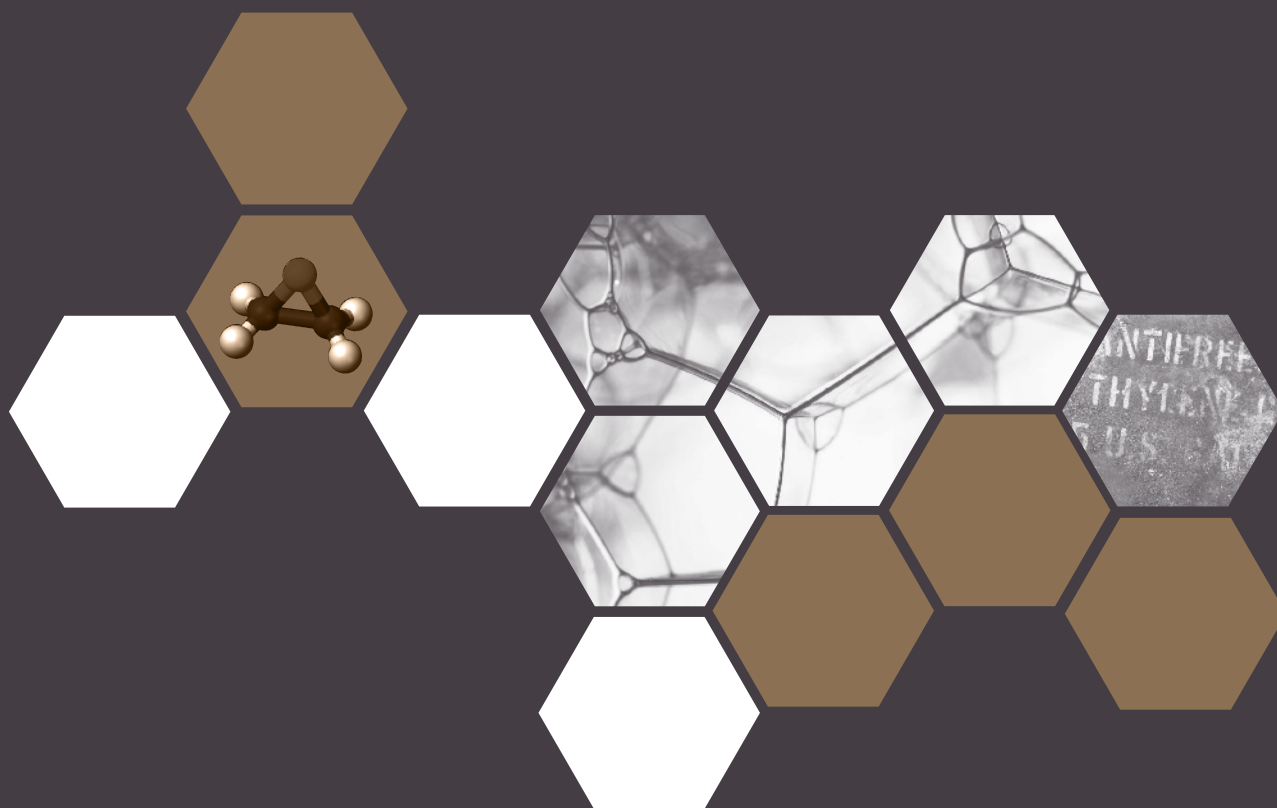


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To the Reader

Manual Preparation

As members and affiliated companies of the American Chemistry Council, we support efforts to improve the industry's responsible management of chemicals. To assist in this effort, the American Chemistry Council's Ethylene Oxide/Ethylene Glycols Panel supported the creation and publication of this manual. The Panel is comprised of the following companies:

Balchem Corporation/ARC Specialty Products

BASF Corporation

Bayer Material Science LLC

Celanese Ltd.

Champion Technologies

Croda, Inc.

The Dow Chemical Company

Eastman Chemical Company

Honeywell

Shell Chemical LP

The development of this manual was led by the Panel's Ethylene Oxide Safety Task Group (EOSTG), a group comprised of producers and users of ethylene oxide. The EOSTG functions to generate, collect, evaluate and share information to support product stewardship with regard to ethylene oxide. The EOSTG formed a manual work group, chaired by Keith Vogel of Lyondell Chemical Company, to lead the development of this document. The following work group members provided significant contributions:

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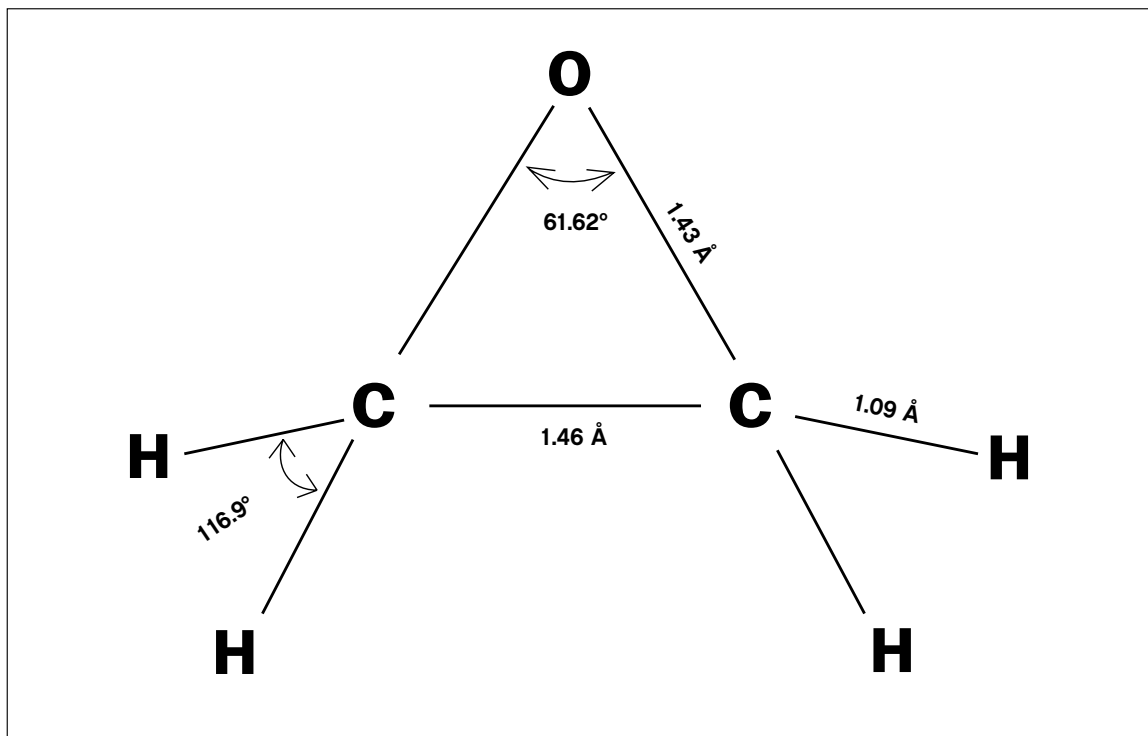
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2.0 Properties of Ethylene Oxide

2.1 Introduction

Figure 2.1 The Ethylene Oxide Molecule



Ethylene Oxide (EO), sometimes referred to as oxirane, is the simplest cyclic ether. It is a colorless gas or liquid and has a sweet, etheric odor. The structure of an EO molecule is shown in Figure 2.1 above. The C-C bond is short and the bond angles strained [1]. Because its highly strained ring can be opened easily, EO is highly reactive.

EO was first prepared in 1859 by Wurtz [2] using potassium hydroxide solution to eliminate hydrochloric acid from ethylene chlorohydrin. The chlorohydrin process developed from Wurtz's discovery and industrial production of EO began in 1914. The direct catalytic oxidation of ethylene, discovered in 1931 by Lefort [3], has gradually superseded the chlorohydrin process. Currently, EO is produced by direct oxidation of ethylene with air or oxygen.

Virtually all EO produced is further reacted (Section 2.4) to derivative products. Its most important derivative is ethylene glycol, which is used for the manufacture of polyester and in

automotive antifreeze. Other EO derivatives include surfactants, solvents, amines and poly(ethylene) glycols. EO also has several direct uses, including use as a sterilant and the treatment of spices and other foodstuffs. United States production of EO in 2004 was 8,315 million (8.3 billion) pounds, according to National Petrochemical & Refiners Association's (NPRA) Petrochemical Surveys 4 Quarter 2003 (published January 27, 2005), highlighting its role as an important industrial chemical.

The highly reactive nature of EO, which helps make it a versatile and commercially important chemical intermediate, also underlies some of the main hazards of EO – in particular, its flammability, reactivity, explosive vapor decomposability and toxicity. Understanding the properties of EO is important to managing its use.

2.2 Physical Properties

Important physical properties of EO are summarized in Table 2.1, below.

Table 2.1 Physical Properties of Ethylene Oxide

Ethylene Oxide			
Chemical Abstracts Name:	Oxirane		
Chemical Abstracts Number:	75-21-8		
PSUID Code:	1441		
UN CODE:	1040		
IUPAC Name:	Oxirane		
Synonyms:	Ethylene Oxide Dihydrooxirene Dimethylene Oxide Epoxyethane	1,2-Epoxyethane Oxacyclopropane Oxidoethane EO, ETO	
Other Names: Ethene oxide; Oxane; Oxirene, Dihydro-; Oxyfume; Oxyfume 12; T-Gas; Aethylenoxid; Amprolene; Anprolene; Anproline; ENT-26263; E.O.; 1,2-Epoxyaethan; Ethox; Ethyleenoxide; Etylenu tlenek; FEMA No. 2433; Merpil; NCI-C50088; a,b-Oxidoethane; Oxiraan; Oxiran; RCRA waste number U115; Sterilizing gas ethylene oxide 100%; C2H4O [37]			
Structural Formula:	CH ₂ OCH ₂		
Property	SI Units	Engineering Units	Note(s)/ [References]
Molecular Weight	44.053	44.053	
Critical Temperature	469.15°K	384.8°F	
Critical Pressure	7,191 kPa	1,043 psia	
Critical Volume	0.00319 cu m/kg	0.051 cu ft/lb	
Critical Compression Factor	0.2588	0.2588	AIChe DIPPR (r) Database
Melting Point	160.65°K	-170.5°F	
Triple Point Temperature	161.46°K	-169.1°F	1
Triple Point Pressure	0.0078 kPa	0.00113 psia	
Normal Boiling Point at 101.325kPa (1atm)	283.6°K	50.8°F	AIChe DIPPR (r) Database
Liq. Sp. Gr. 20°C/20°C (68°F/(68°F))	0.875	0.875	
Liq. Volume @ 25°C (77°F)	0.00113 cu m/kg	0.018 cu ft/lb	2
Coefficient of Cubical Expansion, at 20°C (68°F)	0.00158/°K	0.00088/°F	[37]
Heat of Vaporization	579.5 kJ/kg	249.2 BTU/lb	
Entropy of Vaporization	2.04 kJ/kg*°K	0.488 BTU/lb*°F	[37]
Heat of Formation – Ideal Gas	-1,194.8 kJ/kg	-514 BTU/lb	[37, 58, 59]
Heat of Formation – Liquid	-1766.5 kJ/kg	-760 BTU/lb	[59]
Gibbs Energy of Formation – Ideal Gas	-300.3 kJ/kg	-129.15 BTU/lb	4
Gibbs Energy of Formation – Liquid	-267 kJ/kg	-115 BTU/lb	3
Absolute Entropy – Ideal Gas	5.52 kJ/kg*°K	1.319 BTU/lb*°F	[37, 59]
Absolute Entropy - Liquid	3.494 kJ/kg*°K	0.835 BTU/lb*°F	3 [59]
Heat of Fusion at Melting Point	117.5 kJ/kg	50.52 BTU/lb	[37]

(continued on page 4)

Table 2.1 (continued from page 13)

Property	SI Units	Engineering Units	Note(s)/ [References]
Entropy of Fusion	0.73 kJ/kg*°K	0.175 BTU/lb*°F	[36]
Standard Heat of Combustion, Liquid HHC (HHV) (to water condensed)	-29,076 kJ/kg	-12,509 BTU/lb	5
Standard Heat of Combustion, Gas LHC (LHV) (to water as vapor)	-27,649 kJ/kg	-11,895 BTU/lb	5
Standard Heat of Combustion, Gas HHC (HHV) (to water condensed)	-29,647 kJ/kg	-12,755 BTU/lb	5
Heat of Solution in Water	-142.7 kJ/kg	-61.35 BTU/lb	
Acentric Factor	0.197	0.197	
Radius of Gyration	1.937E-10 m	6.355E-10 ft	
Dipole Moment	6.3E-30 C*m	1.889 Debye	
Liq Dielectric Const at 0°C (32°F)	14.5	14.5	
Vapor Dielectric Const at 15°C (54.5°F)	1.01	1.01	[10]
Electrical Conductivity (liq)	4E-06 Siemens/m	4E-08 mhos/cm	
van der Waals Volume	5.485E-04 cu m/kg	0.008785 cu ft/lb	
van der Waals Area	7.492E+06 m sq/kg	3.658E+07 ft sq/lb	
Refractive Index, n _D at 6.8°C (44.3°F)	1.3597	1.3597	
Flash Point	<255.16°K	<0°F	
Flammability Limits	2.6-100 vol.%	2.6-100 vol.%	
Fundamental Burning Velocity, Pure EO	0.027m/s	0.089 ft/s	[58]
Autoignition Temp (in Air)	718.15°K	833°F	[60]
Decomposition Temp (at 760 mm Hg)	-773°K	-932°F	6, [17]
<p>NOTES:</p> <ol style="list-style-type: none"> 1. Estimated to be equal to the melting point temperature. 2. Determined at the normal boiling point. 3. Estimated from CRC 1994 Handbook of Thermophysical and Thermochemical Data. 4. Calculated from the enthalpy of formation and the absolute entropy. 5. Calculated from heats of formation. 6. Decomposition temperature affected by pressure, container surfaces, volume, and geometry. Decomposition temperature has been reported as low as 842°F (723.2°K) and as high as 1060°F (844°K) 			
<p>WARNING: FLAMMABILITY LIMITS ARE DETERMINED AT 77°F (298°K) AND 1 ATMOSPHERE. HIGHER TEMPERATURES AND/OR HIGHER PRESSURES WILL LOWER THE LOWER LIMIT.</p>			

Graphs and tables of selected temperature-dependent properties of EO are provided in Appendix A.

Ethylene Oxide Water Mixtures

Table 2.2 on the next page shows some of the properties of aqueous EO solutions. Of particular note are the relatively high melting points, which

are due to hydrate formation [4]. Hydrates consist of organic molecules enclosed by water molecules in a cage structure. The highest melting point observed is 52°F (11.1°C) and corresponds to a hydrate composition of C₂H₄O • 6.89 H₂O [5].

Liquid EO and water are completely miscible in each other in all proportions, but due to differences in density, may not initially mix in the absence

Table 2.2 Physical Properties of Aqueous Ethylene Oxide Solutions [9,10]

EO Content wt%	Melting Point °F (°C)	Bubble Point °F (°C)	SG at 50/50°F (10/10°C)	
			Flash Point	°F (°C)
0	32 (0)	212 (100)	1.0000	
0.5				107 (41.5)
1	31.3 (-0.4)			88 (31)
2				37 (3)
3	29.7 (-1.3)			
5	29.1 (-1.6)	136.4 (58)	0.9977	28 (-2)
10	42.1 (5.6)	108.5 (42.5)	0.9944	
20	50.7 (10.4)	89.6 (32)	0.9816	-6 (-21)
30	52 (11.1) max	80.6 (27)	0.9658	-18 (-28)
40	50.7 (10.4)	69.8 (21)	0.9500	-31 (-35)
60	46 (7.8)	60.8 (16)	0.9227	-49 (-45)
80	38.7 (3.7)	55.4 (13)	0.9005	-63 (-53)
100	-169 (-111.7)	50.7 (10.4)	0.8828	-71 (-57)

of any agitation (i.e., it is possible to have two separate phases if one is added beneath the surface of the other without mixing). EO/water mixtures are highly non-ideal and do not follow Raoult's Law. Raoult's Law deviation factors for EO/water mixtures are shown in figures 14 and 15 in Appendix A.

Solubility of Ethylene Oxide Gas

The solubility of EO gas in various compounds has been measured and reported at atmospheric pressure and 72–74°F (22–23°C) by Chaigneau [41]. These compounds include water, alcohols, hydrocarbons, oils, chlorocompounds, esters and waxes.

Solubility of Gases in Ethylene Oxide

The solubility of gases in liquid EO vary, increasing in the order nitrogen, argon, methane and ethane. Increasing temperature tends to increase the solubility. The Henry's Law Constants for these gases in EO at different temperatures are given in Appendix A [7].

2.3 Reactive and Combustive Properties

Understanding the reactivity and combustion properties of EO is important to managing its use. As described in Chapter 5, serious incidents have occurred during the processing, storage, and transportation of ethylene oxide.

Combustion/Flammability

EO is a flammable, explosible chemical. Its fire and explosion characteristics are system-dependent. Some of the characteristics for EO/air mixtures are as follows.

- The minimum value cited for the lower flammable limit of EO air mixtures is 2.6% [20].
- The upper flammable limit is typically stated to be 100% because pure EO can violently decompose with a significant release of heat in the absence of air or oxygen.
- Accordingly, the flammable range of EO-air mixtures is 2.6–100%.

Table 2.3 Heat of Reaction of Various Ethylene Oxide Reactions at 25°C

	kJ/kg	BTU/lb	Note [Reference]
Combustion			
Liquid HHC (to water condensed)	-29,076	-12,509	1
Gas LHC (to water as vapor)	-27,649	-11,895	1
Gas HHC (to water condensed)	-29,647	-12,755	1
Decomposition			
	-3,051	-1,312	[59]
	-3,013	-1,296 (calc from gas heats of formation)	
Isomerization to acetaldehyde			
	-2,621	-1,127	
Polymerization			
	-2,324	-1,000	[13, 17]
Hydrolysis			
	-2064	-887	[46]
<i>NOTE:</i>			
1. Calculated from heats of formation.			

- The autoignition temperature of EO in air at 14.7 psia is 833°F (445°C) [21].

This temperature can be lower with the presence of certain impurities such as water, acetaldehyde, and rust.

Figures 2.2 and 2.3 illustrate the flammable limits for EO, air and either nitrogen or carbon dioxide ternary mixtures at atmospheric (14.7 psia) pressure (101.325kPa) [39]. The literature also indicates some variability in the boundary concentration demarcation separating the flammable and non-flammable regions. [38, 39, 59]. Also, it is important to recognize that mixture pressure also affects the flammability characteristics. Figure 2.4 illustrates the effects of pressure on the flammability region for EO/Nitrogen/Air. Thus, more or less dilution with an inerting gas may be required to maintain a non-flammable condition depending on whether the pressure is greater or less than atmospheric pressure.

The flammable limits of other mixtures of EO with various gases and air can be found in the literature. See Appendix D for examples: EO with H₂O [22]; N₂ [23], [22]; N₂-H₂O [24]; CO₂-H₂O [24]; CH₄ [15]; CO₂ [6], [22], [25]; C₃H₆ [26]; C₄H₉ [26]; N₂-air [6]; CH₄-air [6]; CO₂-air [20]; CF₂Cl₂-air [27], [28]; CO₂-air, N₂-air, R12-air, R134a-air [39]; CO₂-air, N₂-air, Steam-air [24]; MeBr-air [24].

Flammability of Ethylene Oxide and Water Mixtures

Due to the flash characteristics of EO/water mixtures, it can be difficult to extinguish fires of these liquid mixtures until the EO reaches a certain dilution. In closed systems such as sewers, 100 to 1 water to EO dilution ratios (vol/vol) may be required to produce a mixture, the vapor of which will not support combustion. In open systems, such as around an atmospheric spill, water/EO mixtures of less than 22 to 1 (vol/vol) can generate sufficient vapors to support combustion.

Ignition Energy and Static Electricity

Liquid EO is an electrically conductive fluid that cannot accumulate static electricity charges in metal containers having internal parts properly bonded and grounded (see NFPA 77 Static Electricity Guide). Bottom filling is therefore generally not needed unless there are isolated internal areas that might accumulate a charge. If containers have non-conductive linings, such as glass or plastic, use of an uncoated grounded metal device in contact with the contained liquid at all times provides effective grounding of the liquid.

At standard conditions and in the absence of air, pure EO vapor minimum ignition energy (MIE) is about 1000 mJ [9]. While this minimum EO ignition

Figure 2.2 Flammable Region of Ethylene Oxide/Nitrogen/Air Mixtures

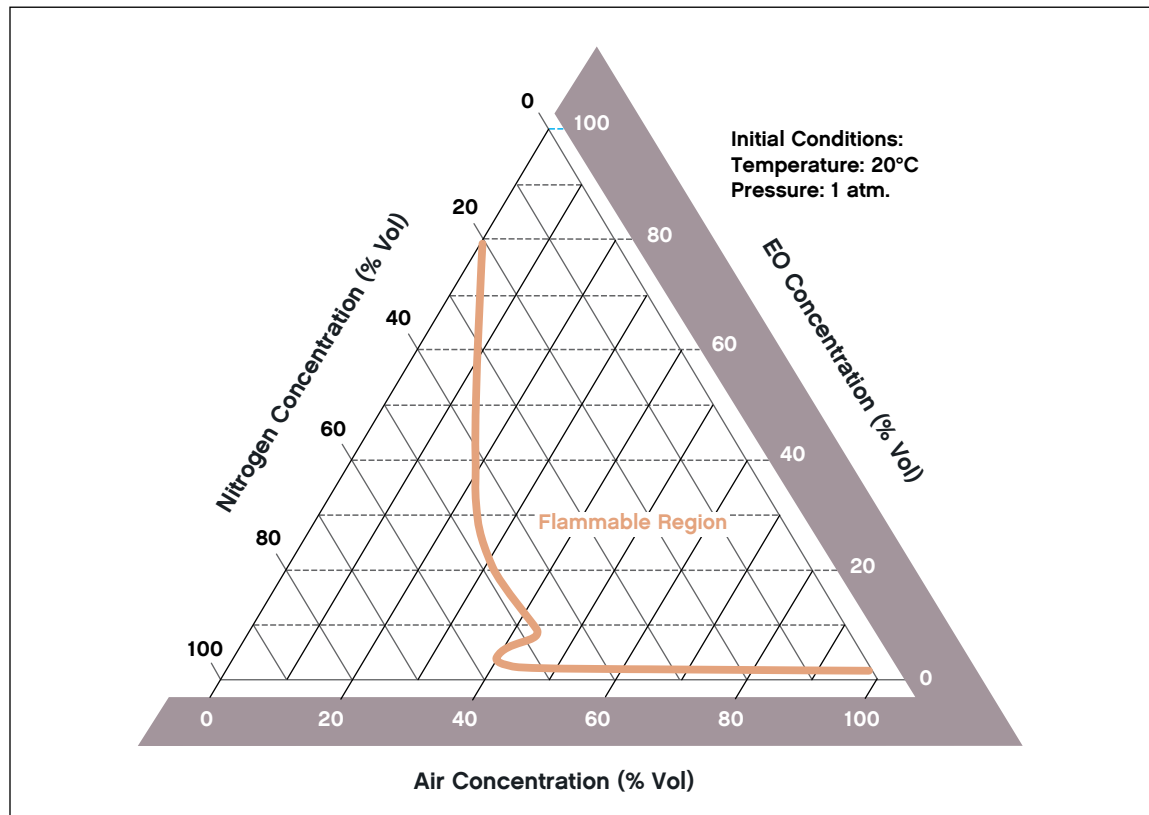


Figure 2.3 Flammable Region of Ethylene Oxide/Carbon Dioxide/Air Mixtures

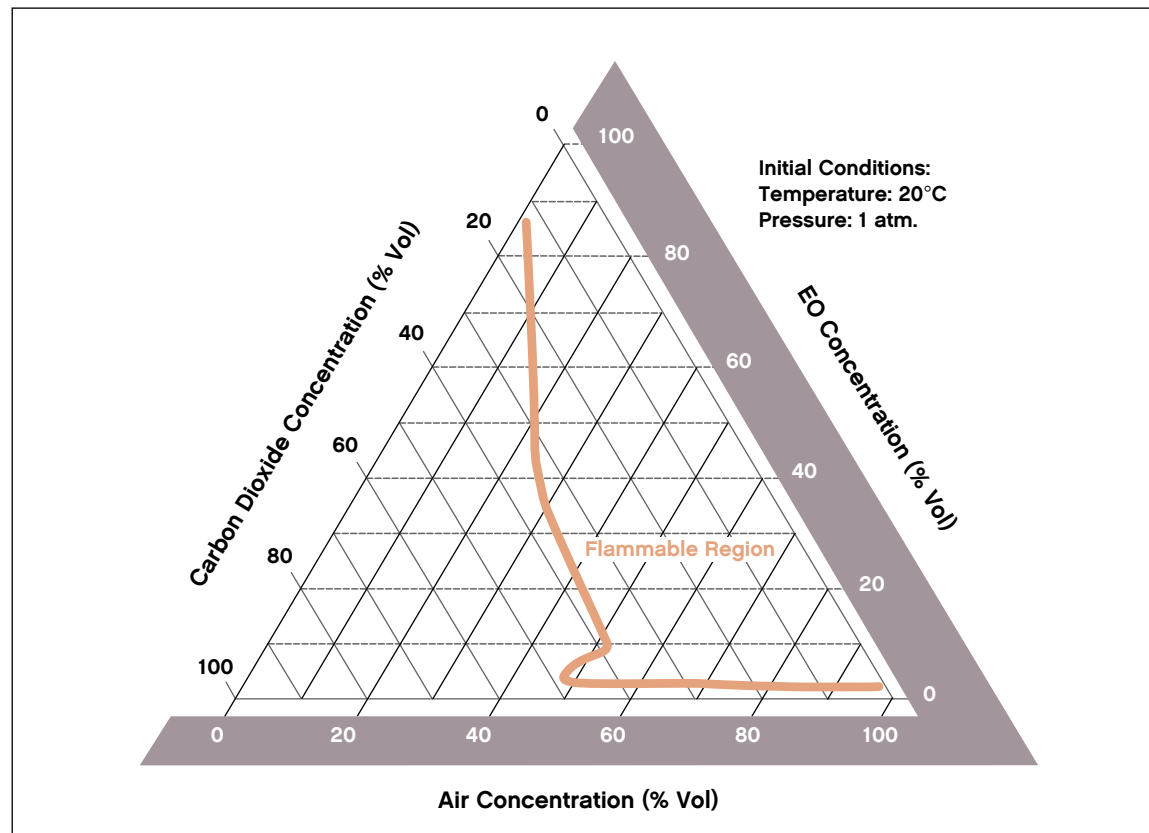
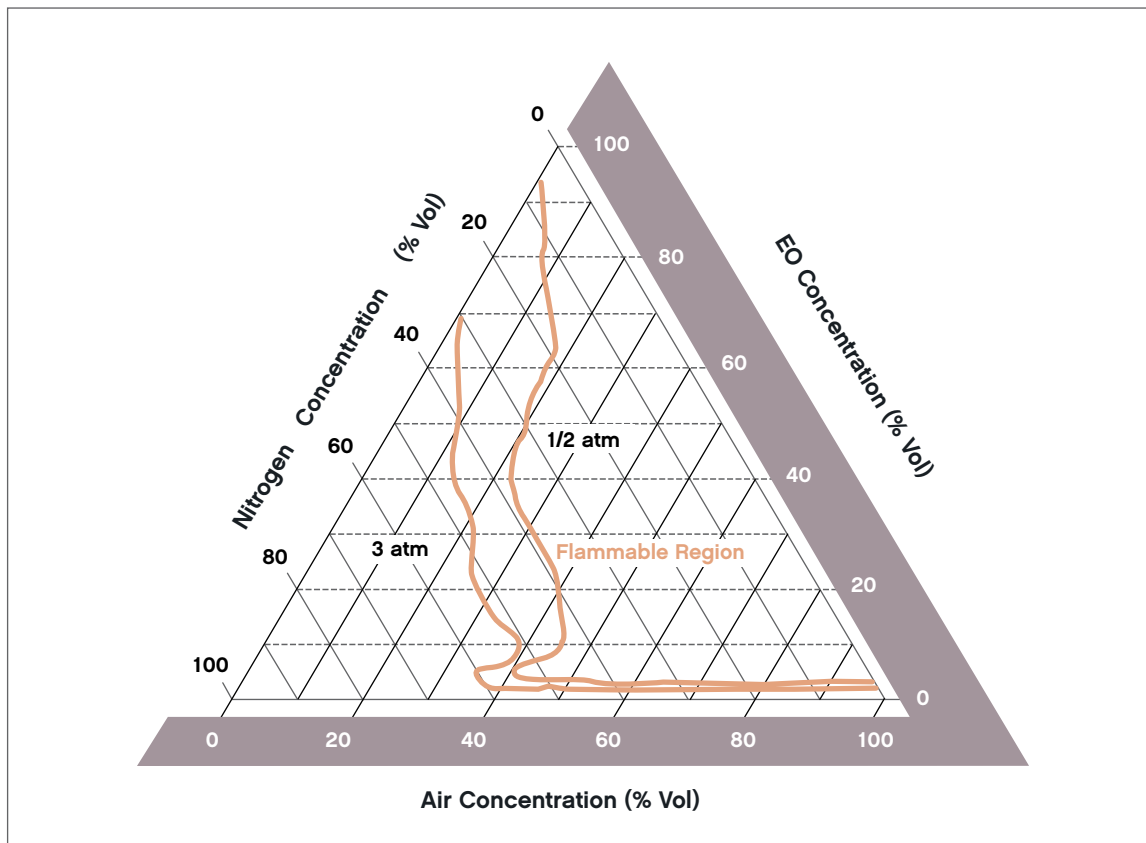


Figure 2.4 Effects of Pressure on Flammable Region of Ethylene Oxide/Nitrogen/Air Mixtures

energy decreases with increased temperature and pressure, a static energy discharge is much lower than the MIE and is not a significant hazard under normal liquid storage and handling conditions. EO liquid discharged into the vapor space of a properly inerted storage tank in the absence of oxygen will not carry sufficient energy to ignite the vapor.

At standard conditions and in the presence of air, the MIE of EO is in the range of 10,000–100,000 mJ at just above the lower flammable limit (2.6 mol%) and is about 1000 mJ at the upper flammable limit (100 mol%) [58]. However, between these upper and lower flammable limits, the ignition energy follows a “skewed parabolic” contour with changes in composition that reaches a minimum value of 0.06 mJ at about 10.4 mol%. Comparing minimum ignition energies, EO in air at these concentrations has a minimum ignition energy less than gasoline vapor (0.24mJ), and only somewhat greater than hydrogen (0.01-0.02mJ). (Routine movement of a person can typically initiate static discharge energy in the range of 1-50 mJ, while the energy

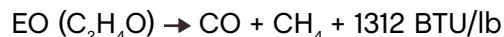
from ordinary spark plugs is ca. 20-30 mJ [31]. Note that people cannot usually feel sparks carrying less than about 2 mJ.) Thus, various mixtures of EO vapor and air can be easily ignited by a static spark, even by the low discharge levels that might be generated by a person. EO in air also has a much wider flammability range (2.6-100%) than either gasoline (1.4-7.6%) or hydrogen (4.0-75%). Consequently, static discharge is a very important consideration in the design and operation of equipment. See Eichel [32] for a discussion of electrostatic calculations.

The NFPA 77 Static Electricity Guide provides guidance for bonding and grounding equipment in EO service. In general, the NFPA Guide provides that flanged connections do not need external bonding wires, but that users should consider using external bonding wires where electrical continuity might appear questionable (for example, where specially coated bolting materials are in use, in areas near swivel joints, or if a non-conductive item of equipment is placed in a line). For static grounding, the NFPA Guide notes that all metal parts should have a resistance to ground of 1M Ω or less.

To minimize the potential for static buildup, samples or small quantities of EO are generally obtained using grounded metal portable containers with conductive linings. Use of non-conductive plastic bottles and pails should be performed only with great caution. If circumstances, such as laboratory settings, necessitate their use, the container should be bottom filled (submerged) using a grounded conductive dip tube resting on the bottom of the container to minimize splashing and turbulence. Where a transparent sample container is required (such as for clarity inspection), use of a glass container helps minimize static charge buildup. Avoid rubbing or cleaning the container immediately prior to filling or emptying as another means of avoiding buildup of static charge. (See Section 6.9 for further discussion of sample system design.)

Decomposition

Pure EO vapor or EO vapor mixed with air or an insufficient amount of inert gases can decompose explosively. The primary decomposition reaction is expressed by the following equation:



The reaction can also produce ethane, ethylene, hydrogen, carbon and acetaldehyde [10, 17].

At atmospheric pressure, thermal decomposition of pure EO vapor occurs at 932°F (500°C) [17]. Both lower and higher gaseous EO decomposition temperatures have been reported – indicating that decomposition temperature is affected by pressure, surface characteristics, volume and geometry. EO can also ignite and decompose explosively below atmospheric pressures, down to a pressure of around 4.8-5.8 psia, but at greater than 932°F (500°C).

Once the decomposition reaction has been initiated, it can be propagated from the ignition source through the gas phase as a flame (i.e., reaction zone) and, under certain conditions, may be explosive. It is important to understand that this reaction can occur in the absence of air or oxygen. (Note that a number of sources consider a flame a region of combustion, whereas combustion is defined as the oxidation of a fuel source.)

High pressure can be generated by decomposition of EO. The maximum theoretical explosive pressure is about 10 times the initial pressure but this can

increase to 20 times the initial pressure if liquid EO is present. This phenomenon occurs because liquid EO evaporates and participates in the decomposition reactions which take place in the vapor phase [15].

EO liquid mists will decompose explosively similarly to EO vapor. The decomposition of these two-phase mixtures yields greater pressures and rates of pressure rise than the vapor alone [17]. Liquid EO can participate in a decomposition that starts in the vapor phase. Explosion of liquid EO, initiated by a strong ignition source within the liquid, was first described in 1980. It is thought that the ignition source vaporizes liquid EO and the decomposition reaction takes place in the gas phase.

It has been reported in the literature that pure EO vapor, when ignited in a closed-end system, can undergo a transition from decomposition flame to a detonation shock wave with a propagation speed of approximately 1 mile (1,600 meters) per second [47]. This phenomenon, which destroyed a 12-inch (0.3 meter) pipe test apparatus, can generate overpressures that are orders of magnitude greater than the maximum theoretical overpressure. The progression of a decomposition flame front to a detonation shock wave can result in a highly destructive event. The literature cited above concluded that certain specific conditions of equipment size, pressure, and temperature were necessary for a deflagration to transition to a detonation. See Chapter 5 for more information and illustrative incidents.

Mixtures of EO with nitrogen, carbon dioxide and methane will not decompose over certain concentration ranges; thus, the risk of vapor decomposition can be minimized by dilution with a suitable inert gas. Nitrogen is most commonly used for dilution, although other inert gases and methane have been used on occasion. Note that carbon dioxide is not typically used as a diluent due to its high solubility in EO. The dilution quantity depends on temperature, pressure and the expected ignition source and duration [9]. The most thorough discussion of the EO decomposition process is presented in Reference [17]. The minimum total pressure for inert blanketing is important [9, 10], and Section 6.5 presents information relevant to the inerting of EO in storage and handling systems. Chapter 9 provides information concerning the inerting of

transportation containers. Inerting of vapor spaces of reactors using EO as feeds or reagents is discussed in Section 6.6.

Deflagration and Detonation of Ethylene Oxide in Piping

Unpublished work by Union Carbide performed in 1956 provided some information on the topic of EO vapor decomposition flame propagation, suggesting that at pressures up to 75 psia, EO decomposition flames would not be expected to propagate indefinitely through vented, horizontal pipe with a diameter of less than 2 inches.

In the late 1990s, the American Chemistry Council's Ethylene Oxide Industry Council (now the Ethylene Oxide/Ethylene Glycols Panel), sponsored work to revisit earlier Union Carbide data and to obtain specific information in two areas: (1) decomposition flame speeds and the extent of flame propagation in long lengths of 2-inch diameter pipe containing pure EO vapor; and (2) maximum flame speeds in long lengths of 12-inch pipe containing pure EO vapor.

This work was completed and results published in 2001[47]. The study showed:

- Indefinite propagation of a slow deflagration flame can occur in 2-inch pipe under certain handling conditions. Flames may fail to propagate under adverse flow conditions or if the flame is forced to propagate downward; however, 2-inch pipe cannot be considered a barrier to indefinite flame propagation.
- A decomposition flame can accelerate from a deflagration to a detonation in 12-inch pipe. Results of the study observed the decomposition flame velocity to have exceeded 3900 ft/sec (1200 meters/sec), but the authors noted that, due to study limitations, the flame front velocity was likely to have been substantially higher at the far end of the pipe. The transition from deflagration to detonation has the potential to create significantly higher pressures than if a direct detonation occurred.

Ethylene Oxide Disproportionation Reactions

Investigation of a major industrial incident that occurred in a North American EO manufacturing facility during the 1990s indicated that EO vapor

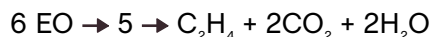
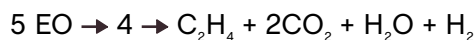
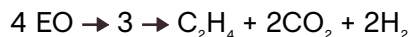
in contact with high surface area metal oxides, such as the gamma form (Fe_2O_3) of iron oxide, can undergo disproportionation reactions that can raise local temperatures above the decomposition temperature of EO.

In this particular incident the disproportionation reaction occurred within the tubes of a distillation column reboiler, in the presence of a deposit of high surface area rust embedded in an EO polymer matrix, when flow through the reboiler was reduced by a process upset. The loss of reboiler circulation allowed for rapid heat buildup in the vicinity of the iron oxide/polymer deposit, accelerating the disproportionation reactions which then progressed into localized temperatures reaching the EO thermal decomposition temperature. The result was an explosion that destroyed the distillation column [42].

A similar incident occurred at a Gulf Coast EO manufacturing facility in 2000 [43], resulting in internal column damage.

Reference 42 provides the following information with regard to this type of reaction:

“The disproportionation of ethylene oxide ... was previously unknown... and not reported in the open literature. It consists of several simultaneous reduction/oxidation reactions.... All three of the stoichiometric reactions ... below were observed experimentally.”



The disproportionation produces ethylene and carbon dioxide, which reduces the vapor-phase EO concentration. As the reference notes, “In order for a propagating decomposition of ethylene oxide to occur, the hot spot temperature must reach the ethylene oxide autodecomposition temperature of about 500°C (932°F) while the vapor phase contains above about 40% EO.”

As the reference points out, the disproportionation reactions have higher activation energies than polymerization. Although disproportionation reactions release approximately the same heat as the polymerization reaction, the disproportionation reaction rates are much faster at higher temperatures. The heat release rates are thus proportionately higher in disproportionation reactions and this mechanism can form a localized hot spot:

“... heat release profiles from the reaction of ethylene oxide with the gamma form (Fe_2O_3) of iron oxide [differ] at ... different temperatures. At 155°C (311°F), EO polymerization occurs, but it occurs over a period of hours so that the maximum heat flow is relatively low. At 200°C (392°F), however, EO disproportionation occurs in minutes, rapidly generating a very high heating rate. In essence, these disproportionation reactions can serve as a chemical ignition source by generating a hot spot within/on the iron oxide containing polymer with a temperature greater than the EO autodecomposition temperature.”

The reference concludes:

“... Small amounts of ethylene oxide polymers are indigenous to ethylene oxide liquid operations. Furthermore, it was found that ethylene oxide polymer binds any metal ions present in the liquid. The key to safe ORS (Oxide Refining Still) operation is to always maintain adequate liquid contact at all heated surfaces, eliminating the possibility of vapor reaching temperatures higher than the boiling point of the equilibrium liquid.”

Reactions with Water, Acids, and Bases

The reaction of EO with water (i.e., hydrolysis) to produce high molecular weight glycols is widely practiced within chemical process industries. Hydrolysis of EO to higher molecular weight glycols is also used in the design of EO vent scrubbers where EO absorbed by water is reacted to glycols. Reactions of this type are exothermic and require appropriately sized heat removal equipment. Adding or mixing water to EO inventories in storage vessels or transportation containers has potentially severe consequences.

Rate expressions for EO in water at neutral pH, acid catalyzed and base catalyzed reactions are available in the open literature [9, 51, 52, 53, 54]. These studies are generally based on first order kinetics with 5 wt.% EO in the solution. However, calculated results from these rate expressions do not agree well with experimental data at significantly higher EO concentrations.

Studies designed to better explain kinetics for the reaction of EO with water at neutral pH were initiated by EO producers [46]. These studies examined varying EO concentrations (up to 99%) in water. The data presented, regarding the kinetics, heat of reaction, stoichiometry, physical properties and vapor-liquid equilibrium for various water-contamination reactions of EO and essentially

neutral pH water, can assist in sizing pressure relief devices for inadvertent water contamination of vessels containing EO.

Polymerization

EO has a tendency to polymerize. As this section will discuss, formation of EO polymer is a function of temperature, time at temperature and exposure to catalysts or contaminants.

A number of sources have observed thermally driven polymerization initiated at different temperatures. Industrial laboratory tests have shown high purity EO self-polymerization to have occurred at temperatures at 320°F (160°C) in a closed and near-adiabatic system. Additionally, there have been reports that thermal initiation of polymerization can occur at temperatures as low as 212° F (100°C). Polymerization can occur at lower temperatures, including ambient temperature (see discussion about catalyzation by rust at ambient temperature, below), but at ambient temperature the polymerization reaction is considerably slower. The polymerization reaction can also be influenced by contaminants for which the initiation point for polymerization appears to be strongly dependent upon the level and type of trace impurities in the EO.

The polymerization reaction is exothermic, releasing 1,000 BTU per pound of EO reacted [13]. If exposed to water at temperatures greater than 122°F (50°C), the polymer reacts to produce sticky polyethylene glycols.

The usual catalysts for EO reactions, such as strong alkali [18], iron oxide (rust) [19], and other metal oxides accelerate the reaction. When catalyzed by rust at ambient temperature, polymerization can create blockages or plugs in operations, such as pluggage of lines, relief valve inlets, and instrumentation taps. Polymerization can also result in off-specification product. Britton [17] has reported a rust catalyzed heat of polymerization of 1102 ± 121 BTU/lb.

The condition of metal surfaces is extremely important in determining the rate of EO polymer formation. It has been reported [19] that even clean carbon steel catalyzes polymerization, although at a much slower rate than rusty steel. For this reason, stainless steel is often chosen as a material of construction, especially when the surface to volume ratio is high. Some other factors that have

been observed to affect the rate of polymerization are:

- Metal surface to volume ratio
- Temperature
- Residence time in equipment

The polymerization reaction has not been found to be auto-catalytic [43]. That is, the presence of a pure EO polymer does not accelerate the polymerization process. However, polymer traps iron oxide particles which is a catalyst for polymerization.

Overheating of EO or contamination of EO with catalysts such as potassium hydroxide (KOH) can lead to runaway polymerization. Reference [18] discusses an EO polymerization (or “polycondensation”) incident involving contamination of an EO-containing cylinder with chlorine and alkali. The result was an 8-hour accelerating or “runaway” reaction that ended in an explosion.

Table 2.4 Physical Properties of Ethylene Oxide Polymer [44]

Molecular Weight	Melting Temp.°F (°C)	Density (g/cc)
200	-85 softening (65)	1.127
600	72 softening (22)	
1000	102 (39)	
3400	131 (55)	1.204
10,000	145 (63)	
100,000	150 (66)	1.130
4,000,000	150 (66)	

Properties of EO Polymer

Pure EO polymers have been characterized [44] as clear viscous liquids (molecular weight less than 600) and as opaque white solids (higher molecular weight). However, in industrial settings, EO polymer is often dark brown or black, due to the presence of magnetite iron oxide (Fe_3O_4) inside the polymer matrix. Note that the density of EO polymer is significantly higher than that of EO, so polymer that

precipitates inside a storage container will tend to collect on the bottom.

Solubility of EO polymer in various solvents, including EO, is a function of molecular weight of the polymer and temperature. In general, higher molecular weight polymer is harder to dissolve. Solubilities of low molecular weight EO polymer in various solvents are set out in Table 2.5. Note the extremely low solubility in the non-polar solvent heptane.

Polymer samples from EO processing and storage equipment have exhibited molecular weights ranging from a few thousand to over one million atomic mass units (amu). At the upper end of this range, the polymer is quite insoluble in solvents and hot water and must be removed by physical means.

Cold Temperature Polymer Precipitation (“Drop-Out”)

There have been reports observing copious amounts of polymer during railcar off-loading in cold climates at temperatures between 20°F - 40°F (-7°C - 4°C), but when these railcars have been returned to warmer climate loading facilities, the polymer is no longer observed. To explore this phenomenon further, an EO producer collected polymer residues from customer sites and plant storage vessels and dissolved the residues in EO. As illustrated in Figure 2.5 below, rapid cooling of the samples, with molecular weights ranging from 50,000-1,000,000, produced an instantaneous dropout temperature that correlated with molecular weight.

Three important observations can be made about the polymer drop-out process.

- First, the polymer fell out as a gel with a volume one hundred times larger than the dry polymer originally placed in the vessel. Thus, reports of copious amounts of polymer appear to be explainable by gel formation.
- Second, the polymer rapidly sank to the bottom upon standing. Therefore, the concentrated and gelled polymer would be expected to be observed at the beginning of the off-loading process.

Table 2.5 Solubility* of Ethylene Oxide Polymer in Various Solvents [45]

Solvent	Mol Wt 500 – 600		Mol Wt 3000 - 3700	
	T=68°F	T=122°F	T=68°F	T=122°F
Water	73	97	62	84
Methanol	48	96	35	S
Acetone	20	S	<1	S
Trichloroethylene	50	90	30	80
Heptane	0.5	.01	<.01	<.01

*Solubility is given in weight percent; S signifies completely soluble

- Third, the temperatures at which the polymer precipitated in this experiment were lower than the off-loading temperatures of 20°F to 40°F (-7°C to 4°C) where polymer has been observed.

Comparison of “long-term” drop-out temperatures to “instantaneous” ones appears to resolve the discrepancy of the third observation. Figure 2.6 shows that, after about four days exposure to 40°F (4°C), most polymers above 180,000 amu precipitate. It is not uncommon for a railcar shipped to a colder destination to sit for several days before unloading. Since the temperature

of the EO in a railcar shipped to a colder climate would be expected to decrease over several days in such conditions, it may be expected for the once-soluble polymer to precipitate out of solution. This analysis helps explain the polymer drop-out phenomenon observed at off-loading temperatures of 20°F to 40°F (-7°C to 4°C).

Low molecular weight polymer of 45,000 amu, however, failed to drop out after three weeks at 40°F (4°C). It appears that there is a region below 180,000 amu where polymer would not be expected to drop out of solution at 40°F (4°C) during routine railcar holding times.

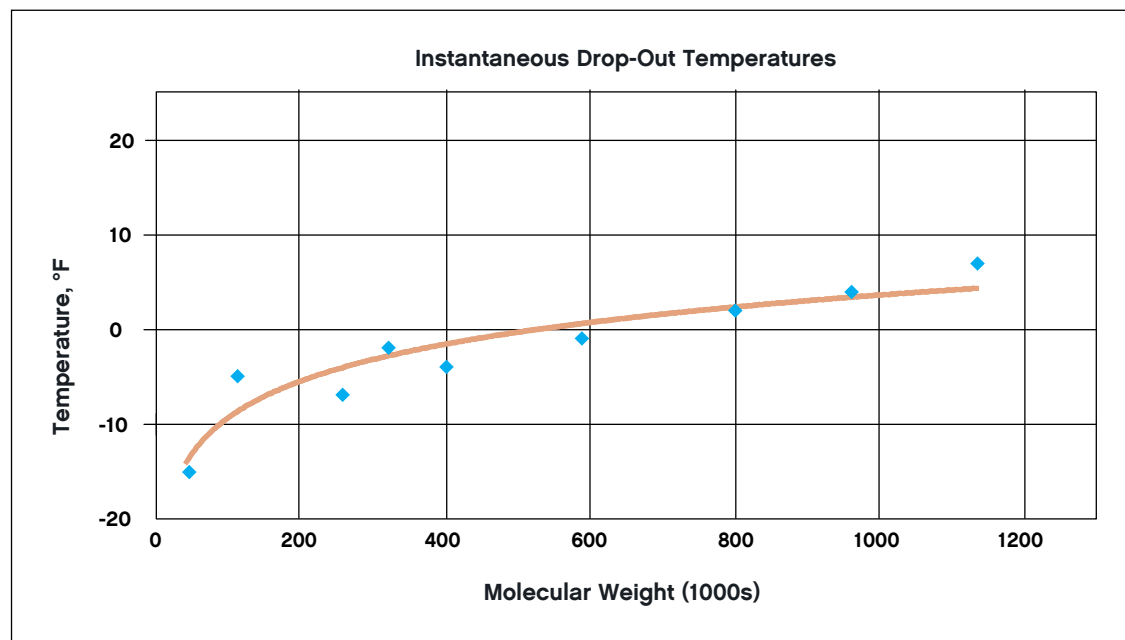
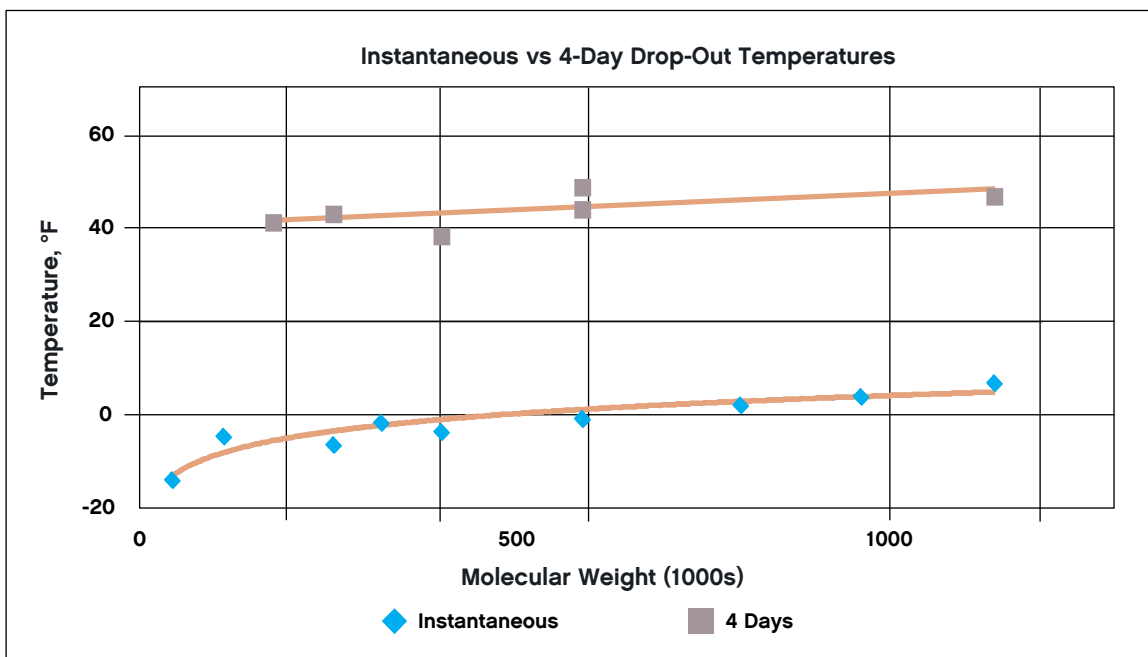
Figure 2.5 Ethylene Oxide Polymer Instantaneous Drop-Out Temperatures [46]

Figure 2.6 Ethylene Oxide Polymer Drop-Out Temperatures after 4 Days [47]

2.4 Commercial Chemistry

EO is a highly versatile molecule. Considerable energy is stored in the ring structure of the EO molecule. Its reactions proceed mainly via ring opening and are highly exothermic. Only a few of the large number of possible reactions are briefly discussed here. More detailed information can be found in references [8]-[14].

Addition to Compounds with a Reactive Hydrogen Atom

EO reacts with compounds containing a reactive hydrogen atom to form a product containing a hydroxyethyl group. Examples of compounds with a reactive hydrogen atom (XH) include: HOH, H₂NH, HRNH, R₂NH, RCOOH, RCONH₂, HSH, RSH, ROH, N=CH, and B₂H₆ (R= alkyl or aryl). The reaction is accelerated by acids and bases. All common acids and Lewis acids as well as zeolites, ion exchangers [29], and aluminum oxide are effective catalysts. A detailed discussion of reaction mechanisms and chemistry can be found in references [12] and [30].

The end product of this reaction contains at least one hydroxyl group, so it can react successively with additional EO to produce long chain

polyether polymers, which are sometimes called poly-oxyethylene-glycols. The molecular weight distribution of the polymers depends on the reaction conditions, the catalysts employed, and the ratio of reactants.

This type of reaction is commercially important because the reaction of EO with water produces ethylene glycols. The production of poly(ethylene) glycols by this route is also of commercial importance.

When used with starting materials other than water (e.g., phenols, ammonia, fatty amines, fatty alcohols and fatty acids), the resulting reaction, often referred to as ethoxylation, is used to produce the bulk of the other commercially important EO derivatives.

Addition to Double Bonds

EO can add to compounds with double bonds, such as carbon dioxide, to form cyclic products. EO also adds to other double bond systems, e.g., to R₂C=O, SC=S, O₂S=O, RN=CO, and OS=O.

Catalytic Isomerization to Acetaldehyde

Aluminum oxide (Al₂O₃), phosphoric acid and phosphates, iron oxides, and, under certain conditions, silver, catalyze the isomerization of EO to acetaldehyde.

Other Reactions

EO reacts with many other compounds such as hydrogen (catalytic reduction to ethanol); hydrogen sulfide and mercaptans; Grignard reagents; halides; hydrogen cyanide; dimethyl ether; and compounds with active methylene or methyne.

2.5 Uses of Ethylene Oxide

Products derived from EO have many different uses. Some of these products (or uses) include:

- **Monoethylene Glycol:** Antifreeze for engines, production of polyethylene terephthalate (polyester fibers, film, and bottles), and heat transfer liquids and deicing of aircraft and runways.
- **Diethylene Glycol:** Polyurethanes, polyesters, softeners (cork, glue, casein and paper), plasticizers, gas drying and solvents.
- **Triethylene Glycol:** Polyurethanes, lacquers, solvents, plasticizers, gas drying and humectants (moisture-retaining agents).

- **Poly(ethylene) Glycols:** Cosmetics, ointments, pharmaceutical preparations, lubricants (finishing of textiles and ceramics), solvents (paints and drugs) and plasticizers (adhesives and printing inks).
- **Ethylene Glycol Ethers:** Brake fluids, detergents, solvents (paints and lacquers), and extractants for SO₂, H₂S, CO₂ and mercaptans from natural gas and refinery gas.
- **Ethanolamines:** Chemicals for textile finishing, cosmetics, soaps, detergents and natural gas purification.
- **Ethoxylation products of fatty alcohols, fatty amines, alkyl phenols, cellulose, poly(propylene glycol):** Detergents and surfactants (nonionic), biodegradable detergents, emulsifiers and dispersants.

EO also has direct uses as a sterilizing agent for medical devices and equipment and as a fumigant for spices. In sterilization applications, it is sometimes referred to as EtO.