and τ are fluid-dependent correlation parameters.

The other thermodynamic parameters can then be obtained through analytic derivatives of the Helmholtz energy terms. For instance, the pressure is given by

$$p = \rho RT \left[1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau} \right]$$

and the specific internal energy by

$$\frac{u}{RT} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right]$$

and the specific enthalpy by

$$\frac{h}{RT} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right] + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau} + 1$$

which can also be written as

$$\frac{h}{RT} = \frac{u}{RT} + \frac{p}{\rho RT}$$

The specific entropy is given by

$$\frac{s}{R} = \tau \left[\left(\frac{\partial \alpha^0}{\partial \tau} \right)_{\delta} + \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta} \right] - \alpha^0 - \alpha^r$$

and the specific heats at constant volume and constant pressure respectively are given by

$$\frac{c_v}{R} = -\tau^2 \left[\left(\frac{\partial^2 \alpha^0}{\partial \tau^2} \right)_{\delta} + \left(\frac{\partial^2 \alpha^r}{\partial \tau^2} \right)_{\delta} \right]$$

$$\frac{c_p}{R} = \frac{c_v}{R} + \frac{\left[1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta}\right)_{\tau} - \delta \tau \left(\frac{\partial^2 \alpha^r}{\partial \delta \partial \tau}\right)\right]^2}{\left[1 + 2\delta \left(\frac{\partial \alpha^r}{\partial \delta}\right)_{\tau} + \delta^2 \left(\frac{\partial^2 \alpha^r}{\partial \delta^2}\right)_{\tau}\right]}$$

The EOS is set up with temperature and density as the two independent properties, but often other inputs are known, most often temperature and pressure because they can be directly measured. As a result, if the density is desired for a known temperature and pressure, it can be obtained iteratively.

3.1.2 First law for flow process

The control volume sketched in Fig. 3.1, seprated from the surrounding by a control surface, is used as a basis for the analysis of an open thermodynamic system with flowing streams (fs) in and out, according to (Smith, Van Ness, and Abbott 1996)

A general mass balance or continuity equation can be written:

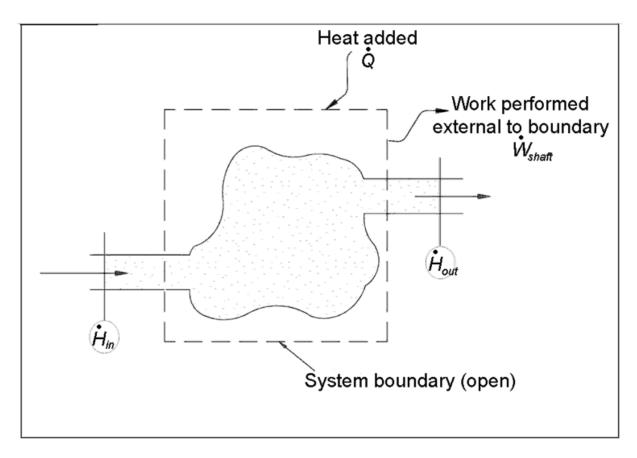


Figure 3.1: Control volume with one entrance and one exit. The image has been sourced from (WikiMedia 2008,).

$$\frac{m_{cv}}{dt} + \Delta \left(\dot{m}\right)_{fs} = 0 \tag{3.1}$$

The first term is the accumulation term i.e. the rate of change of the mass inside the control volume , $m_c v$, and the Δ in the second term represents the difference between the outflow and the inflow

$$\Delta \left(\dot{m}\right)_{fs} = \dot{m}_2 - \dot{m}_1$$

An energy balance for the control volume, with the first law of thermodynamics applied, needs to account for all the energy modes with can cross the control surface. Each stream has a total energy

$$U + \frac{1}{2}u^2 + zg$$

where the first term is the specfic internal energy, the second term is the kinetic energy and the last

term is the potential energy. The rate at which each stream transports energy in or out of the control volume is given by

$$\dot{m}(U + \frac{1}{2}u^2 + zg)$$

and in total

$$\Delta \left[\dot{m}(U + \frac{1}{2}u^2 + zg) \right]_{fs}$$

Further work (not to be confused with shaft work) is also associated with each stream in order to move the stream into or out from the control volume (one can think of a hypothetical piston pushing the fluid at constant pressure), and the work is PV on the basis of the specific fluid volume. The work rate for each stream is

$$\dot{m}(PV)$$

and in total

$$\Delta \left[\dot{m}(PV)\right]_{fs}$$

Further, heat may be transferred to (or from) the control volume at a rate \dot{Q} and shaft work may be applied, \dot{W}_{shaft} . Combining all this with the accumulation term given by the change in total internal energy the following general energy balance can be written

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\dot{m}(U + \frac{1}{2}u^2 + zg) \right]_{fs} + \Delta \left[\dot{m}(PV) \right]_{fs} = \dot{Q} + \dot{W}_{shaft}$$

Applying the relation H=U+PV, setting $\dot{W}_{shaft}=0$ since no shaft work is applied to the vessel, and assmuning that kinetic and potential energy changes can be omitted the energy balance simplifies to

$$\frac{d(mU)_{cv}}{dt} + \Delta \left[\dot{m}H\right]_{fs} = \dot{Q}$$

The equation can be further simplified if only a single port acting as either inlet or outlet is present

$$\frac{d(mU)_{cv}}{dt} + \dot{m}H = \dot{Q} \tag{3.2}$$

where the sign of \dot{m} determines if the control volume is either emptied of filled. The continuity equation eq. 3.1 and the energy balance eq. 3.2 combined with the equation of state are the key equations that shall be solved/intergrated in order to calculate the change in temperature and pressure as a function of time.

3.2 Flow devices

3.2.1 Restriction Orifice

When a fluid flows through a constriction or opening such as an orifice, the velocity will be affected by conditions upstream and downstream. If the upstream pressure is high enough, relative to the downstream pressure, the velocity will reach the speed of sound (Ma = 1) and the flow rate obtained will be the critical flow rate. The maximum downstream pressure for the flow to still be sonic (Ma = 1), is when $P_d = P_c$. The ratio of the critical and upstream pressure is defined by equation eq. 3.3.

$$\frac{P_c}{P_u} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} \tag{3.3}$$

- P_c is the critical pressure. [kPa]
- P_d is the downstream pressure. [kPa]
- P_u is the upstream pressure. [kPa]
- k is the isentropic expansion factor, approximated by the ideal gas heat capacity ratio C_p/C_v . [-]

In order to calculated the mass flow rate through an orifice equation 5.49 is used based on literature from the Committee for the Prevention of Disasters (Bosch and Weterings 2005). It is assumed that only gas exits the orifice, as the PSV is positioned on the top of the vessel

To account for the difference in choked and non-choked flow a set limit pressure is introduced as in equation eq. 3.4. If the downstream pressure, P_{down} , is below the pressure limit, \$ P_{limit}\$, then the flow is choked, and the pressure used, P_{used} , in equation eq. 3.5 should be the pressure limit, P_{limit} . Otherwise if the downstream pressure, P_{down} , is greater than or equal to the pressure limit, P_{limit} , the flow is no longer choked and the pressure used should be the downstream pressure, P_{down} (Bosch and Weterings 2005).

$$P_{limit} = P_{up} \cdot \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}} \tag{3.4}$$

$$\dot{m}_{flow} = C_d \cdot A \cdot \sqrt{\left(\frac{2k}{k-1}\right) \cdot P_{up} \cdot \rho \cdot \left(\frac{P_{used}}{P_{up}}\right)^{\frac{2}{k}} \left(1 - \left(\frac{P_{used}}{P_{up}}\right)^{\frac{k-1}{k}}\right)}$$
(3.5)

- ρ is the density of the gas upstream. $[kg/m^3]$
- P_{limit} is the pressure limit of the upstream absolute pressure. [bara]
- P_{up} is the absolute pressure upstream of the orifice. [bara]
- k is the ratio of the heat capacities at constant pressure, C_p , and at constant volume, C_v .
- P_{down} is the absolute pressure downstream of the orifice. [bara]
- P_{used} is the pressure used in the mass flow equation based on choked or non-coked conditions. [bara]
- \dot{m}_{flow} is the mass flow through the orifice. [kg/s]
- C_d is the discharge coefficient of the orifice opening. [-]
- A is the cross sectional area of the orifice. $[m^2]$

3.2.2 Pressure safety valve / Relief valve

A PSV / relief valve is a mechanical device actuated by the static pressure in the vessel and a conventional PSV is often used for gas/vapor systems. A conventional PSV is a spring-loaded device which will activate at a predetermined opening pressure, and relieve the vessel pressure until a given reseat pressure has been reached. Both the opening pressure and the reset pressure is above the vessel operating pressure, and the PSV will remain closed until the pressure inside the vessel increases to the opening pressure. The operation of a conventional spring-loaded PSV is based on a force balance. A conventional PSV can be seen in Fig. 3.2. A spring exerts a force on a disc blocking the inlet of the PSV. When the pressure inside the vessels reaches the opening pressure, the force exerted on the disc by the gas, will be larger than the force exerted by the spring and the PSV will open and allow the gas to flow out of the vessels. The flow of gas out of the vessels will lower the pressure and thereby also the force exerted on the disc. When the pressure in the vessels is reduced to the reset pressure, the PSV will close and the disc will again hinder the gas flow.

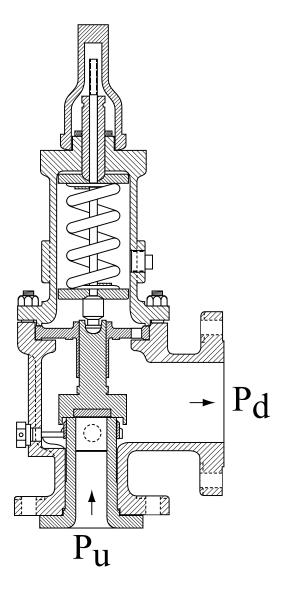


Figure 3.2: Conventional/pop action PSV adapted from (Eriksen and Bjerre 2015) and (API 2014)

The relief valve model implemented in HydDown is the API 520 equations (API 2014) for gas relief for both sonic/critical as well as subcritical flow. No corrections factors are implemented in HydDown.

For sonic flow (critical flow), as indicated in equation, the mass flow thorugh the PSV can be determined by equation eq. 3.6.

$$W = \frac{AC \cdot K_d \cdot K_b \cdot K_c \cdot P_1}{\sqrt{\frac{T \cdot Z}{M}}} \tag{3.6}$$

- A is the effective discharge area. [mm²]
- W is the mass flow through the device. [kg/h]

- C is a coefficient, as a function of k, as defined in equation eq. 3.7.
- K_d , K_b , and K_c are correction factors.
- P_1 is the allowable upstream absolute pressure. [kPa]
- T is the temperature of the inlet gas at relieving conditions. [K]
- M is the molecular mass of the gas at relieving conditions. [kg/kmol]
- Z is the compressibility factor for the gas.

 K_d is the effective coefficient of discharge, with a typical value of 0.975, for an installed PSV. K_b is a back-pressure correction factor between 0 and 1, assumed to be 1. K_c is a correction factor used when a rupture disk is installed upstream, otherwise it is 1. In the present implementation a value of 1 is assumed.

$$C = 0.03948\sqrt{k\left(\frac{2}{k+1}\right)^{\left(\frac{k+1}{k-1}\right)}}$$
 (3.7)

For subsonic flow (subcritical flow), the effective discharge area of the PSV is determined by equation eq. 3.8.

$$W = \frac{A \cdot F_2 \cdot K_d \cdot K_c}{17.9 \sqrt{\frac{T \cdot Z}{M \cdot P_1 \cdot (P_1 - P_2)}}}$$
(3.8)

 F_2 is the coefficient of subcritical flow which can be determined from eq. 3.9.

$$F_2 = \sqrt{\left(\frac{k}{k-1}\right)r^{\left(\frac{2}{k}\right)}\left(\frac{1-r^{\left(\frac{k-1}{k}\right)}}{1-r}\right)}$$
(3.9)

where r is the ratio of backpressure to upstream relieving pressure, P_2/P_1 .

When modelling a pop action PSV/relief valve under dynamic conditions, the valve will go from closed to fully open in a short period of time when the set pressure, P_{set} , is reached. The pop action is illustrated in Fig. 3.3 which shows the opening and closing hysteresis of the PSV as a function of pressure. In order to close the shall be reduced below the reseat pressure.

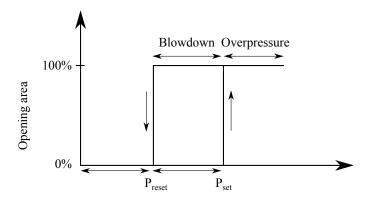


Figure 3.3: Relief valve hysteresis adapted from (Eriksen and Bjerre 2015)

When specifying PSV's it is comon to use standrd API sizes as shown in tbl. 3.1

Table 3.1: Standard PSV orifice sizes according to API

Size	Area [in ²]	Area [m ²]
D	0.110	$7.09676 \cdot 10^{-5}$
Ε	0.196	$1.26451 \cdot 10^{-4}$
F	0.307	$1.98064 \cdot 10^{-4}$
G	0.503	$3.24515 \cdot 10^{-4}$
Н	0.785	$5.06450 \cdot 10^{-4}$
J	1.287	$8.30320 \cdot 10^{-4}$
K	1.838	$1.18580 \cdot 10^{-3}$
L	2.853	$1.84064 \cdot 10^{-3}$
М	3.600	$2.32257 \cdot 10^{-3}$
N	4.340	$2.79999 \cdot 10^{-3}$
Р	6.380	$4.11612 \cdot 10^{-3}$
Q	11.050	$7.12901 \cdot 10^{-3}$
R	16.000	$1.03225 \cdot 10^{-2}$
T	26.000	$1.67741 \cdot 10^{-2}$

3.2.3 Control Valve

For calculating the the mass flow through a control valve the ANSI/ISA (Borden 1998)(ISA 1995) methodology also described in IEC 60534 (IEC 2011).

The flow model for a compressible fluid in the turbulent regime is

$$W = CN_6F_PY\sqrt{x_{sizing}p_1\rho_1}$$

or equivalent

$$W = CN_8 F_P Y \sqrt{\frac{x_{sizing} M}{T_1 Z_1}}$$

- C is the flow coefficient (C_v or K_v)
- N_8 is a unit specific constant, 94.8 for C_v and bar as pressure unit
- F_P is a piping geometry factor [-]
- Y is the expansion factor [-]
- x_{sizing} is is the pressure drop used for sizing[-]
- p_1 is the upstream pressure [bar]
- ρ_1 is the upstream density [kg/m³]
- M is the molecular weight [kg/kmol]
- T_1 is the upstream temperature [K]
- Z_1 is the upstream compressibility [-]

In HydDown the piping geometry factor is not yet implemented and assumed to be 1. The pressure drop ratio x_{sizing} used for sizing is determined as the lesser of the actual pressure drop ratio, x, and the choked pressure drop ratio x_{choked} . The actual pressure drop ratio is given by:

$$x\frac{\Delta p}{p_1}$$

The pressure drop ratio at which flow no longer increases with increased value in pressure drop ratio, is the choked pressure drop ratio, given by the following equation

$$x_{choked} = F_{\gamma} x_{TP}$$

The factor x_T is based on air near atmospheric pressure as the flowing fluid with a specific heat ratio of 1.40. If the specific heat ratio for the flowing fluid is not 1.40, the factor F_{γ} is used to adjust x_T . Use the following equation to calculate the specific heat ratio factor:

$$F_{\gamma} = \frac{\gamma}{1.4}$$

where γ is the ideal gas C_p/C_v . It should be noted that the above equation has been derived from perfect gas behaviour and externsion of an orifice model with γ in the range of 1.08 to 1.65. If used outside the assumptions flow calculations may become inaccurate.

The expansion factor Y accounts for the change in density as the fluid passes from the valve inlet to the vena contracta. It also accounts for the change in the vena contracta area as the pressure differential is varied.

$$Y = 1 - \frac{x_{sizing}}{3x_{choked}}$$

3.3 Heat transfer

3.3.1 Natural convection

Experiments have indicated that the internal heat transfer mechanism for a vessel subject to depressurisation can be well approximated by that of natural convection as found from measured Nusselt numbers being well correlated with Rayleigh number, with no apparent improvement in model performance by included the Reynold number (Woodfield, Monde, and Mitsutake 2007).

To determine the heat transfer for the gas-wall interface, Newton's law of cooling is applied, as given in equation eq. 3.10.

$$\frac{dQ}{dt} = -hA(T_s - T_{gas}) \tag{3.10}$$

- dQ is the change in thermal energy due to convective heat transfer. [J]
- dt is the change in time during the heat transfer. [s]
- h is the convective heat transfer. [W/m 2 · K]
- A is the area normal to the direction of the heat transfer. $[m^2]$
- T_s is the surface temperature of the geometry. [K]
- T_{gas} is the temperature of the surrounding gas. [K]

Equation [eq. ??] indicates the heat transfer to the surface of any geometry such as a plate or cylindrical wall, by means of heat convection from its surroundings (Çengel and Ghajar 2011)(Geankoplis 1993).

The convective heat transfer will need to be estimated for the the gas-wall interface, by the use of empirical relations for the Nusselt number. The Nusselt number describes the ratio of convective heat transfer to conductive heat transfer, normal to a surface area, as given in equation eq. 3.11.

$$Nu = \frac{hL}{k} \tag{3.11}$$

- Nu is the Nusselt number. [-]
- h is the convective heat transfer. [W/m²·K]
- L is a characteristic length of the geometry. [m]
- k is the thermal conductivity of the gas. [W/m·K]

The characteristic length L used is the height of the gas volume.

The empirical correlations used to calculate the Nusselt number of the gas-wall interface is a function of the Rayleigh number, which can be defined by the Grashof number and Prandtl number, as in equation eq. 3.12.

$$Ra = Gr \cdot Pr \tag{3.12}$$

- Ra is the Rayleigh number. [-]
- Gr is the Grashof number. [-]
- Pr is the Prandtl number. [-]

The Grashof number is a dimensionless number which approximates the ratio of the buoyancy forces to viscous forces, as given in equation [eq. 3.13]. The Prandtl number is a dimensionless number defined as the ratio of the momentum diffusivity to thermal diffusivity, as given in equation eq. 3.14.

$$Gr = \frac{\beta g \rho^2 L^3 \Delta T}{\mu^2} \tag{3.13}$$

$$Pr = \frac{c_p \mu}{k} \tag{3.14}$$

- β is the coefficient of volume expansion. [1/K]
- g is the standard acceleration of gravity. [m/s²]
- ρ is the gas density. [kg/m³]
- ullet L is the characteristic length. [m]
- ΔT is the temperature difference of the surface and gas. [K]
- μ is the dynamic viscosity. [kg/m·s]
- c_p is the heat capacity of gas. [J/kg·K]
- k is the thermal conductivity of gas. [J/m·K]

It is important to note that the properties in the above equations shall be evaluated at the fluid film temperature which can be approximated by the average of the the fluid bulk temperature and the vessel wall temperature (Geankoplis 1993).

3.3.2 Mixed convection

Experiments have indicated that the internal heat transfer mechanism for a vessel subject to filling can be well approximated by that of combined natural convection and forced convenction as found from measured Nusselt numbers being well correlated with Rayleigh and Reynolds number (Woodfield, Monde, and Mitsutake 2007).

For mixed convection the effective Nusselt number, Nu, can be approximated by

$$Nu = (Nu_{forced}^n + Nu_{natural}^n)^{\frac{1}{n}}$$

During charging with different gases (H_2 , N_2 and Argon), Woodfield *et al.* demonstrated that in roder to provide a good fit to the experimentally determined Nusselt number a correlation based on both Reynolds and Rayleigh number was necessary. They found a good fit with the following formula (n=1)

$$Nu = Nu_{forced} + Nu_{natural} = 0.56Re_d^{0.67} + 0.104Ra_H^{0.352}$$

3.3.3 Conduction

For accurate prediction of the outer and especially the inner wall temperature for correct estimation of internal convective heat transfer and the average materials temperature, the general equation of 1-D unsteady heat transfer shall be solved:

$$\frac{\delta T}{\delta t} = \frac{k}{C_p} \frac{\delta^2 T}{\delta x^2}$$

- T is temperature
- x is the spatial (1-D) coordinate
- · k is the thermal conductivity
- C_p is the heat capacity

Here it is written in Cartesian coordinates, but for most applications to pressure equipment, cylindrical coordinates are applicable, at elast for the shell. To be solved the initial values and boundary values must be specified. In its present state HydDown does not include the unsteady heat tranfer model i.e. the assumption is that the temperature from outer to inner surface is uniform and equal to the average temperature. This is obviously a crude approaximation, but might be justified depending in the Biot number:

$$Bi = \frac{hL}{k}$$

The Biot number is a simple measure of the ratio of the heat transfer resistances at the surface of a body to the inside of a body. The ratio gives an indication to which extent the temperature will vary in space (gradient) when the body is subject to a displacement in temeprature at the surface boundary layer. Striednig *et al.* (Striednig et al. 2014) concluded that for a type I (steel) cylinder the Biot number was approx. 0.03 and hence the error in assuming a uniform temperature in the vessel wall was low.

With a typical thermal conductivity of 45 W/mK for steel and a heat transfer coefficient up to 600 W/m^2K (Woodfield, Monde, and Mitsutake 2007) the Biot number for a vessel with a wall thichness of 2 cm is 0.27. This is significant higher that approximated by (Striednig et al. 2014). Anyway, the Biot number is lower than 1, and the assumption of a uniform temperature is reasonable. However, for increased wall thicness, and/or for different materials with lower thermal conductivity the error may grow to an unacceptable level.

3.3.4 Fire heat loads

The heat transfer from the flame to the shell is modelled using the recommended approach from Scandpower (Hekkelstrand and Skulstad 2004). The heat transfer from the flame to the vessel shell is divided into radiation, convection and reradiation as seen in equation eq. 3.15.

$$q_f = \underbrace{\alpha_s \cdot \varepsilon_f \cdot \sigma \cdot T_f^4}_{\text{Radiation}} + \underbrace{h_f \cdot (T_f - T_s(t))}_{\text{Convection}} - \underbrace{\varepsilon_s \cdot \sigma \cdot T_s(t)^4}_{\text{Reradiation}}$$
(3.15)

- q_f is the flame heat flux. [W/m²]
- α_s is the vessel surface absorptivity. [-]
- ε_f is the flame emissivity. [-]
- σ is the Stefan-Boltzmann constant, σ = $5.67 \cdot 10^{-8}$ [W/m $^2 \cdot$ K 4]
- T_f is the flame temperature. [K]
- h_f is the convection heat transfer coefficient between the flame and the surface. [W/m 2 ·K]
- $T_s(t)$ is the time dependent surface temperature. [K]
- ε_s is the surface emissivity. [-]

This model assumes that the pressure vessel is fully engulfed by the flame. This means that the view factor for the radiation is unity and is therefore not taken into consideration. The convective heat transfer coefficients for a jet fire and a pool fire, and recommended values for the emissivity and absorptivity, are given by Scandpower as (Hekkelstrand and Skulstad 2004)

- $h_{iet\ fire} = 100 \, [W/m^2 \cdot K]$
- $h_{pool\ fire}$ = 30 [W/m²·K]
- $\alpha_s = 0.85$

- ε_s = 0.85
- $\varepsilon_f = 1.0$ (optical thick flames, thickness > 1 m)

The flame temperature is found by solving equation eq. 3.16 for the incident heat flux in relation to the ambient conditions. The flame temperature is kept constant throughout the simulation.

$$q_{total} = \sigma \cdot T_f^4 + h_f \cdot (T_f - T_{amb}) \tag{3.16}$$

- q_{total} is the incident flame heat flux as given in table tbl. 3.2. [W/m²]
- T_{amb} is the ambient temperature pprox 293 K (20 $^{\circ}$ C)

The heat flux used to calculate the flame temperature is given in table tbl. 3.2.

Table 3.2: Incident heat fluxes for various fire scenarios given by Scandpower (Hekkelstrand and Skulstad 2004)

	Small jet fire [kW/m²]	Large jet fire [kW/m²]	Pool fire [kW/m²]
Peak heat load	250	350	150
Background heat load	0	100	100

3.4 Model implementation

A simple (naive) explicit Euler scheme is implemented to integrate the mass balance over time, with the mass rate being calculated from an orifice/valve equation. For each step, the mass relief/ left in the vessel is known. Since the volume is fixed the mass density is directly given. For the calculation methods (isentropic,isenthalpic,isenergetic etc), Coolprop allows specifying density and either H,S or U directly - this is very handy and normally only TP, PH, TS property pairs are implemented, and you would need to code a second loop to make it into am UV, VH or SV calculation. Coolprop is very convenient for this, however for a cubic EOS and for multicomponent Helmholtz energy EOS coolprop only supports a subset of state variables to be specified directly (T,P,quality). For this reason single component HEOS is the main target of this project.

- **3.4.1** Isothermal process
- 3.4.2 Isentropic process
- 3.4.3 Isenthalpic process

4 Validation

The code is provided as-is. However, comparisons have been made to a few experiments from the literature.

The following gases and modes are considered:

- High pressure hydrogen filling
- High pressure hydrogen discharge
- · High pressure nitrogen discharge
- Low pressure air discharge
- · Low pressure air filling

4.1 Hydrogen discharge

Calculations with HydDown for high pressure hydrogen vessel discharge has been compared to three experiments from (Byrnes, Reid, and Ruccia 1964). Byrnes *et al.* (Byrnes, Reid, and Ruccia 1964) have reported a number of rapid depressurisation experiments using bith nitrogen and hydrogen, with blowdown times being varied between 14 seconds to 33 minutes. The vessel used was a type "K" gas cylinder with a volume of 0.0499 m³, an ID of 8.56 inched and shell length of 55 inches. The vessel is placed in a vertical position. A control valve is mounted on the neck of the cylinder with a fixed opening percentage during each experiment, set to provide the required depressurisation rate. It is mentioned that the gas cylinder is placed inside a weather proof cabinet with perlite insulation in order to emulate adiabatic conditions, however the simulation run here are with a finte heat transfer coefficient on the outside of the cylinder. In their paper detailed pressure and temperature traces are provided for thre experimental runs: 7, 8, and 9 with depressurisation from 2,000 psia in 30 seconds, 480 seconds and 14 seconds, respectively. These experiments are simulated in Fig. 4.1, Fig. 4.2 and Fig. 4.3.

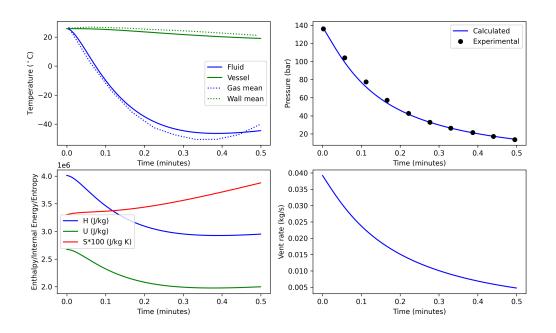


Figure 4.1: Calculations of hydrogen discharge experiment run 7 from (Byrnes, Reid, and Ruccia 1964). The figure shows calculated gas and wall temperature (full lines) compared to experiments (upper left), calculated and experimental pressure (upper right), specific thermodynamic state variables (lower left), and the calculated vent rate (lower right).

The figure layout is general for all the validation studies conducted and will described in brief for eased readability. Each experiement figure is divided in 4 subplots; the upper left shows the simulated bulk gas temperature and vessel wall (average) temperature with measured values include (if available), the upper rigth shows the simulated and measured pressure (if available), the lower left shows the specific enthalpy, specific internal energy and the specific entropy of the bulk gas content as a function of time, the lower right shows the simulated mass rate leaving or entering the vessel.

As seen from Fig. 4.1, Fig. 4.2 and Fig. 4.3, the calculations generally compare well with the experimental results. The faster depressurisation times are predicted the best it seems as seen from run 7 and 9. The much slower run 8 does not have as a good a fit, considering the bulk gas temperature. However, on an absolute scale the results are still within 5°C of the experimentally determined gas temperature. The trend in *goodness of fit* could indicate that the heat transfer from the outside of the vessel to the gas lacks some details, which become detectable at the very slow depressurisation. For the fast depressurisation the heat transfer from the outside is of less importance and the inside heat transfer coefficient may be predicted better.

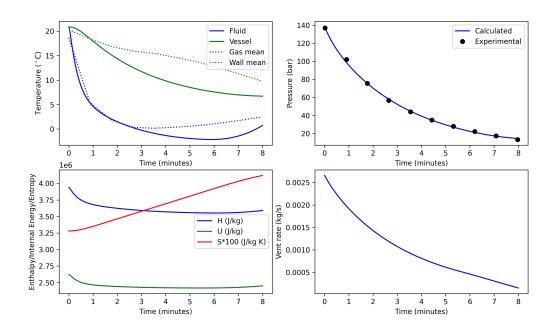


Figure 4.2: Simulation of run 8 from (Byrnes, Reid, and Ruccia 1964).

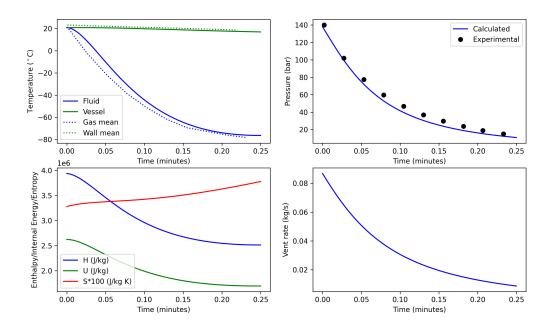


Figure 4.3: Simulation of run 9 from (Byrnes, Reid, and Ruccia 1964).

4.2 Hydrogen filling

4.3 Nitrogen discharge

Calculations with HydDown is compared to experiment I1 from ref. (Haque et al. 1992). The experiment is a blowdown of a vertically oriented cylindrical vessel with flat ends. The vessel length is 1.524 m, the inside diameter is 0.273 m and the wall thickness is 25 mm. The vessel is filled with N_2 at 150 bar, at 15°C. Ambient temperature is 15°C. The blowdown orifice diameter is 6.35 mm. The results are shown in Fig. 4.4. The didirscharge coefficient of the orifice has been set to 0.8 in order to match the vessel pressure profile. The back pressure is set to atmospheric conditions.

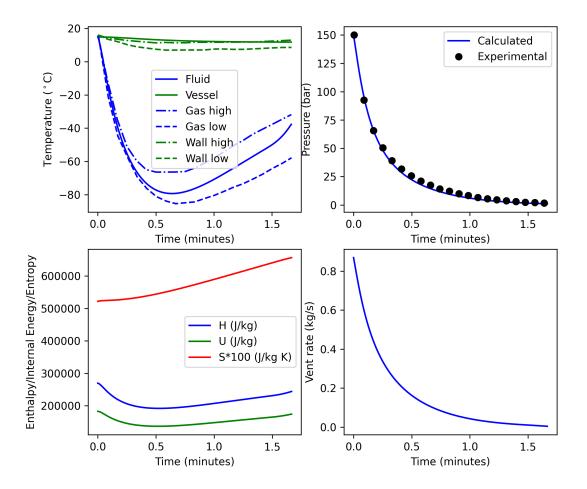


Figure 4.4: Calculations of nitrogen discharge emulating experiment I1 from (Haque et al. 1992). The figure shows calculated gas and wall temperature (full lines) compared to experiments (upper left), calculated and experimental pressure (upper right), specific thermodynamic state variables (lower left), and the calculated vent rate (lower right).

As seen from Fig. 4.4, the calculations compare well with the experimental results. The calculated temperature of the bulk vapor is within the experimental range of measured temperature at all times during the simulation. It is also noted that the minimum temperature is reached at approx. the same time as in the experiments. The calculated vessel inner wall temperature does not decline as rapidly as the experiments—but from around a calculation time of 60 s, the temperature is within the experimentally observed inner wall temperature. The main reason for the inability to match the vessel wall temperature is that the model ignores the temperature gradient from the outer to the inner wall

surface and uses an average material temperture. Especially at the beginning of the discharge it is considered likely that a significant temperature gradient will exist.

4.4 Air discharge/filling

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