PHYSICAL AND CHEMICAL PROPERTIES OF ETHYLENE OXIDE.

PHYSICAL PROPERTIES.

Ethylene oxide is a colourless gas that condenses at low temperatures into a mobile liquid. It is miscible in all proportions with water, alcohol, ether, and most organic solvents. Its vapours are flammable and explosive. The physical properties of ethylene oxide are given in Tables-1.

Table-1. Some Physical Constants of Ethylene Oxide, C_2H_4O

Property	Value
Molecular weight	44.05
Boiling point,°C at 101.3 kPa	10.4
Coefficient of cubical expansion at 20°C, per °C	0.00158
Critical pressure, Mpa	7.19
Critical temperature,°C	195.8
Explosive limits in air, %	
Upper	100
Lower	3

Flash point, Tag open cup,°C	<-18
Freezing point, °C	-111.7
Heat of combustion at 25°C, KJ/Kmol	-1218
Heat of fusion, KJ/Kmol	5.17
Refractive index, n_D	1.3597

Table 2. Solubility of Ethylene Oxide in Water, mL vapour/ mL solvent

Pressure	Temperature, °C		
	5	10	20
20	45	33	20
27	60	46	29
40	105	76	49
53	162	120	74
67	240	178	101
80		294	134
93			170
101			195

Clathrate formation

Ethylene oxide forms a stable clathrate with water. It is nonstoichiometric, with 6.38 to 6.80 molecules of ethylene oxide to 46 molecules of water in the unit cell. The maximum observed melting point is 11.1°C. An X-ray structure of the clathrate revealed that it is a type I gas hydrate, with six equivalent tetrakaidecahedral (14-sided) cavities fully occupied by ethylene oxide, and two dodecahedral cavities 20-34% occupied.

CHEMICAL PROPERTIES.

Ethylene oxide is a highly reactive compound, and so is used industrially as an intermediate for many chemical products. The three-membered ring is opened in most of its reactions. These reactions are very exothermic because of the tremendous ring strain in ethylene oxide, which has been calculated.

REACTIONS

Polymerisation: The reaction of ethylene oxide with a nucleophile introduces the hydroxyethyl group:

$$ROH + C_2H_4O \longrightarrow ROCH_2CH_2OH$$

This product of this reaction can also react with ethylene oxide; if this process is repeated many times, a polymer is formed:

$ROCH_2CH_2OH + C_2H_4O \longrightarrow ROCH_2CH_2O\text{-}(CH_2CH_2O)_nH$

Low molecular polymers of ethylene oxide, ploy ethylene glycol, are formed by allowing ethylene oxide to react with water or alcohols under the proper conditions. The average molecular weight can be varied from 200 to 14000. Polymers with much higher average molecular weights from 90,000 to 4X 10_6 are formed by a process of coordinate anionic polymerization.

Crown ethers: Ethylene oxide forms cyclic oligomers (crown ethers) in the presence of fluorinated Lewis acids such as boron trifluoride, phosphorous pentafluoride, or antimony pentafluoride. Hydrogen fluoride is the preferred catalyst.

Other reactions:

1. With water:

Wurtz was the first to obtain ethylene glycol by heating ethylene oxide with water in a sealed tube. Diethylene glycol and triethylene glycol are formed as byproducts. This was the first synthesis of polymeric compounds of well- defined structure. Hydration is slow at ambient temperatures and neutral conditions, but is much faster with either acid or base catalysis. The type of anion in the catalysing acid is relatively unimportant.

2. **With Alcohol:** These reactions parallel those of ethylene oxide with water. The primary products are monoethers for ethylene glycol;
3. **With Ammonia and Amines:** Ethylene oxide reacts with ammonia to forma a mixture of mono-, di-, triethanolamines. Complex compounds of nitrogen are formed form the reaction of alkyl amines with ethylene oxide. Diethyl amine and ethylene oxide react to yield diethylaminoethanol.
4. **With phenol:** The 2-hydroxyethyl aryl ethers are prepared from the reaction of ethylene oxide with phenols at elevated temperatures and pressures. 2-phenoxyethyl alcohols is a perfume fixative. The water-soluble alkyl phenol ethers of the higher polyethylene glycols are important surface-active agents.
5. **With Acyl Halides, Hydrogen Halides And Metallic Halides:**

Ethylene oxide reacts with acetyl chloride at slightly elevated temperatures in the presence of hydrogen chloride to give the acetate of ethylene chlorohydrin.

Hydrogen halides react to form the corresponding halohydrins.

Aqueous solutions of ethylene oxide and a metallic halide can result in the precipitation of the metal hydroxide. E.g.: The halides of aluminium, chromium, iron, thorium, and zinc in dilute solution react with ethylene oxide to form sols or gels of the metal oxide hydrates and ethylene halohydrin.

6. With Hydrogen Sulphides And Mercaptans:

Ethylene oxide reacts with hydrogen sulfide to yield 2-mercaptoethanol and thiodiglycol (bis-2-hydroxyethyl sulfide). Reaction conditions determine the proportions of each derivative.

Three moles of ethylene oxide react with one mole of hydrogen sulfide in water to give the strong base tris (hydroxyethyl) sulfonium hydroxide, $[(HOCH_2CH_2)3SOH-]$. The reaction of ethylene oxide with long-chain alkyl mercaptans yields polyoxyethylene mercaptans, (some of which are nonionic surfactants).

7. With Hydrogen Cyanide:

Ethylene oxide reacts readily with hydrogen cyanide in the presence of alkaline catalysts, such as diethylamine, to give ethylene cyanohydrin. This product is easily dehydrated to give acrylonitrile in 80-90% yield:

$$HCN + CH_2\text{----}CH_2 \longrightarrow HOCH_2CH_2CN$$

$$HOCH_2CH_2CN \longrightarrow CH_2 = CHCN + H_2O$$

Other reactions are there in the reference: 6