

Phosgene Safety Practices

for design, production and processing

PSP Appendices

Appendix 1 - Phosgene synthesis and properties

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III caveat

The information herein is presented in good faith, is believed to be accurate and reliable, but may well be incomplete and /or not applicable to all conditions or situations that may be encountered.

No representation, guarantee or warranty is made as to the accuracy, reliability or completeness of this report, or that the application or use of any of the information, analysis, methods and recommendations herein will avoid, reduce or ameliorate hazard, accidents, losses, damages or injury of any kind to persons or property. Readers are therefore cautioned to satisfy themselves as to the applicability and suitability of said information, for the purposes intended, prior to use.

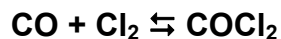
1 Phosgene production

Phosgene (COCl_2) is produced by an exothermic reaction of a gaseous mixture of anhydrous chlorine (Cl_2) and high-purity carbon monoxide (CO) in the presence of an activated carbon catalyst.

The crude phosgene (COCl_2) can be used directly in the gaseous state or as a liquid either condensed or dissolved in a solvent and then further processed. Any uncondensed residual gases with excess CO are sent to an off-gas purification unit or recovered.

For more information see also the references in section 5 below.

2 Main reaction



The heat of reaction is: 1093 kJ/kg COCl_2 (exothermic). The maximum temperature on the active carbon bed is about 550°C.

The reaction equilibrium is described by:

$$K_p = p_{\text{COCl}_2} / (p_{\text{CO}} \times p_{\text{Cl}_2})$$

where:

p_i [atm] = partial pressure of the component i

$$K_p = \exp(-dH_o / (RT) + dS_o / R)$$

$$dH_o = -110440 \text{ J/mol}$$

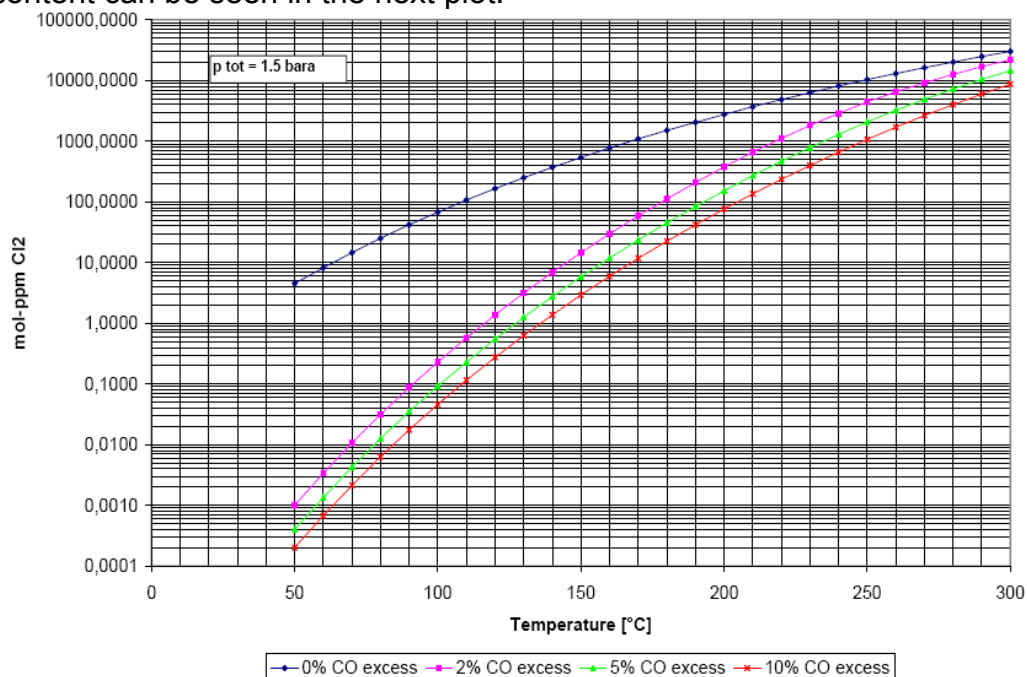
$$dS_o = -135.5 \text{ J/molK}$$

$$K_p [1/\text{atm}] = \exp(A + B / T [\text{K}])$$

$$A = -16.3$$

$$B = 13100$$

The influence of the temperature, pressure and excess CO on the equilibrium Cl_2 content can be seen in the next plot.

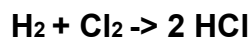


3 Side reactions

The purity of CO and Cl₂ gases are important since impurities can lead to the following side reactions.

3.1 Chlorine-hydrogen reaction

The exothermic reaction is:



The equilibrium lies always at the HCl side.

If the mixed gas contains more than 4 volume % of hydrogen, a chlorine-hydrogen reaction may cause an explosion. This can be seen in a triangular explosion diagram of Cl₂, inert gas and hydrogen. Such a diagram can show the curves of nitrogen or CO₂ as an inert gas at various temperatures. It can also show the curve for the lower ignition limit at various temperatures.

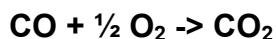
The ignition temperature cannot be specified because the ignition temperature is lowered by the catalytic influence of the metallic surface.

To avoid chlorine-hydrogen reactions, the recommended limit value for the hydrogen concentration in the mixed gas is set to <2 volume% H₂ (50% below the lower explosion limit). It is important that this limit value should not be exceeded and controlled by means of protective measures.

The permissible H₂ concentration in the mixed gas (sum of the H₂ content in CO gas and chlorine gas) is assured by restricting the H₂ concentration at the suppliers (CO and chlorine production units).

At temperatures below the explosion limit, the reaction also leads to a temperature increase in the mixed gas. A concentration of 1 volume % H₂ in CO results in a ca. 30°C temperature increase in the mixed gas.

3.2 Carbon monoxide-oxygen reaction



Ignition Temperature: 605°C

The CO/O₂/N₂ system has an explosion range. The recommended maximum O₂ concentration is 5 volume % (at 50°C, 1 bar). This value decreases as the temperature rises (ca. 1 volume %/100°C).

When Cl₂ is added to this system, the explosion range becomes smaller and the O₂ limit concentration increases.

The maximum recommended oxygen concentration in the mixed gas (with H₂ contents of <3 volume %) was determined to be 3.0 volume % O₂. This is ~50% of the oxygen limit concentration in the mixed gas and nearly 100% of the oxygen concentration in the chlorine-free system CO/O₂/N₂.

The low oxygen limit concentration for the system CO/O₂/N₂ can be tolerated since it occurs only for short periods during production and under conditions where it can be expected that there are no sources of ignition (start-up with CO):

- In a generator packed with fresh activated carbon, the ignition temperature cannot be reached due to the low heat of adsorption of CO.
- When CO is sent to a generator that has been operated previously, COCl₂ is always desorbed by the carbon and acts as a dilutant.

Since in an on-stream phosgene generator a source of ignition may exist at any time (hot reaction zone); it is important that protective measures are taken to assure that the O₂ concentration will not exceed the permissible maximum. Because phosgene generators are always operated under positive pressure and the units are carefully monitored for leaks, it is essential that the O₂ specification for CO and Cl₂ gas streams are met.

In coke CO units and in reformers where the separation step is operated under vacuum (often called VSA or PSA units: vacuum/pressure swing adsorption) it is important that the O₂ concentration be monitored via a mandatory protective measure in the CO production unit. CO produced in reformers with a cold-box separation step does not contain O₂, even under upset conditions. Therefore, the attention should mainly be directed at the chlorine production unit.

3.3 Chlorine-iron reaction

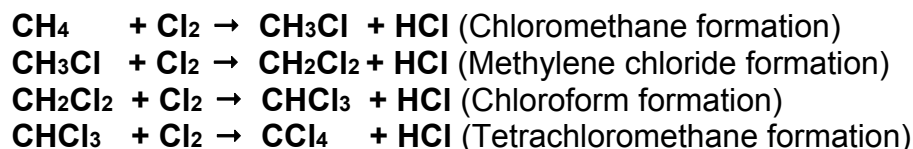


The auto-ignition temperature for a chlorine-iron reaction is about 250°C. Depending on the surface conditions, the ignition temperature may be significantly lower.

“Euro-Chlor GEST” (European Chlorine Recommendations) 79/82 lists a maximum operating temperature of 120°C. In phosgene units, the permissible temperature in the chlorine line and in the mixed gas is limited to T_{max} < 120°C.

Limiting the temperature is a mandatory protective measure.

3.4 Methane chlorination



The above reactions are all exothermic and the reaction equilibrium lies always at the chloromethane side.

Remarks:

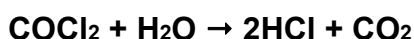
- In the phosgene generator CCl₄ is mostly found as a final chlorinated product:
$$\text{CH}_4 + 4\text{Cl}_2 \rightarrow \text{CCl}_4 + 4\text{HCl}_{\text{gas}}$$
- Tetrachloromethane can also be produced through dissociation of phosgene:
$$2 \text{ COCl}_2 \rightleftharpoons \text{CCl}_4 + \text{CO}_2$$

The reaction leads to a temperature increase in the phosgene reactor/mixed gas. A limit value for a permissible CH₄ concentration in the mixed gas (or CO gas) cannot be provided.

Table: Temperature increase as a function of the methane concentration in volume%::

CH ₄ in CO	Temperature Increase ΔT (°C)
2%	62
4%	98
8%	166

3.5 Reaction with water (hydrolysis)



The formation of hydrogen chloride in the presence of water leads to the formation of hydrochloric acid and subsequently leads to corrosion. However, the reaction rate depends strongly on the pH. And since basic conditions are normally required for phosgene decomposition any acid formed will be neutralised (see Part 2 - section 2.2.7).



Chlorine dissolves in aqueous systems and partially reacts to hypo-chlorous acid, which is also corrosive. At temperatures below +12°C, solid chlorine hydrate separates from moist (due to water vapour) chlorine. HClO can also form in solid chlorine hydrate.

3.6 Formation of NCl_3



The reaction is exothermic. The presence of ammonia can normally be neglected except in CO produced by desulphurisation on activated carbon with NH_3 addition.

3.7 Phosphorus chloride formation



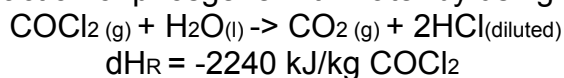
The reaction is strongly exothermic and may initiate a chlorine-iron fire. In a coke CO unit, white phosphorus may be formed and separated. The use of non-P containing cokes is recommended otherwise it is important to take appropriate measures to eliminate P.

4 Phosgene decomposition

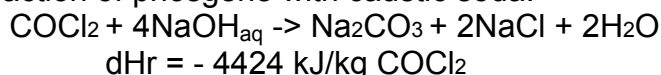
For safe operation of phosgene generating or processing units it is important that systems are provided that will decompose phosgene under upset operating conditions so that the amounts and/or concentrations at the unit outlet do not exceed allowed values stated in the unit operating permit.

Two main reactions are used in those decomposition systems:

- Reaction of phosgene with water by using an activated carbon catalyst:



- Reaction of phosgene with caustic soda:



Detailed information about the requirements of those decomposition systems are described in the Part 2 - section 2.2.8.

5 References

Dunlap, K. L. (2010). Phosgene. *In*: 'Kirk-Othmer Encyclopedia of Chemical Technology.' [Online ed.] Wiley, New York.

Schneider, W. and Diller, W. (2000). Phosgene. *In*: 'Ullmann's Encyclopedia of Industrial Chemistry.' [Online ed.] Wiley, New York.

6 **Abbreviations and acronyms**

°C	Degree Celsius
CCl ₄	Tetrachloromethane or carbon tetrachloride
CH ₄	Methane
CH ₃ Cl	Chloromethane
CH ₂ Cl ₂	Dichloromethane (DCM) or methylene chloride
CHCl ₃	Chloroform or trichloromethane
Cl ₂	Chlorine
CO	Carbon monoxide
CO ₂	Carbon dioxide
COCl ₂	Phosgene
Fe	Iron
FeCl ₃	Ferric chloride
H ₂	Hydrogen
HCl	Hydrogen chloride, hydrochloric acid
HClO	hypo-chlorous acid
H ₂ O	Water
K _p	equilibrium constant
N ₂	Nitrogen
NaCl	Sodium chloride
Na ₂ CO ₃	Sodium carbonate
NaOH	Sodium hydroxide
NCl ₃	Nitrogen trichloride
NH ₃	Ammonia
NH ₄ Cl	Ammonium chloride
O ₂	Oxygen
P	Phosphorous
PCl ₅	Phosphorus chloride
pH	Measure of the acidity of a solution (potential of Hydrogen)
p _i	partial pressure of component i
PSA	Pressure swing adsorption
T	Temperature
VSA	Vacuum swing adsorption