

Health effects due to evaporation of (hazardous) liquids



More than 5000 liters of ink was spilled from storage containers (Source: Kent Fire and Rescue).

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1 Introduction

When liquids are released somewhere, the liquid vapor can have an effect on human health. Various factors play a role in this, for example vapor pressure, threshold limit values and dispersion. During a hazard identification, such as a HAZOP study, scenarios are often discussed in which a spill of a certain substance from a process installation is a potential danger. Sometimes it is quite difficult to determine the dangers of such a chemical release. There are various complex software packages that can calculate how much liquid will be released in case of such an event and subsequently determine the concentration of the chemical (vapor) in the air using dispersion calculations. This report will focus on some theory first with regard to vapor pressure, dispersion calculations and threshold limit values. A number of sources for chemical properties and threshold limit values are discussed and two simple (free) tools are presented for performing dispersion calculations. Two examples are included in which the theory is applied.

2 Theory

2.1 Vapor pressure

The vapor pressure is the pressure that the vapor (gas) of a certain substance exerts on the walls of a closed space. Usually mbar or kPa is used as a unit to display the vapor pressure. The vapor pressure depends on the temperature and volatility of the substance.

Water has a vapor pressure of 23 mbar (2,3 kPa) at 20°C. At a temperature of 50°C, the vapor pressure of water is 123 mbar. At 100°C the vapor pressure is 1013 mbar, equal to 1 atm; the water will boil. As soon as the vapor pressure becomes equal to the ambient pressure, the liquid will boil.

The vapor pressures at 20°C and 50°C are shown below for a number of substances. It is only a small selection of substances, but it is clear from this that the vapor pressure can vary greatly between different substances.

Substance	Vapor pressure 20°C (mbar)	Vapor pressure 50°C (mbar)
Acetone	247	814
Ethanol	59	293
Ethylene glycol	0,1	1,1
Hexane	162	540
Water	23	123

Acetone has a high vapor pressure. At 50°C it is 814 mbar (0,8 atm), which means that the substance is almost at the boiling point. The boiling point is 56°C. Ethylene glycol, for example, has a very low vapor pressure.

The Antoine equation can be used to approximate the vapor pressure at different temperatures.

$$\log_{10} P_{DS} = A - \frac{B}{T + C}$$

Which can be rewritten to:

$$P_{DS} = 10^{\left[A - \frac{B}{T+C}\right]}$$

In Which P_{DS} is the vapor pressure, T the temperature and A , B and C are the so-called Antoine coefficients. These values differ per substance and are determined for various substances and

temperature ranges. The values will always state which units of pressure and temperature are applicable.

For ethanol, these Antoine coefficients have been determined for various temperature ranges. Below is an example of a set of coefficients.

A	B	C	T
5,37229	1670,409	-46,424	273 – 351,7 K

(vapor pressure in bar and temperature in Kelvin)

If we use these values in the Antoine equation for 20°C (293,15 K) and 50°C (323,15 K) then this yields the following vapor pressure:

$$P_{DS}(293,15 K) = 10^{\left[5,37229 - \frac{1670,409}{293,15 - 46,424}\right]} = 0,0587 \text{ bar} = 58,7 \text{ mbar}$$

$$P_{DS}(323,15 K) = 10^{\left[5,37229 - \frac{1670,409}{323,15 - 46,424}\right]} = 0,294 \text{ bar} = 294 \text{ mbar}$$

These values are very close to the documented values of 59 and 293 mbar.

Antoine coefficients can be found in the literature, for example the [NIST Chemistry WebBook](#). This database also contains a lot of information about other chemical properties.

2.2 Saturated vapor concentration

The saturated vapor concentration can be calculated from the vapor pressure.

$$C[\text{vol}\%] = \frac{P_{DS} [\text{mbar}]}{P_{Total} [\text{mbar}]} \times 100\%$$

$$C[\text{ppm}] = \frac{P_{DS} [\text{mbar}]}{P_{Total} [\text{mbar}]} \times 1.000.000 \text{ ppm}$$

In which C is the saturated vapor concentration in $\text{vol}\%$, P_{DS} is the vapor pressure in mbar and P_{Total} is the total pressure in mbar .

In case of atmospheric pressure ($\sim 1000 \text{ mbar}$), the formulas below apply.

$$[\text{vol}\%] = \frac{P_{DS} [\text{mbar}]}{1.000 [\text{mbar}]} \times 100\%$$

$$C[\text{ppm}] = \frac{P_{DS} [\text{mbar}]}{1.000 [\text{mbar}]} \times 1.000.000 \text{ ppm} = P [\text{mbar}] \times 1.000$$

Monochloroacetic acid (MCA, 80% in water) has a vapor pressure of 16 mbar at 20°C. When MCA is stored in an atmospheric tank, the vapor in the vapor space in the top of the tank will become saturated with MCA vapor. The saturation concentration above the liquid will then be:

$$C = \frac{16 [\text{mbar}]}{1000 [\text{mbar}]} \times 100\% = 1,6 \text{ vol}\%$$

$$C = \frac{16 [\text{mbar}]}{1000 [\text{mbar}]} \times 1.000.000 \text{ ppm} = 16.000 \text{ ppm}$$

With an emission of MCA vapor from the tank, the initial concentration (directly at the opening) will therefore be around 16.000 ppm. The life-threatening value of MCA is around 50 ppm. Depending on

where this emission takes place and the degree of ventilation and air renewal, this can be a very serious concern for health.

2.3 Dispersion calculations

To be able to assess the hazards of the vaporizing of a substance in the event of a spill (LOC - Loss of Containment), it is important to be able to estimate or calculate the amount of the substance that can be released.

This may involve a relatively small opening in a pipe or a tank, for example due to a failing flange joint, an unintentionally open drain valve or corrosion of material. But it can also be a (catastrophic) crack in a tank where a large amount of chemicals is released at once.

When a hole exists in a tank or pipe, the substance will come out at a certain speed. The speed is determined by, among other things, the pressure in the system, temperature of the substance, substance properties such as boiling point, vapor pressure, molecular weight and density and of course the size of the hole.

It is often interesting to subsequently determine how much of this substance will be released as vapor, the so-called Airborne Quantity. In the case of liquids, there are generally three mechanisms that cause vapor formation.

- **Flashing of the liquid** - Due to pressure reduction, a part of the substance immediately changes to vapor upon release.
- **Aerosol formation** - Because the substance escapes from the system at a certain speed, small droplets may form which then evaporate quickly and form a mist.
- **Evaporation from a fluid pool** - The spilled fluid will form a pool with a certain size (depending on the quantity). Evaporation can then take place from this pool.

Depending on the prevailing conditions and the substance in question, a certain amount of vapor will develop. For example, if it is very cold outside, the evaporation from a liquid puddle may be very low.

The vapor will spread further into the environment (dispersion). To assess the dangers of, for example, a leakage, dispersion models can be used. With these models it is possible to determine what the concentration of the substance is at a certain distance from the installation or how high the concentration can rise in an indoor situation with a certain degree of ventilation.

There are various (complex) software packages on the market to perform dispersion calculations. However, there are also some simpler tools available to assess the dangers of a spill. CHEF (Chemical Hazard Engineering Fundamentals) is a tool originally developed by Dow Chemical. Dow has donated CHEF to the Center for Chemical Process Safety (CCPS) and the European Process Safety Center (EPSC), so that the tool is now accessible to everyone. See the [CHEF-website](#) for more information. The website also contains the CHEF Manual in which the applied formulas are discussed.

With CHEF it is possible to estimate the amount of chemicals that can be released in the event of a spill and how much vapor can be produced (Airborne Quantity) on the basis of substance properties, system properties and environmental parameters. A dispersion calculation can then be made, for example to assess the toxic effect or the explosion limits at a certain distance.

An alternative is [CAMEO](#), which is developed in America. This software contains CAMEO to look up substance properties and threshold limit values, ALOHA to perform dispersion calculations and MARPLOT to display dispersion calculations on a map.

CHEF and ALOHA can therefore be used to estimate how far a released substance can still present a hazard, both in terms of toxicity and flammability (risk of explosion).

2.4 Threshold limit values

In order to determine whether a hazardous concentration occurs, it is possible to test against the threshold limit values of the substance in question. There are different types of threshold limit values for different situations. A broad distinction can be made between the threshold limit values for the workers and workplace (Occupational Health and Safety legislation) and intervention values in the event of incidents and calamities.

2.4.1 Threshold limit values (Occupational Health and Safety legislation)

In situations where people can be exposed to certain substances for a longer period of time, **time-weighted averages** (TWA) are often used. In the Netherlands, these threshold limit values are often indicated as TGG (Dutch TWA) and a time format. These TGG values apply to exposure to hazardous substances during daily work. In the past, these values were known as the MAC value of a substance.

The **TGG-8h** indicates the maximum average concentration in which someone can work for a day (8 hours). Within this 8-hour period, concentration levels may occur that are higher than the threshold limit value. However, these must then be compensated by lower values so that the average over 8 hours is not exceeded.

In addition, a **TGG-15min** is often specified, also known as STEL (Short Term Exposure Limit). This threshold limit value is intended for short peak exposures to hazardous substances. In some countries it has been established that one may be exposed 4 times a day to substances with a concentration up to the STEL value (in the Netherlands this rule does not apply). There must be at least one hour between each exposure between the increased exposures. Working in a concentration above the TGG-15min or STEL is unacceptable.

A ceiling value has been defined for some substances. This ceiling value may never be exceeded. With exposures above the ceiling values, irreversible health effects may occur.

For exposures that remain below the TGG threshold limit values, an employee will in principle not incur any health effects during a 40-year working period.

A threshold limit value applies to exposure to one substance. When exposed to multiple (harmful) substances with a similar effect on health, the addition rule is applied (the sum of the individual concentrations divided by the individual threshold limit value must be less than 1). The harmful effect can also be enhanced or weakened when exposed to multiple substances. In addition, threshold limit values apply to healthy persons who perform work with a normal load. In heavy work, where breathing is accelerated, for example, a dangerous substance can be absorbed more quickly in the body, in which case the threshold limit value may have to be lowered.

The degree of exposure can be tested by taking measurements at the workplace. It is important that measurements are carried out in accordance with NEN-EN 689 (Exposure at the workplace).

2.4.2 Intervention threshold values

In addition to threshold limit values that relate to working with hazardous substances on a daily basis, there are also values that relate to incidents. These are also called intervention values. The RIVM (Dutch National Institute for Public Health and the Environment) has determined intervention values for a large number of substances. These are determined for different durations (10 minutes, 30 minutes, 1 hour, 2 hours, 4 hours and 8 hours). These values mainly apply in the event of incidents,

such as a spill. These values are often mentioned in the Chemical Safety Cards with an exposure duration of 1 hour.

Information target value (Dutch VRW) - the concentration that is most likely to be perceived as a nuisance by the exposed population, or above which slight health effects are possible.

Alarm limit value (Dutch AGW) - the concentration above which irreversible or other serious health effects may occur, or where, due to exposure to the substance, persons are less able to bring themselves to safety.

Life threatening value (Dutch LBW) - the concentration above which possible death or life-threatening conditions may occur.

These values are in line with the Acute Exposure Guideline Level (AEGL) and Emergency Response Planning Guidelines (ERPG) values used in the United States.

Sometimes an **immediately dangerous to life or health (IDLH)** value is also mentioned. Above this value, respiratory protection must be used.

Systems to look up threshold limit values:

- Chemical Safety Cards
- [RIVM](#)
- [SER](#)
- [Reach](#) (EU)
- [GESTIS](#) (Germany)
- [CAMEO](#) (USA)
- [IDLH-database](#) (USA)

3 Practical applications

3.1 Examples

Two scenarios have been worked out. Example 1 concerns a leakage of acetic anhydride during a tank truck unloading. A large quantity is spilled in an outdoor environment. In the example, CHEF is used to assess this scenario.

Example 2 concerns a minor leakage of acetone in a garage box with minimal ventilation. CHEF is also used here to assess the scenario.

3.2 Discussion

The release and dispersion calculations provide a rough approximation of reality. The results of dispersion calculations can be used to get an idea of how a scenario can develop. For example, several assumptions are used in the calculations and a worst-case consideration is often made. This means, for example, that the calculated concentration at a certain distance mainly applies downwind of the source.

Many hazardous substances have an odor threshold that is considerably lower than the hazardous concentrations (threshold limit values). A (well-trained) person will quickly leave the location if a hazardous substance is smelled. However, there are also substances that slowly affect the sense of smell, so that the substance is no longer (or strongly reduced) detected by the nose. The same applies to the common cold. As a result, the actual danger of certain substances may be greater than one suspects in terms of odor.

Health effects due to evaporation of (hazardous) liquids

Another important aspect is the threshold limit values. These are usually determined based on experimental studies on animals, but in some cases also with humans. In Example 1, testing is performed against an IDLH limit value of 200 ppm. This value is based on animal testing, but very conservative because there is no data available for the influence of acetic anhydride on humans. Previously, the IDLH limit value was 1.000 ppm. This threshold limit value was once determined based on tests on rats. With a 4-hour exposure to 2.000 ppm acetic anhydride, all rats died within 14 days. During tests with 1.000 ppm, all rats survived the tests. Ultimately, 1.000 ppm was chosen because 2.000 ppm is perceived as too high. (Source: <https://www.cdc.gov/niosh/idlh/108247.html>).

Threshold limit values often contain quite large safety margins. Many threshold limit values are based on the LC01 (Lethal Concentration) value, determined based on animal studies. This value is an estimate where 1 in 100 people will die when exposed to this concentration (for a certain period of time). This is usually accompanied by an uncertainty factor, for example a factor of 10.

The chance that a person actually dies after an exposure to a value above the Life-threatening value (LBW) or the immediately dangerous to life or health (IDLH) may be low, but cannot be excluded.

For long-term and repeated exposures, for example when working with dangerous chemicals during daily work, the time-weighted averages such as the TGG 8h and TGG-15 min are used. For carcinogens, the Health Council derives recommended exposure limits for an additional risk of cancer of 4 per 1000 and 4 per 100 000 respectively as a result of constant exposure to the substance during a working life of 40 years.

Yet all those safety margins are not nonsense. The determination of a threshold limit value is based on exposure to one substance and a healthy population. If several substances are released, there is the possibility that they reinforce each other's negative effects on health (synergism). A person is also exposed to many more substances during work, but also outside (at home, in traffic, etc.). It will therefore have to be assessed per scenario and per substance which threshold limit value can best be used to assess a scenario.

Example 1 - Spill of acetic anhydride during tank truck unloading

A tank truck delivers 20 tons of acetic anhydride to a company. For this purpose, the tank truck is connected to the unloading installation by means of a discharge hose (DN65). The unloading is based on static pressure.

A potentially dangerous scenario is breaking loose or tearing of the release hose during the unloading. The acetic anhydride will be able to flow out uncontrolled until the tanker is almost empty. A puddle of acetic anhydride will be formed. In this example we determine how much acetic anhydride will evaporate and to what concentrations this will lead to the air.

Threshold limit values

Acetic anhydride has no legally determined limit values in the Netherlands. Different limits for acetic anhydride have been determined. The RIVM has determined intervention values at different exposure times. The life-threatening value (10 minutes) is 290 mg / m³. In the United States an ERPG-3 value of 100 ppm and an IDLH of 200 ppm is used.

In this example we work with the IDLH of 200 ppm. This concentration can quickly become dangerous for a person exposed to it. A person involved in an acetic anhydride spill will soon leave the location due to the irritating odor.

Dispersion modeling

In this example a number of assumptions have been made for the analysis.

- Outside temperature 20°C
- Diked area 50 m² (can contain full contents of tank truck)
- Height tank truck 2 m
- Height release point 1 m

We use CHEF to determine how much acetic anhydride will evaporate and to what concentrations in the air this will lead to.

Airborne Quantity

The starting point is the Airborne Quantity tab. First, we fill in the type of leakage at STEP 1. In this case we opt for a Hole Size. We assume that the release hose will fully break loose or tear completely. The hole will be the same as the hose diameter, DN65 (65mm). At STEP 2 we fill in the size of the gap and some process information. The pressure in the tanker is atmospheric. The liquid will therefore flow mainly under free fall. Because it is not possible to enter 0 as pressure, it has been decided to enter a very low pressure of 0,001 kPa. As a result, the pressure factor in the calculations becomes negligibly small.

Clear Inputs

AIRBORNE QUANTITY INPUT INFORMATION

Required Inputs are Shaded "Yellow"

STEP 1 - Select Type of Release Hole Size

STEP 2 - Enter Required Release Information

Input Units may be changed - Input Values in "blue" will be converted to appropriate equation units

Release Inputs:

	<u>Input Value</u>	<u>Input Units</u>	<u>Equation Input</u>	<u>Equation Units</u>
Hole Size, d	65	mm	0,065	m
Coefficient C_d <i>(typically Square Edged Hole)</i>	Rounded Nozzle		1	dimensionless
Heat Input Rate, q				Kwatt
Specified Rate <i>(at either specified Hole Size or Release Pressure)</i>				Kg/sec

Process Inputs:

	<u>Input Value</u>	<u>Input Units</u>	<u>Equation Input</u>	<u>Equation Units</u>
Release Temperature, T	20	C	20	C
Release Pressure (gauge), $P_0 - P_A$	0,001	kPa	0,001	kPa gauge
Total Inventory <i>(Leave Blank for 1 hour leak)</i>	20000	Kg	20000	Kg

All chemical properties are entered in STEP 3. If the substance is already present in CHEF, it is sufficient to select the substance in the dropdown menu. The data will then be entered automatically. For substances that are not standard in CHEF, or to correct certain properties, the data can also be entered manually. Most parameters depend on the temperature and are automatically corrected for the temperature entered in STEP 2.

STEP 3 - Enter Chemical Properties (or Select Chemical Name from Pic List)

Cas No.

Chemical Name Acetic Anhydride 108-24-7

(Leave Input Value Blank to accept Chemical Data Table Values)

	<u>Data Table Value</u>	<u>Input Value</u>	<u>Input Units</u>	<u>Equation Input</u>	<u>Equation Units</u>
Physical State	Liquid			Liquid	
Molecular Weight, Mw	102,1			102,1	
Normal Boiling Point, T_B	138,6			138,6	C

Liquid Properties at Release Temperature:

Vapor Pressure, P^{sat}	0,5			0,5	kPa absolute
Liquid Density, ρ_L	1078			1078	Kg/cu m
Liquid Heat Capacity, C_S	1,513			1,513	Kjoule/Kg C
Heat of Vaporation, ΔH_V	459,6			459,6	Kjoule/Kg

In STEP 4 we fill in the location (indoor or outdoor) and we can indicate whether, for example, a dike (or drip tray) is present to collect liquids. Here we can indicate that the dikes area is 50 m². It is also

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indicated that the liquid height in the tanktruck is around 2 meters and that the release takes place at a height of 1 meter.

A wind speed of 0,1 m / s is used for a leak indoors. A wind speed of 3 m / s is used for a leak outdoors.

STEP 4 - Enter Equipment and Plant Layout Information				
	<i>Input Value</i>	<i>Input Units</i>	<i>Equation Input</i>	<i>Equation Units</i>
Equipment Location	Outdoor		<i>(Assumed Outdoor if Blank)</i>	
Equipment Volume, V _{Equip}				cu m
Estimated Contained Mass <i>(for Reference if volume and density entered)</i>				Kg
Liquid Height within Equipment, h'	2	m	2	m
Diked Area <i>(Leave Blank if No Dike)</i>	50		50	sq m
Leak Elevation above Surface, h	1		1	m

Based on the data entered, CHEF has calculated that an liquid releas of 24,2 kg / sec acetic anhydride will occur. This quantity is mainly based on a 65 mm hole and the static liquid height of 2 meters in the tank.

ESTIMATED LIQUID RELEASE RATE				
<i>Hole Size - Subcooled Liquid (equation 12):</i>				
$L = 1.2 c_d d^2 \{ \rho_L [1000 (P_0 - P_A) + 9.8 \rho_L h'] \}^{1/2}$ <i>Bemoulli equation</i>				
$L = 1.2 (1) (0,065)^2 \{ (1078) \{ [1000 (0,001) + 9.8 (1078) (2)] \}^{1/2} =$				
L =	24,2	Kg/sec	- or -	3190
				lb/min
1 hr Release =	20000	Kg	- or -	44000
				lb

From the chemical properties and the prevailing conditions, it is subsequently calculated how much acetic anhydride will evaporate (Evaporation rate). First, it is determined how large the pool of liquid will become. If a dike or drip tray is present, this will limit the formation of a pool somewhat. In this case the size of the puddle is limited to 50 m² (diked area surface). Without a dike or shelter, the pool will be around 1800 m² in size. This can be determined by leaving the Diked Area empty in STEP 4.

From the evaporation rate and the size of the puddle it is then determined that Airborne Quantity is 0,012 kg / s. The factors for flashing and aerosol formation are almost negligible.

LIQUID RELEASE - ESTIMATED POOL EVAPORATION

Estimated Pool Temperature = **20** C (293,15 K)
 Vapor Pressure at Pool Temp, P^{sat} = **0,500** kPa
 Assumed Wind Speed (Outdoor Location) = 3 m/sec
(may be conservative as does not account for evaporative cooling)

Evaporation Rate (equation 35), $m_p = 0.0021 Mw^{2/3} u^{0.78} P^{sat} / T_p$
 $0.0021 (102,1)^{2/3} (3)^{0.78} (0,5) / (273,15 + 20) =$ **0,000185** Kg/sec m²

Release Duration, $t_L = \text{Inventory} / L = 20000 / 24,2 =$ **826,45** sec

Estimated Liquid Rate to Pool, $L' = L (1 - F_v) (1 - F_D) =$
 $24,2 (1 - 0,000001) (1 - 0,0001) =$ **24,1976** Kg/sec

Estimated Pool Area (equation 33), $A_p = L' / [\rho_L / (100 t_L) + m_p / 2] =$
 $24,1976 / [1078 / \{100 (826,45)\} + 0,000185 / 2] =$ **50** m²
 limited to dike area

Pool Evaporation = $m_p A_p = (0,000185) (50) =$ **0,01** Kg/sec

LIQUID RELEASE - ESTIMATED AIRBORNE QUANTITY

Liquid Release - Airborne Quantity = $L [F_v + F_D (1 - F_v)] + m_p A_p =$
 $24,2 [0 + 0,0001 (1 - 0)] + 0,01 =$ **0,0124** Kg/sec - or - **1,64** lb/min

Liquid Release - Airborne Quantity for Equipment Rupture
If Initial Vapor / Total Vapor or 2,02 kg / 37,98 kg < 0.01, Use Maximum Pool Evaporation Rate
 or **0,0124** Kg/sec - or - **1,64** lb/min

1 hour Airborne Quantity = **37,98348** Kg - or - **83,6** lb
based on pool evaporation for 1 hour

Vapor Dispersions

On the Vapor Dispersions tab you can determine how high the concentration of acetic anhydride vapors will be at a certain distance from the acetic anhydride spill.

To do this, enter the location and the type of leakage at STEP 1. We can then enter a concentration for which we want to know at what distance it will be reached. It is also possible to enter a distance to determine how high the concentration will be at that distance.

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The concentration here is the IDLH of 200 ppm. Exposure to this concentration can already cause serious health problems. In addition, 5 meters is entered as Distance of interest to get an idea of the concentration to which an operator or driver can be exposed if it is 5 meters away.

Clear Inputs

VAPOR DISPERSION INPUT INFORMATION

Required Inputs are Shaded "Yellow"

STEP 1 - Select Location, Type of Release, Concentration and Distance of Interest

Release Location *(Assumed Outdoor if Blank)* Outdoor

Type of Release *(Assumed Vapor if Blank)* Vapor ▼

Use Averaging Time Correction for Flammable Release No If "Yes" dispersion concentration is approximately doubled

Input Units may be changed - Input Values in "blue" will be converted to appropriate equation units

	Input Value	Input Units	Equation Input	Equation Units
Concentration of Interest	200	ppm	200	ppm
Concentration of Interest for Hazard Analysis is typically 1/2 LFL, LFL, ER-2, ER-3 or LC ₅₀				
Outdoor Downwind Distance of Interest, X	5	m	5	m
Distance of Interest is typically to the property limit, to an unrestricted work area, or to an occupied building				

The substance properties are entered again in STEP 2.

STEP 2 - Enter Chemical Properties (or Select Chemical Name from Pic List)

Cas No.

Chemical Name Acetic Anhydride 108-24-7

	Data Table Value		
Lower Flammable Limit, LFL	2,7	vol %	For reference in determining concentration of interest
ERPG-3 Concentration	200	ppm	
ERPG-2 Concentration	5	ppm	

Vapor Molecular Weight, Mw

	Input Value	Leave Blank to accept Chemical Data Table Mw	Equation Input
	102,1		102,1

In STEP 3 we fill in how much acetic anhydride evaporates (Airborne Quantity). This is calculated on the Airborne Quantity tab.

STEP 3 - Enter Process Information

Process Inputs:

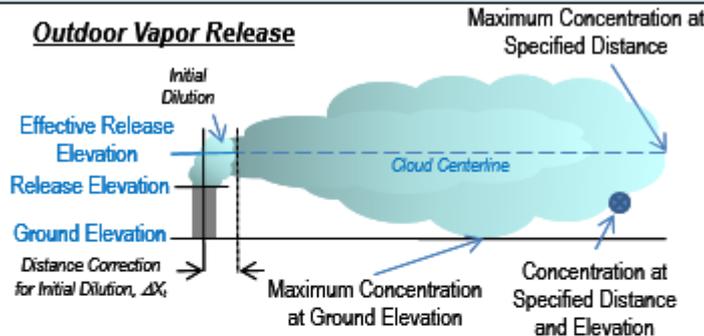
	Input Value	Input Units	Equation Input	Equation Units
Airborne Rate, AQ	0,0124		0,0124	Kg/sec
Release Temperature, T	20		20	C
Total Release Quantity, AQ _{Total} <i>(Leave Blank if Unlimited)</i>				Kg

In STEP 4, some additional information is requested regarding the location. If the leakage should take place in an indoor environment, the volume and the ventilation rate of the relevant room can be entered here.

STEP 4 - Enter Equipment and Plant Layout Information

Equipment and Plant Layout Inputs:	Input Value	Input Units	Equation Input	Equation Units
Diameter of Hole or Discharge Piping, d_o <i>The hole size for vapor release estimate or diameter of relief system discharge piping</i>	65	mm	0,065	m
Release Elevation, h <i>(Blank assumed at Ground)</i>				m
Release Direction <i>(Assumed Horizontal if Blank)</i>	Horizontal			
Enclosed Process Area Volume, V_{Eidg}				cu m
Enclosed Process Area Ventilation Rate		Air Changes/Hr		<i>(Assumed 1 if Blank)</i>

SIMPLE VAPOR DISPERSION for 3 m/sec Wind Speed, Class D Atm Stability, and Industrial Surface Roughness



Test for Plume versus Puff Model at Dispersion Conditions: (equation 50)

If $AQ > 0.04 \text{ Total } AQ^{2/3} \text{ Mw}^{1/3}$ ---> Instantaneous Model for 3 m/sec D weather

No Total Release Quantity Entered, Assumed Continuous Dispersion

Continuous

Estimated Exposure Duration - Continuous Dispersion (Equation 51)

$$(0 \text{ Kg} / 0,01 \text{ Kg/sec}) = 3600,0 \text{ sec}$$

Maximum Downwind Distance to Concentration of Interest (equation 39)

$$\text{Continuous (equation 37): } X = 35000 [AQ (F) / (Mw u C_c)]^{0.5} - \Delta X_t$$

$$= 35000 [(0,0124) (1) / \{ 102,1 (3) (200) \}]^{0.5} - 0,1 = 15 \text{ m}$$

Maximum Concentration at Downwind Distance of Interest for $X > \Delta X_t$

$$\text{Continuous (equation 40): } C_c = 1.2 \times 10^9 F AQ / [Mw u (X + \Delta X_t)^2]$$

$$= 1.2 \times 10^9 (1/F) [(0,0124) / \{ 102,1 (3) (5 + 0,1)^2 \}] = 1867,7 \text{ ppm}$$

The calculations show that the IDLH concentration of 200 ppm can be present until about 15 meters from the pool. This is the worst-case concentration where someone would stand downwind of the spill.

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At a distance of 5 meters (downwind) the estimated concentration is almost 1.900 ppm.

With CHEF it is very easy to calculate the effect of a diked area. This can be determined by entering another area in the Diked Area under Airborne Quantity (STEP 4). If a 100 m² diked area is present, then the acetic anhydride pool can become 100 m². This results in a vapor development of 0,022 kg/s. The downwind distance to the IDLH concentration of 200 ppm is hereby 21 meters. At a distance of 5 meters from the source, the concentration will increase to more than 3.000 ppm.

Explosion area

The dispersion calculation was tested against the IDLH concentration of 200 ppm. It is also possible to test against the Lower Explosion Limit (LEL). For acetic anhydride, the LEL is 2,7 vol%. We can fill this in at STEP 1 of the Vapor Dispersions. CHEF will then convert this to a ppm value.

	<u>Input Value</u>	<u>Input Units</u>	<u>Equation Input</u>	<u>Equation Units</u>
Concentration of Interest	2,7	vol %	27000	ppm

Concentration of Interest for Hazard Analysis is typically 1/2 LFL, LFL, ER-2, ER-3 or LC₅₀

The calculation now shows that the distance of the LEL area reaches approximately 1 meter. Beyond that, the concentration will be below LEL.

Maximum Downwind Distance to Concentration of Interest (equation 39)

Continuous (equation 37): $X = 35000 [AQ (F) / (Mw u C_c)]^{0.5} - \Delta X_t$

$= 35000 [(0,0124) (1) / \{ 102,1 (3) (27000) \}]^{0.5} - 0,1 = 1 \text{ m}$

Example 2 – Jerrycan of acetone is running empty in a garage box

Acetone is used in a garage box at home. During the work, a jerry can with acetone falls to the floor and about 10 liters of acetone flow over the floor.

In this example we determine how much acetone will evaporate and to what concentrations this will lead in the air.

Threshold limit values

Acetone has a legal limit value of 1.210 mg / m³ (TGG 8h) and 2.420 mg / m³ (TGG 15 min). The Dutch RIVM has drawn up a number of intervention values for incident follow-up.

Interventiewaarden		10 min.	30 min.	1 uur	2 uur	4 uur	8 uur
Voorlichtingsrichtwaarden	VRW (mg/m ³)	480	480	480	480	480	480
Alarmeringsgrenswaarden	AGW (mg/m ³)	22.000*	12.000*	7.800*	5.200*	3.500	2.300
Levensbedreigende	LBW (mg/m ³)	40.000**	21.000*	14.000*	9.200*	6.100*	4.100
Datum vaststelling: 13-05-2009				1 mg/m ³ = 0,414 ppm; 1 ppm = 2,42 mg/m ³			

Dispersion modeling

In this example a number of assumptions have been made for the analysis.

- Temperature garage box 20°C
- Volume garage box 50 m³
- Air refresh rate garage box 1x per hour

We use CHEF to determine how much acetone will evaporate and to what concentration this will lead within the garage box.

Airborne Quantity

The starting point is the Airborne Quantity tab. First, we fill in the type of leakage at STEP 1. In this case we opt for an Equipment Rupture, the jerry empties on the floor very quickly.

STEP 1 - Select Type of Release	Equipment Rupture
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At STEP 2 we only enter the temperature and the amount of liquid that flows over the floor. 10 liters of acetone weighs 7,8 kg.

Process Inputs:	<u>Input Value</u>	<u>Input Units</u>	<u>Equation Input</u>	<u>Equation Units</u>
Release Temperature, T	20		20	C
Release Pressure (gauge), P ₀ - P _A				kPa gauge
Total Inventory <i>(Leave Blank for 1 hour leak)</i> <i>Inventory Must be Entered for Equipment Rupture</i>	7,8	Kg	7,8	Kg

All chemical properties are entered in STEP 3. Here we choose acetone from the dropdown menu.

STEP 3 - Enter Chemical Properties (or Select Chemical Name from Pic List)

Cas No.

Chemical Name	Acetone	67-64-1
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(Leave Input Value Blank to accept Chemical Data Table Values)

	<i>Data Table Value</i>	<i>Input Value</i>	<i>Input Units</i>	<i>Equation Input</i>	<i>Equation Units</i>
Physical State	Liquid			Liquid	
Molecular Weight, Mw	58,1			58,1	
Normal Boiling Point, T _B	56			56	C

Liquid Properties at Release Temperature :

Vapor Pressure, P ^{sat}	24,7			24,7	kPa absolute
Liquid Density, ρ _L	784,4			784,4	Kg/cu m
Liquid Heat Capacity, C _S	2,193			2,193	Kjoule/Kg C
Heat of Vaporation, ΔH _V	541,9			541,9	Kjoule/Kg

In STEP 4 we enter Indoor as location. For a leakage indoors, a wind speed of 0.1 m/s is then used for calculations.

STEP 4 - Enter Equipment and Plant Layout Information

	<i>Input Value</i>	<i>Input Units</i>	<i>Equation Input</i>	<i>Equation Units</i>
Equipment Location	Indoor		<i>(Assumed Outdoor if Blank)</i>	
Equipment Volume, V _{Equip}				cu m
Estimated Contained Mass <i>(for Reference if volume and density entered)</i>				Kg
Liquid Height within Equipment, h'				m
Diked Area <i>(Leave Blank if No Dike)</i>			No Dike	sq m
Leak Elevation above Surface, h			1	m

From the evaporation rate and the size of the puddle it is then determined that the Airborne Quantity is 0,00044 kg / s. The factors for flashing and aerosol formation are almost negligible. The dispersion calculation can then be done with this value.

LIQUID RELEASE - ESTIMATED POOL EVAPORATION		
Estimated Pool Temperature =	20	C (293,15 K)
Vapor Pressure at Pool Temp, P^{sat} =	24,700	kPa
Assumed Wind Speed (Indoor Location) =	0,1	m/sec
<i>(may be conservative as does not account for evaporative cooling)</i>		
Evaporation Rate (equation 35), $m_p = 0.0021 M_w^{2/3} u^{0.78} P^{sat} / T_p$		
	$0.0021 (58,1)^{2/3} (0,1)^{0.78} (24,7) / (273,15 + 20) =$	0,000441 Kg/sec m ²
Release Duration, $t_L = \text{Inventory} / L = 7,8 / 0 =$		sec
Estimated Liquid Rate to Pool, $L' = L (1 - F_v) (1 - F_D) =$		
	$0 (1 - 0,000001) (1 - 0,0011) =$	
Estimated Pool Area (equation 33), $A_p = L' / [\rho_L / (100 t_L) + m_p / 2] =$		
	$7,8 (0,000001 + (1 - 0,000001) 0,0011) 100 / 784,4 =$	1 m ²
Pool Evaporation = $m_p A_p = (0,000441) (1) =$	0,00044	Kg/sec
limited to pool fill rate		

Vapor Dispersions

On the Vapor Dispersions tab you can then determine how high the concentration of acetone will be in the garage box.

VAPOR DISPERSION INPUT INFORMATION		
<i>Required Inputs are Shaded "Yellow"</i>		
STEP 1 - Select Location, Type of Release, Concentration and Distance of Interest		
Release Location <i>(Assumed Outdoor if Blank)</i>	Indoor	
Type of Release <i>(Assumed Vapor if Blank)</i>	Vapor	
Use Averaging Time Correction for Flammable Release		<i>If "Yes" dispersion concentration is approximately doubled</i>

The substance properties are entered again in STEP 2.

STEP 2 - Enter Chemical Properties (or Select Chemical Name from Pic List)

Chemical Name	Acetone		Cas No.	67-64-1
Lower Flammable Limit, LFL	3,6	vol %	} For reference in determining concentration of interest	
ERPG-3 Concentration	57000	ppm		
ERPG-2 Concentration	32000	ppm		
Vapor Molecular Weight, Mw	58,1	<i>Input Value</i>	Leave Blank to accept Chemical Data Table Mw	<i>Equation Input</i> 58,1

In STEP 3 we fill in how much acetone evaporates (Airborne Quantity). This is calculated on the Airborne Quantity tab.

STEP 3 - Enter Process Information

Process Inputs:	<i>Input Value</i>	<i>Input Units</i>	<i>Equation Input</i>	<i>Equation Units</i>
Airborne Rate, AQ	0,00044		0,0004	Kg/sec
Release Temperature, T	20		20	C
Total Release Quantity, AQ _{Total} (Leave Blank if Unlimited)				Kg

In STEP 4, some additional information is requested regarding the location. Here we indicate that the garage has a volume of 50 m³ and the ventilation rate is 1x per hour.

STEP 4 - Enter Equipment and Plant Layout Information

Equipment and Plant Layout Inputs:	<i>Input Value</i>	<i>Input Units</i>	<i>Equation Input</i>	<i>Equation Units</i>
Diameter of Hole or Discharge Piping, d ₀ <i>The hole size for vapor release estimate or diameter of relief system discharge piping</i>				m
Release Elevation, h (Blank assumed at Ground)				m
Release Direction (Assumed Horizontal if Blank)				
Enclosed Process Area Volume, V _{Bldg}	50		50	cu m
Enclosed Process Area Ventilation Rate	1	Air Changes/Hr (Assumed 1 if Blank)		

The calculations show that the concentration can rise to almost 12.000 ppm (~ 29.000 mg/m³). It is assumed that the evaporation continues and that no immediate action is taken.

CONCENTRATION FOR RELEASE WITHIN ENCLOSED PROCESS AREA

Check Limit for Total Release Divided by Enclosed Volume (equation 57)

$$C_{Limit} = 2.45 \times 10^7 (Total\ AQ) / [Mw (V_B)] = 5 \times 10^7 (1,44) / [58,1 (50)] = \mathbf{12144,6\ ppm}$$

"Steady State" Concentration within Enclosed Process Area (equation 56)

$$C_{Indoor} = 8.8 \times 10^{10} (AQ / Mw) / (VR V_B + 88020 AQ / Mw) = \\ 8.8 \times 10^{10} (0,0004 / 58,1) / [1 (50) + 88020 (0,0004) / 58,1] = \mathbf{11971,9\ ppm}$$

The calculated value, 29.000 mg/m³, lies somewhere between the Life-threatening Value (LBW) of 10 and 30 minutes. This means that an acetone released can indeed be a danger to a person who may be present.

In this example, it is probably best to open the door (s) and to refresh the air in the garage as much as possible. If we enter a ventilation rate of 4 at STEP 4, the concentration will be reduced to around 3.000 ppm (~ 7.300 mg/m³). This is still considerably high, but will not immediately be life threatening.

"Steady State" Concentration within Enclosed Process Area (equation 56)

$$C_{Indoor} = 8.8 \times 10^{10} (AQ / Mw) / (VR V_B + 88020 AQ / Mw) = \\ 8.8 \times 10^{10} (0,0004 / 58,1) / [4 (50) + 88020 (0,0004) / 58,1] = \mathbf{3020,1\ ppm}$$

In the event of such a spill, it is probably good to allow the acetone pool to evaporate in a controlled manner in a well-ventilated area (doors open).