# Hydrogen in chlorine




November, 2016

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# Introduction

- Production of chlorine and hydrogen are coupled
  - $2\ NaCl + 2\ H_2O \longrightarrow Cl_2 + H_2 + 2\ NaOH$
- Unless you make use of ODC technology
  - $2\ NaCl + ½\ O_2 + H_2O \longrightarrow Cl_2 + 2\ NaOH$
- Independent from the technology used:
  - $H_2$ will be present in your chlorine gas
- Hydrogen reacts easily with $Cl_2$ and/or $O_2$
  - Explosions or even detonations can occur

# Explosion limits

- The explosion limits are defined as an increase of 5% of the initial pressure
- Detonations occur when the reaction is so fast that a shock wave propagates;
  - this can cause extreme high pressures ( up to 50 times the initial pressure)

# Explosion limits

- Explosion limits and effect of temperature[1)]

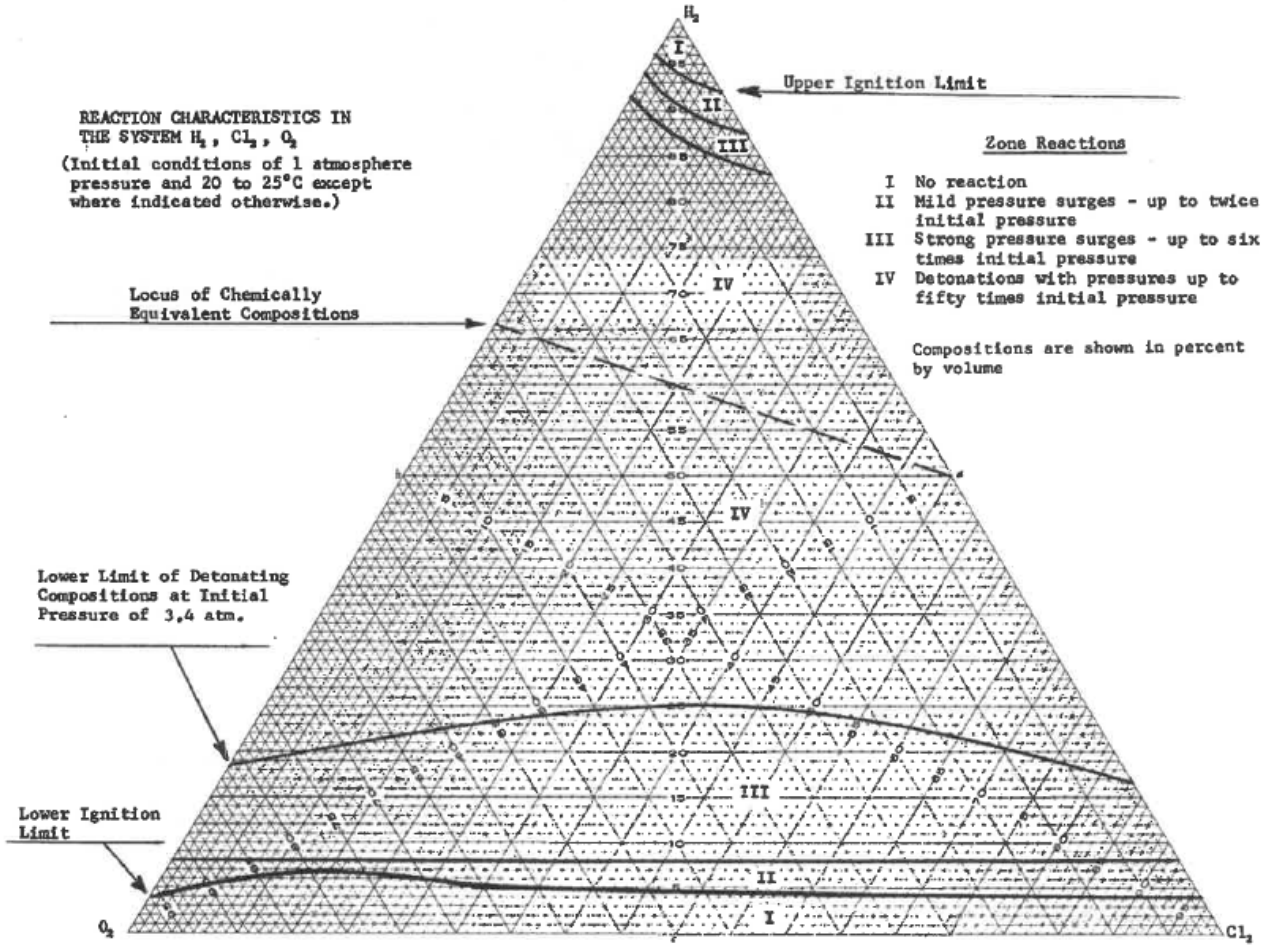
| Temp. in °C | $H_2$ – Air (vol% $H_2$) | $H_2$ – $O_2$ (vol% $H_2$) | $H_2$ - $Cl_2$ (vol% $H_2$) |
|---|---|---|---|
| Minus 60 | 4.0 – 69 | 4.0 – 96 | 5.0 – 90 |
| Minus 40 | 4.0 – 71 | 4.0 – 96 | 4.0 – 90.5 |
| Minus 20 | 4.0 – 72 | 4.0 – 96 | 4.0 – 91.5 |
| 0 | 4.0 – 73 | 4.0 – 96 | 3.5 – 92 |
| 20 - 25 | 4.0 – 75 | 4.0 – 96 | 3.0 – 92.5 |
| 50 | 3.7 – 76 | 4.0 – 96 | 3.0 – 93 |
| 100 | 3.0 - 80 | 4.0 – 97 | 3.0 – 93 |

- The effect of pressure is limited[1)]
  - The lower explosion limit at 13.5 bar(a) is 2.5 – 3%



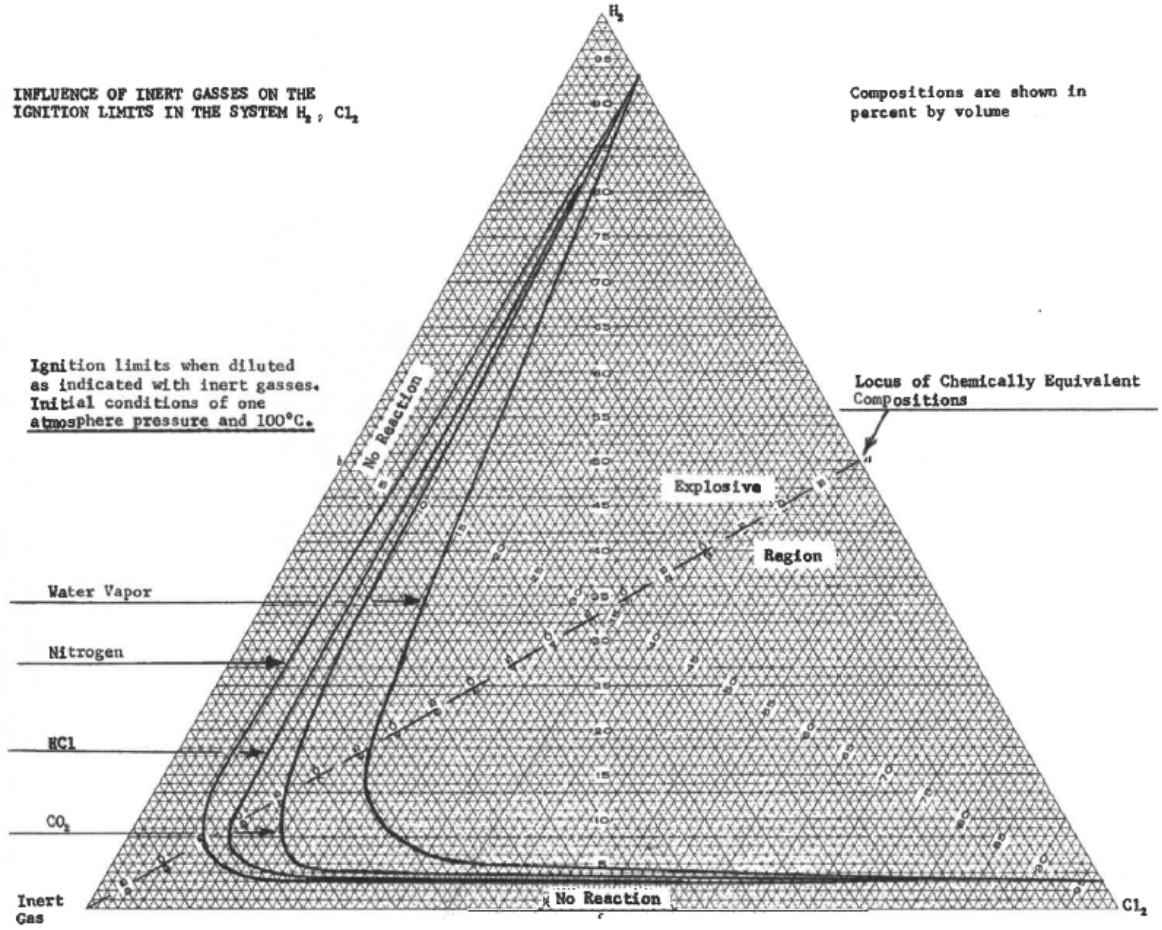
[1)] See GEST 91/168 Chapter 9

# Explosion limits



# Explosion limits

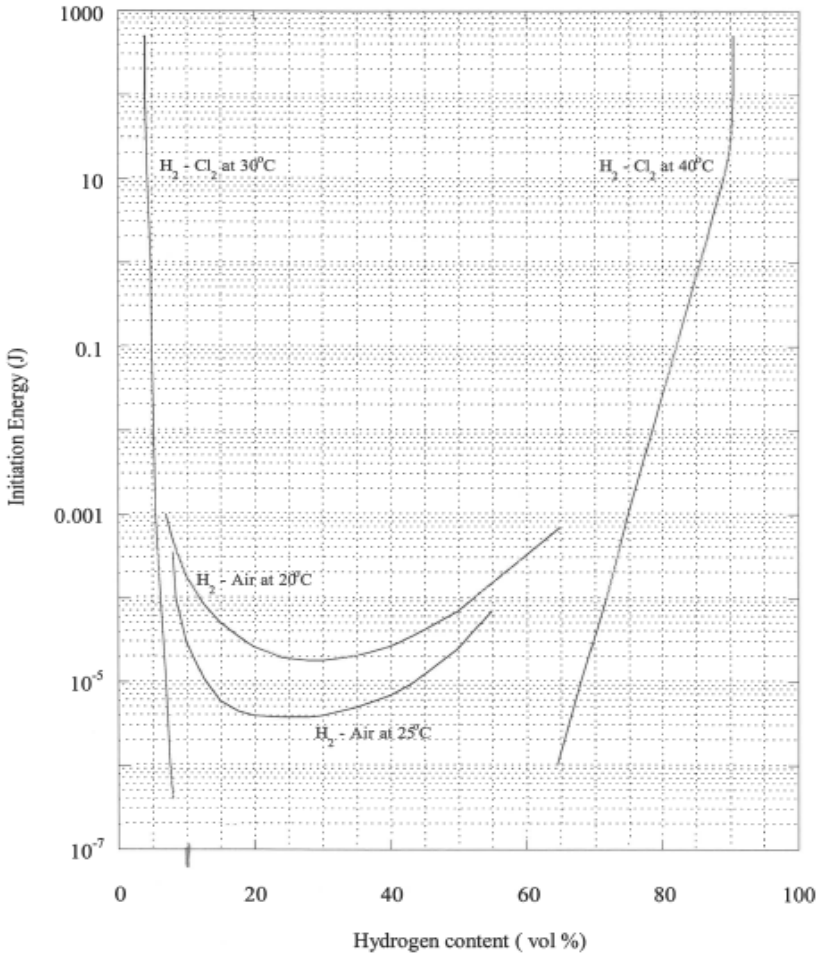
- Effects of Inert gases is limited



# Explosion limits

- $H_2$ – $Cl_2$ (explosive) mixtures can easily be ignited, $10^{-7}$ J, see graph

- Auto ignition temperature of $H_2$ – $Cl_2$ mixtures in 207 $^0$C (for $H_2$-air it is 400 $^0$C)



# The risks in a chlorine plant

## The electrolyser

- Normal operating conditions:
  - $Cl_2$: 97.0 – 99.9 vol% (dry basis)
  - $O_2$: 0.1 – 2.5 vol% (dry basis)
  - $H_2$: 0.0 - 0.5 vol% (dry basis)
  - $H_2O$: 40.0 – 60.0 vol% (highly influenced by operating temp.)
  - The water reduces the concentrations and with that the risk of having an explosive mixture
- Be aware: water concentration is decreasing dramatically during cooling and drying of the $Cl_2$-gas, So do not count on the dilution effect of water
- Main risk: when hydrogen levels increase above normal; e.g. membrane leakages

# The risks in a chlorine plant

## Chlorine liquefaction (1)

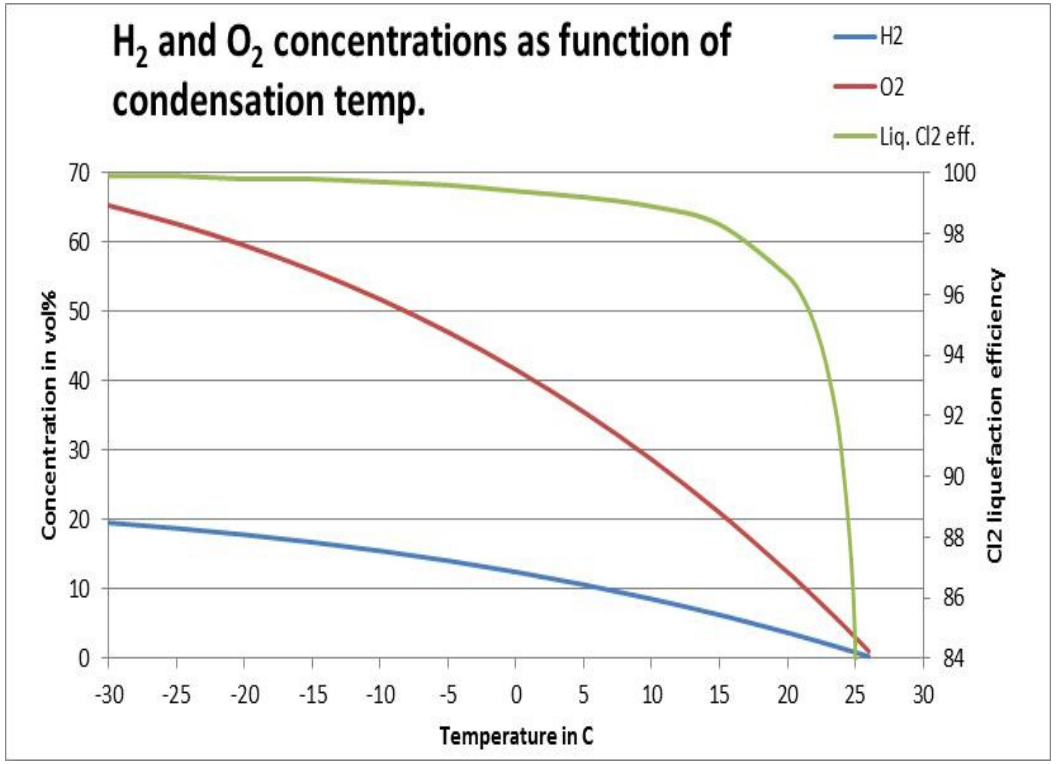
- After cooling & drying  normal operating conditions:
  - $Cl_2$:  97.0 – 99.9 vol% (dry basis)
  - $O_2$:  0.1 –  2.5 vol% (dry basis)
  - $H_2$:  0.0 -  0.5 vol% (dry basis)

- What happens during the liquefaction
  - When cooling the gas the $Cl_2$ content will decrease and the $H_2$ and $O_2$ content will increase
  - An explosive mixture could occur

# The risks in a chlorine plant

## Chlorine liquefaction (2)

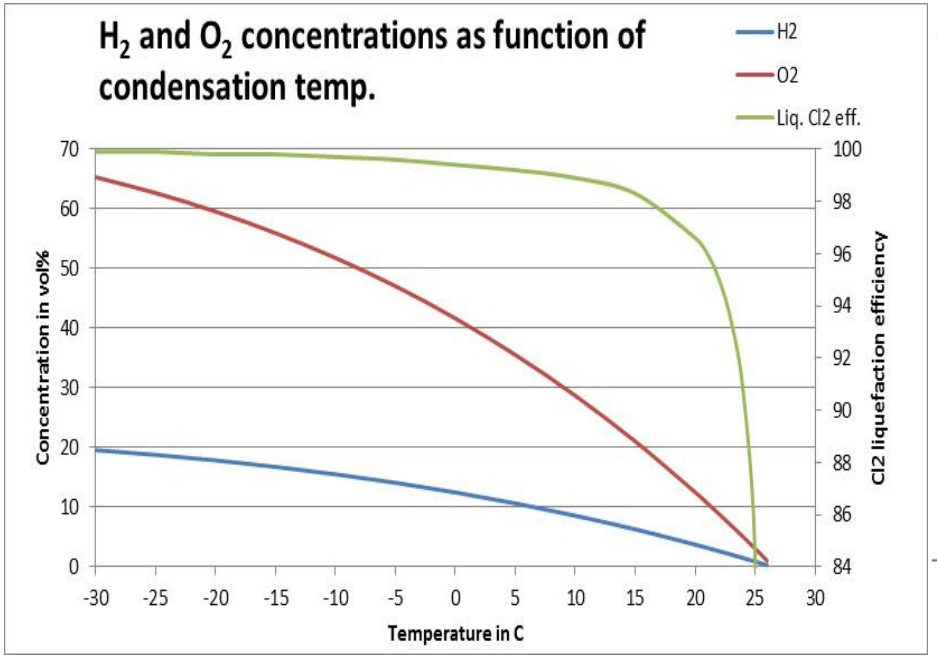
- Assume the following conditions:
  - $Cl_2$: 99.35 vol%
  - $O_2$: 0.50 vol%
  - $H_2$: 0.15 vol%
  - 8 bar(abs) and 90 °C
- Condensation starts at 26,2 °C
- In the graph the $H_2$ and $O_2$ concentrations are presented as function of the condensation temperature

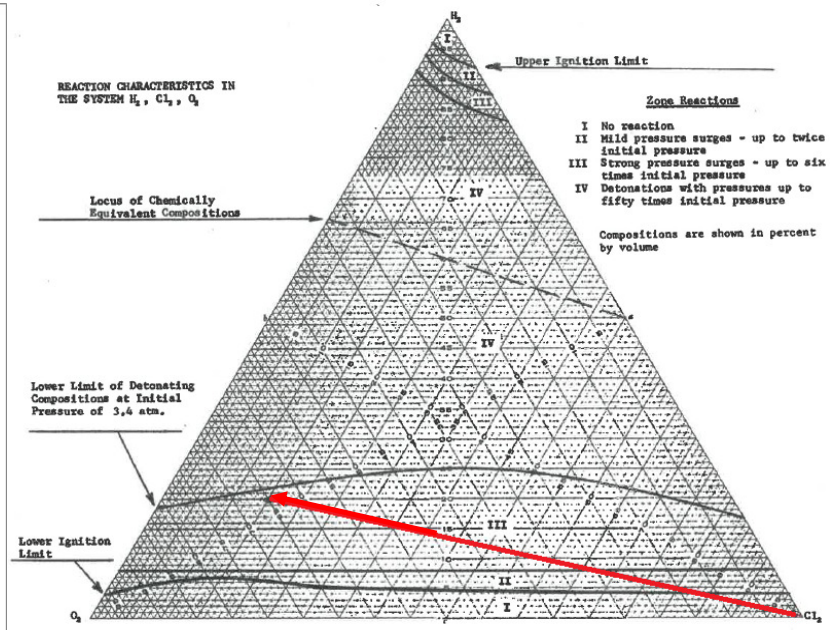


# The risks in a chlorine plant

## Chlorine liquefaction (3)

- At temperatures < 21 C the gas mixture is explosive
  - liquefaction efficiency 96%
- At temperatures < -40 the gas mixture is in the detonation zone



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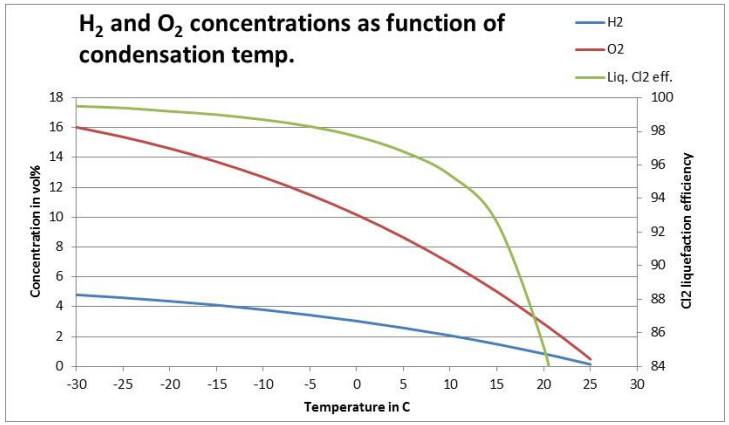
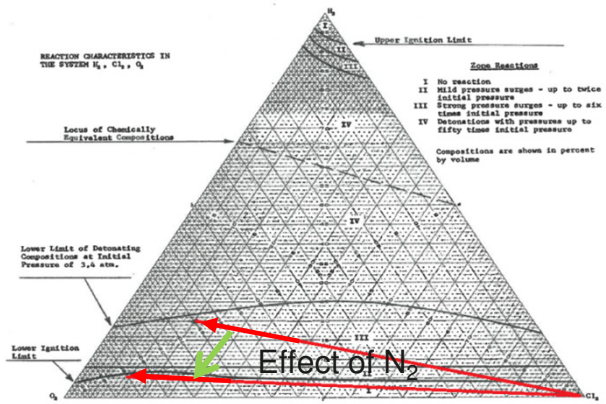
# The risks in a chlorine plant

## Chlorine liquefaction (4)

- How to avoid the explosive mixture during liquefaction
  - Stop condensation before the explosive mixture appears
    - Liquefaction efficiency only 96% ☹
  - Add e.g. $N_2$ during/before condensation
    - Liquefaction efficiency can be increase at the costs of lower temperatures; condensation starts at 25 $^0$C and 99.5% eff. at -30 $^0$C



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# The risks in a chlorine plant

## Chlorine liquefaction (5)

- What happens if suddenly the $H_2$ level in the gas from the electrolyser increases?
- Take the previous example; and assume $H_2$ in cell gas increases from 0.15% to 0.3%
- Condensation at approx. -25 $^0$C

| $H_2$ content in cell gas | 0.15 % | 0.30 % |
|---|---|---|
| $H_2$ content after condensation | 4.61% | 8.73% |

- What to do?
  - Increase temperature to + 6.5 $^0$C
  - Increase nitrogen flow to condenser

# The risks in a chlorine plant

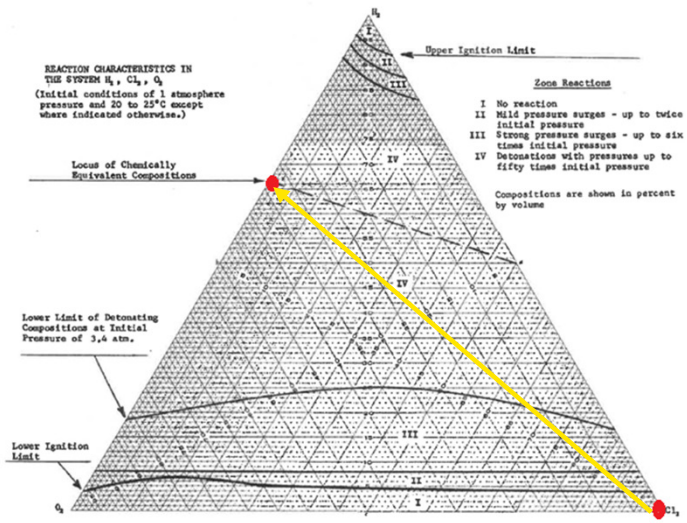
## Chlorine absorption (1)

- In the $Cl_2$ absorption all kind of gasses containing $Cl_2$ are treated.
- These gases will also contain $H_2$
- In the absorption the $Cl_2$ will react but the $H_2$ and $O_2$ remains
- Two cases will be reviewed
  - An electrolyser produces gas with High $H_2$ (e.g. 1% instead of 0.15%)
  - Normal absorption of the vent gas form the condensation

# The risks in a chlorine plant

## Chlorine absorption (2)

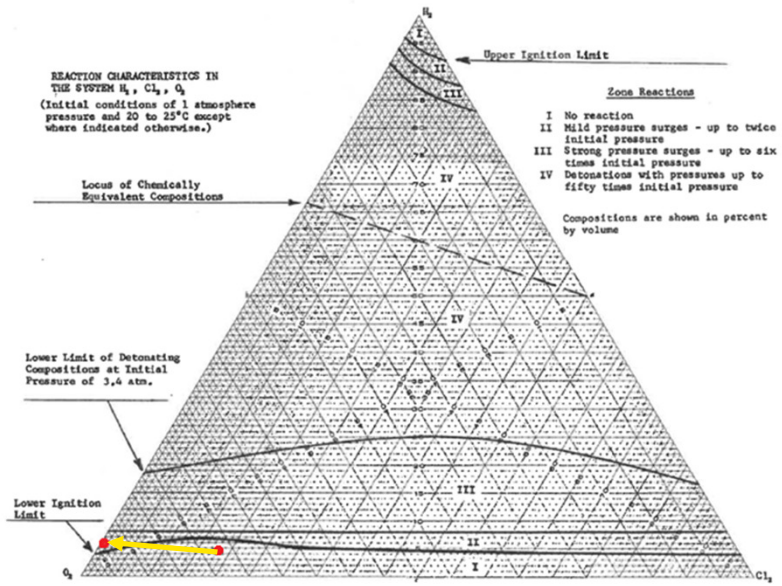
- An electrolyser produces gas with High $H_2$ (e.g. 1.0% instead of 0.15%)
- Due to abnormal situation and risks in liquefaction it will be rerouted directly to absorption
- What happens:
  - In absorption mixture becomes detonative
- What to do?
  - Add always sufficient Air to absorption



# The risks in a chlorine plant

## Chlorine absorption (3)

- Normal absorption of the vent gas from the condensation
- Composition:
  - after condensation: $Cl_2$ 18.5%; $O_2/N_2$ 76.9%; $H_2$ 4.6%
- What happens:
  - In absorption mixture becomes explosive
- What to do?
  - Add always sufficient Air to absorption



# Conclusions

- The $Cl_2$ will always contain a small amount of $H_2$
- Dangers situations can occur every ware in the process
- It is advised to measure hydrogen:
  - After the electrolysers
  - After the condensation or in between the different condensation steps
- Have sufficient control in the condensation when $H_2$ levels increase
  - Adding $N_2$ or (dry) Air
  - Increase condensation temperature
- Add always sufficient amounts of fresh air to the absorption to avoid explosive/detonative mixtures

# Thank you very much

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