3.0 Properties of Phosgene

Introduction

The information presented in this section is a general composite of information about the properties of phosgene including the names, formulas, physical properties, reactivity, instability and combustion, commercial chemistry and use.

The information provided in this section should not be considered as a directive or as an industry standard that readers must adopt or follow. Instead, the information is intended to provide helpful ideas and guidance that users may wish to consider in a general sense (See Section 1.1 Preface and Legal Notice). Also included is a reference list of useful resources.

Contents
3.1 The Phosgene Molecule ................................................................. 2
3.2 Names ......................................................................................... 3
3.3 Physical Properties ..................................................................... 3
3.4 Reactivity, Instability and Combustion Properties ...................... 5
3.5 Commercial Chemistry ............................................................... 6
3.6 Uses ............................................................................................ 7
References ........................................................................................ 8
3.1 The Phosgene Molecule

Phosgene was synthesized by the British chemist John Davy (1790–1868) in 1812 by exposing a mixture of carbon monoxide and chlorine to sunlight. He named it "phosgene" in reference of the use of light to promote the reaction; from Greek, phos (light) and gene (born). It gradually became important in the chemical industry as the 19th century progressed, particularly in dye manufacturing. It is also a valued industrial reagent and building block in synthesis of pharmaceuticals and other organic compounds.
3.2 Names

Chemical Name - Phosgene
Chemical Abstract Registry Number - 0000 75-44-5

Other Names:
CARBON DICHLORIDE OXIDE
CARBONE (OXYCHLORURE DE) [FRENCH]
CARBONIC DICHLORIDE
CARBONIO (OSSICLORURCI DI) [ITALIAN]
CARBON OXYCHLORIDE
CARBON OXYCHLORIDE
CARBONYLCHLORID [GERMAN]
CARBONYL CHLORIDE
CARBONYL DIC*LORIDE
CG
CHLOROFORMYL CHLORIDE
FOSGEEN (DUTCH)
FOSGEN (POLISH)
FOSGENE (ITALIAN)
FOSGENO (SPANISH)
HSDB 796
KOOLSTOF OXYCHLORIDE (DUTCH)
NCI-C60219
PHOSGEN (GERMAN)
PHOSGENE
RCRA WASTE NUMBER P095

Formula:
COCl₂
CCl₂O

3.3 Physical Properties

Grade and Strength - Commercial 100%

Properties & Characteristics
Color and Physical State - At room temperature and pressure, phosgene is a colorless, non-flammable, potentially highly toxic gas. At sufficiently lower temperatures or higher pressures or both, it is a highly toxic colorless liquid.

Note: Phosgene, in the presence of high humidity, water, fog or ammonia, may produce a white cloud.
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>English Units</th>
<th>Value</th>
<th>Metric Units</th>
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<tbody>
<tr>
<td>Molecular Weight</td>
<td>98.9158</td>
<td>lbm/lbmol</td>
<td>98.9158</td>
<td>g/mol</td>
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<tr>
<td>Critical Temperature</td>
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<td>F</td>
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<td>C</td>
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<tr>
<td>Critical Pressure</td>
<td>822.97462</td>
<td>psia</td>
<td>5.67E+07</td>
<td>dyne/cm²</td>
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<td>Critical Volume</td>
<td>3.04351</td>
<td>ft³/lbmol</td>
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<td>cm³/mol</td>
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<td>Critical Compressibility Factor</td>
<td>0.285</td>
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<td>0.285</td>
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<td>Melting Point</td>
<td>-198.004</td>
<td>F</td>
<td>-127.78</td>
<td>C</td>
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<td>Triple Point Temperature</td>
<td>-198.004</td>
<td>F</td>
<td>-127.78</td>
<td>C</td>
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<tr>
<td>Triple Point Pressure</td>
<td>0.0001335</td>
<td>psia</td>
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<td>dyne/cm²</td>
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<td>Normal Boiling Point</td>
<td>45.608</td>
<td>F</td>
<td>7.56</td>
<td>C</td>
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<td>Liquid Molar Volume</td>
<td>1.12992</td>
<td>ft³/lbmol</td>
<td>70.5389</td>
<td>cm³/mol</td>
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<tr>
<td>Ideal Gas Heat of Formation</td>
<td>-9.42E+04</td>
<td>BTU/lbmol</td>
<td>-2.19E+12</td>
<td>erg/mol</td>
</tr>
<tr>
<td>Ideal Gas Gibbs of Formation</td>
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<td>BTU/lbmol</td>
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<td>erg/mol</td>
</tr>
<tr>
<td>Ideal Gas Absolute Entropy</td>
<td>67.81556</td>
<td>BTU/lbmol-R</td>
<td>2.84E+09</td>
<td>erg/mol-K</td>
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<tr>
<td>Standard Absolute Entropy</td>
<td>67.81556</td>
<td>BTU/lbmol-R</td>
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<td>erg/mol-K</td>
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<tr>
<td>Standard Heat of Formation</td>
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<tr>
<td>Standard Gibbs of Formation</td>
<td>-8.81E+04</td>
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<td>erg/mol</td>
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<tr>
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<td>BTU/lbmol</td>
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<td>Heat of Combustion</td>
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<td>-1.75E+12</td>
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<tr>
<td>Acentric Factor</td>
<td>0.201309</td>
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<td>0.201309</td>
<td>cm</td>
</tr>
<tr>
<td>Radius of Gyration</td>
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<td></td>
<td>2.88E-08</td>
<td>cm</td>
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<tr>
<td>Solubility Parameter</td>
<td>92.45383</td>
<td>(BTU/ft³)^½</td>
<td>5.64E+04</td>
<td>(erg/cm³)^½</td>
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<tr>
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<td>cm³/mol</td>
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<td>Flash Point</td>
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<td>Unknown</td>
<td>C</td>
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<tr>
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<td>Unknown</td>
<td>vol% in air</td>
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<tr>
<td>Lower Flammability Limit</td>
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<td>vol% in air</td>
<td>Unknown</td>
<td>vol% in air</td>
</tr>
<tr>
<td>Upper Flammability Temperature</td>
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<td>Unknown</td>
<td>C</td>
</tr>
<tr>
<td>Lower Flammability Temperature</td>
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<td>Auto-ignition Temperature</td>
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</tbody>
</table>

Odor: At low concentrations, its odor is similar to that of green corn or newly mown hay; at high concentrations, its odor can be sharp and suffocating. There may be perceived odors at the lower threshold value but recognition of the odor as phosgene is usually at a higher value.

Odor Threshold: >0.125 ppm (odor perception), >1.5 ppm (recognition of odor)¹

Permissible Exposure Limit Threshold Limit Value (by volume in air): 0.1 ppm.²
3.4 Reactivity, Instability and Combustion Properties

Phosgene is a stable compound at normal ambient temperatures (21°C or 70°F). At temperatures above 250°C (482°F), phosgene decomposes to form mixtures of carbon monoxide (CO), chlorine (Cl₂), carbon dioxide (CO₂) and carbon tetrachloride (CCl₄).

Phosgene reacts slowly with water to form carbon dioxide and hydrochloric acid. Phosgene reacts readily with caustic solution and even more readily with ammonia and ammonia water.

When fighting fires, minimize the reactivity hazards through precautionary measures such as those described in Section 5.0 Emergency Response.

Reactivity hazards exist when attempts are made to neutralize liquid spills because the heat of neutralization increases the rate of vaporization of liquid phosgene. Various techniques for minimizing the rate of vaporization from a liquid spill are listed in Section 5.0 Emergency Response.

Hazardous chemical reactions involving phosgene include the following:

**t-Butyl azidoformate** - In the formation of tert-butyl azidoformate by the addition of phosgene to alcohols followed by the addition of sodium nitride or hydrazoic acid in the presence of pyridine, reaction of phosgene with the azide can cause the formation of explosive carbazide. To prevent this reaction, completely remove excess phosgene; pass nitrogen into the solution prior to addition of the azide.

**Aluminum** - Powdered aluminum burns in the vapor of phosgene.

**Alcohols** - Phosgene reacts with all alcohols; two examples follow:

**2,4-Hexadiyne-1,6-diol** - The reaction between 2,4-hexadiyne-1,6-diol and phosgene produces 2,4-hexadiyne-1,6-bischloroformate which is a shock-sensitive compound.

**Isopropyl Alcohol** - The reaction between isopropyl alcohol and phosgene forms isopropyl chloroformate and hydrogen chloride. At temperatures slightly above ambient isopropyl, chloroformate can decompose explosively in the presence of iron salts.

**Secondary Amines** - Phosgene may react with secondary amines to form hazardous products.

**Potassium** - A mixture of potassium and phosgene explodes when subjected to shock.
Sodium - Vapors of sodium and phosgene react with luminescence at about 260°C.

3.5 Commercial Chemistry

Phosgene is obtained commercially by passing carbon monoxide and chlorine over activated carbon. The reaction is exothermic, producing heat that must be removed from the reactor.

The formula for the reaction to produce phosgene is:

\[
\text{CO} + \text{Cl}_2 \xrightarrow{\text{Activated}} \text{COCl}_2 + \text{Heat}
\]

Carbon Monoxide Chlorine Carbon Phosgene

Hydrogen and methane impurities in the carbon monoxide feed gas react with chlorine to produce hydrogen chloride and carbon tetrachloride respectively. The formulas for these two impurity reactions are:

\[
\text{H}_2 + \text{Cl}_2 \xrightarrow{\text{Heat}} 2\text{HCl} + \text{Heat}
\]

\[
\text{CH}_4 + 4\text{Cl}_2 \xrightarrow{\text{Heat}} \text{CCl}_4 + 4\text{HCl} + \text{Heat}
\]

Hydrogen and methane react with chlorine without catalyst, therefore the reaction can take place in the piping prior to the reactors. Normally, these impurities are at very low concentrations and the impurities formed are not significant. If a high concentration of either impurity exists, these reactions can generate enough heat to melt the pipe. Since chlorine is an oxidizer, and methane, hydrogen and carbon monoxide are fuels, a fire can occur in the pipeline without oxygen. At temperatures above 250°F, chlorine will start reacting with steel, weakening the piping and vessels. At 483°F, chlorine will ignite iron and produce a fire. Detection of these impurity generated reactions can be noticed by a rapid rise in the temperature of the feed gas after the carbon monoxide and chlorine mixing point. The use of high mixing temperature automatic shutdown is a useful method to help eliminate this type of failure.

Carbon tetrachloride and carbon dioxide can also be formed at high temperature by the reaction of two phosgene molecules. In the center of the reaction tubes temperatures are sufficiently hot to cause a small amount of this impurity reaction. The formula for this reaction is:

\[
2\text{COCl}_2 + \text{Heat} \rightarrow \text{CCl}_4 + \text{CO}_2
\]
### 3.6 Uses

Phosgene is a widely used chemical intermediate, primarily manufactured for the synthesis of isocyanate-based polymers, carbonic acid esters and acid chlorides. It is also used in the manufacture of dyestuffs, some insecticides and pharmaceuticals and in metallurgy.

Phosgene consumption is summarized below:

Practically all phosgene manufacture is captive; it is used in the manufacture of other chemicals within the plant boundary. Globally, approximately 75% of phosgene is consumed for isocyanates, 20% for polycarbonates, and about 5% for fine chemicals.

**TDI Reaction:** The overall reaction of toluene diamine with phosgene to form toluene diisocyanate (TDI) is shown below:

\[
\text{CH}_3\text{-C}_6\text{H}_3(\text{NH}_2)_2 + 2 \text{ COCl}_2 \rightarrow \text{CH}_3\text{-C}_6\text{H}_3(\text{NCO})_2 + 4 \text{ HCl}
\]

**MDI Reaction:** The overall reaction of Diaminodiphenyl methane with phosgene to form Methyl diphenyl diisocyanate (MDI) is shown below:

\[
2\text{(C}_6\text{H}_4)\text{-CH}_2\text{-2(NH}_2) + 2 \text{ COCl}_2 \rightarrow 2\text{(C}_6\text{H}_4)\text{-CH}_2\text{-2(NCO)} + 4 \text{ HCl}
\]

**Polycarbonate Reaction:** The reaction of Bisphenol-A with phosgene gives the very hard and strong polycarbonate plastics that can be molded and extruded.

\[
x(\text{HO-C}_6\text{H}_4\text{-C(CH}_3\text{)z-C}_6\text{H}_4\text{-OH}) + x(\text{COCl}_2) \rightarrow 2x \text{ HCl} + [-\text{OCO-O-C}_6\text{H}_4\text{-C(CH}_3\text{)z-C}_6\text{H}_4\text{-}]x
\]

When phosgene reacts with alcohols, the alkyl chloroformate is formed first and further reaction gives the alkyl carbonate.

\[
\text{COCl}_2 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CICOOC}_2\text{H}_5 + \text{HCl}
\]

\[
\text{CICOOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{OC(OC}_2\text{H}_5)_2 + \text{HCl}
\]
References

2. American Conference of Governmental Industrial Hygienists, TLV Annual Publication.