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CHAPTER 2 SOLUTIONS

2.1 a. Dew point pressure at 120°F = 48.9°C = 322 K

$$f\{P_{BP}\} = \sum_i x_i - 1 = 0$$

$$\sum_i \frac{y_i}{K_i} - 1 = 0$$

$$\sum_i \frac{y_i P}{P_i^s} - 1 = 0$$

$$P\sum_i \frac{y_i}{P_i^s} - 1 = 0$$

$$P = \frac{1}{\sum_i \frac{y_i}{P_i^s}} = \frac{1}{\frac{y_1}{P_1^s} + \frac{y_2}{P_2^s}}$$

Vapor pressure data – interpolation

	T, °C	P^s, atm	$1/T$, K^{-1}	ln P^s
Pentane	36.1	1	0.003234	0
	58.0	2	0.003020	0.694
	48.9	1.51	0.003105	0.418
Hexane	31.6	0.2632	0.003281	-1.3348
	49.6	0.5263	0.003098	-0.6419
	48.9	0.5125	0.003105	-0.6684

$$P = \frac{1}{\frac{0.5}{1.51} + \frac{0.5}{0.5125}} = 0.765 \text{ atm}$$

b. Bubble point temperature at 1 atm

$$f\{T_{BP}\} = \sum_i y_i - 1 = 0$$

$$= \sum_i K_i x_i - 1 = 0$$

$$= \sum_i \frac{P_i^s}{P} x_i - 1 = 0$$

$$= P_1^s\{T\}x_1 + P_2^s\{T\}x_2 - 1 = 0$$

$$= 0.5[P_1^s\{T\} + P_2^s\{T\}] - 1 = 0$$

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At $T = 120°F$

$$f\{120°F\} = 0.5[1.51 + 0.5125] - 1 = 0.01 \cong 0$$

$$T_{BP} \cong 120°F$$

c. Vapor fraction at 120°F and 0.9 atm

$$f\{\alpha\} = \sum_i \frac{z_i(1-K_i)}{1+(K_i-1)\alpha} = 0$$

$$= \frac{z_1(1-\frac{P_1^s}{P})}{1+(\frac{P_1^s}{P}-1)\alpha} + \frac{z_2(1-\frac{P_2^s}{P})}{1+(\frac{P_2^s}{P}-1)\alpha} = 0$$

$$= \frac{0.5(1-\frac{1.51}{0.9})}{1+(\frac{1.51}{0.9}-1)\alpha} + \frac{0.5(1-\frac{0.5125}{0.9})}{1+(\frac{0.5125}{0.9}-1)\alpha} = 0$$

$$= \frac{-0.6778}{1+0.6778\alpha} + \frac{0.4306}{1-0.4306\alpha} = 0$$

Rearranging:

$$\alpha = 0.424$$

$$x_j = \frac{z_j}{1+(K_j-1)\alpha}$$

$$x_1 = \frac{0.5}{1+(\frac{1.51}{0.9}-1)0.424} = 0.388$$

$$x_2 = \frac{0.5}{1+(\frac{0.5125}{0.9}-1)0.424} = 0.612$$

$y_j = K_j x_j$

$$y_1 = 0.651$$

$$y_2 = 0.349$$

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2.2

	z_i	P^s_i, bar
nC_5	0.34	10.29
nC_7	0.66	2.17

a. BP pressure

$$\sum_i y_i = 1$$
$$\sum_i K_i x_i = 1$$

Ideal mixture

$$\sum_i \frac{P_i^s}{P} x_i = 1$$
$$\sum_i \frac{P_i^s}{P} z_i = 1$$
$$P = \sum_i P_i^s z_i = 10.29 \times 0.34 + 2.17 \times 0.66$$
$$= 4.93 \text{ bar}$$

b. $$y_i = K_i x_i \cong \frac{P_i^s}{P} z_i$$

$$y_1 = \frac{10.29}{4.93} 0.34 = 0.7095; \qquad y_2 = \frac{2.17}{4.93} 0.66 = 0.2905$$

$0.7095 + 0.2905 = 1$ - correct

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2.3 Thermophysical Property Data – from Reid et al., *Properties of Gases and Liquids*, McGraw-Hill (1987) – Appendix A – for vinyl chloride

Molecular weight	62.499
Normal freezing point, T_{nfp}	119.4 K
Normal boiling point, T_{nbp}	259.8 K
Critical temperature, T_c	425 K
Critical pressure, P_c	51.5 K
Critical volume, V_c	169 cc/mol
Critical compressibility factor, z_c	0.265
Acentric factor, ω	0.122
Ideal gas heat capacity, J/(mol-K)	$c_p = a + bT + cT^2 + dT^3$, T in K
a	5.949
b	0.2019
c	-1.536×10^{-4}
d	4.733×10^{-8}
Heat of formation at 298 K, ΔH_f	35,170 J/mol
Gibbs free energy of formation at 298 K, ΔG_f	51,540 J/mol
Vapor pressure	$\ln\{P^s/P_c\} = (1-x)^{-1}ax + bx^{1.5} + cx^3 + dx^6$ where $x = 1 - (T/T_c)$
a	-6.5
b	1.21422
c	-2.57867
d	-2.00937
Liquid density at 259 K	0.969 g/cc

From Woods, *Data for Process Design and Engineering Practice*, Prentice-Hall (1995)

Latent heat of freezing at 25°C	76 kJ/kg
Latent heat of vaporization at 25°C	333 kJ/kg
Liquid heat capacity at 25°C	1.361 kJ/(kg-K)

Toxicity and Flammability Data – from Woods (1995)

National Fire Protection Agency (NFPA)
Ratings (Table Da-1) – scale of 0 – 4,
0 = harmless, 4 = extremely hazardous

Hazard to health (toxicity)	2
Flammability hazard	3
Reactivity or Stability Hazard	2

Note that Crowl and Louvar, *Chemical Process Safety: Fundamentals with Applications*, Prentice-Hall (1990), provide a method for estimating the

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flammability limits for hydrocarbons, but the method does not apply to chlorinated hydrocarbons, such as vinyl chloride.

Also note that the data above are for vinyl chloride only. Similar data are needed for ethylene, acetylene, chlorine, 1,2-dichloroethane, and HCl.

Cost Data – from the *Chemical Market Reporter*, August 17, 1998

Ethylene	0.215 $/lb
Chlorine	255 $/short ton (0.128 $/lb)
Vinyl chloride	0.155 $/lb
Hydrogen chloride	320 $/ton (0.16 $/lb)

From the 1996 *Stanford Research Institute Yearbook*:

Acetylene	0.60 – 0.70 $/lb

MSDS (Material Safety Data Sheet) for Ethylene – obtained using the URL – www.ilpi.com/msds/. The MSDS displayed below was copied from the Cornell University data base. Similarly, MSDSs can be obtained for chlorine, vinyl chloride, HCl, and acetylene.

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Division of Facilities Services

DOD Hazardous Material Information (ANSI Format)
For Cornell University Convenience Only

ETHYLENE, GASEOUS - C2H4

Section 1 - Product and Company Identification
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Section 1 - Product and Company Identification
ETHYLENE, GASEOUS - C2H4

Product Identification: ETHYLENE, GASEOUS - C2H4
Date of MSDS: 10/31/1996 Technical Review Date: 12/22/1999
FSC: 6830 NIIN: LIIN: 00N093296
Submitter: N EN
Status Code: A
MFN: 01
Article: N
Kit Part: N

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Manufacturer's Information

Manufacturer's Name: AIRGAS INC
Manufacturer's Address1: 259 RADNOR-CHESTER ROAD, SUITE 100
Manufacturer's Address2: RADNOR, PA 19087-5240
Manufacturer's Country: US
General Information Telephone: 610-687-5253
Emergency Telephone: 800-424-9300 (CHEMTREC)
Other Number for MSDS Information: P-0022
Emergency Telephone: 800-424-9300 (CHEMTREC)
Chemtec Telephone: (800)424-9300
Proprietary: N
Reviewed: Y
Published: Y
CAGE: 0MN39

Contractor Information

Contractor's Name: AIRGAS INC
Contractor's Address1: 100 MATSONFORD RD SUITE 550
Contractor's Address2: WAYNE, PA 19087
Contractor's Telephone: 215-687-5253
Contractor's CAGE: 0MN39

Section 2 - Composition/Information on Ingredients
ETHYLENE, GASEOUS - C2H4

Ingredient Name: ETHYLENE
Ingredient CAS Number: 74-85-1 Ingredient CAS Code: T
RTECS Number: KU5340000 RTECS Code: T
=WT: =WT Code:
=Volume: =Volume Code:
>WT: 99.5 >WT Code: M
>Volume: >Volume Code:
<WT: <WT Code:
<Volume: <Volume Code:
% Low WT: % Low WT Code:
% High WT: % High WT Code:
% Low Volume: % Low Volume Code:
% High Volume: % High Volume Code:
% Text:
% Environmental Weight:
Other REC Limits: N/K (FP N)
OSHA PEL: N/K (FP N) OSHA PEL Code: M
OSHA STEL: N/K (FP N) OSHA STEL Code: M
ACGIH TLV: N/K (FP N) ACGIH TLV Code: M

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ACGIH STEL: N/K (FP N) ACGIH STEL Code: M
EPA Reporting Quantity:
DOT Reporting Quantity:
Ozone Depleting Chemical: N

Ingredient Name: MAXIMUM IMPURITIES
Ingredient CAS Number: Ingredient CAS Code: X
RTECS Number: RTECS Code: X
=WT: =WT Code:
=Volume: =Volume Code:
>WT: >WT Code:
>Volume: >Volume Code:
<WT: .5 <WT Code: M
<Volume: <Volume Code:
% Low WT: % Low WT Code:
% High WT: % High WT Code:
% Low Volume: % Low Volume Code:
% High Volume: % High Volume Code:
% Text:
% Environmental Weight:
Other REC Limits: N/K (FP N)
OSHA PEL: N/K (FP N) OSHA PEL Code: M
OSHA STEL: N/K (FP N) OSHA STEL Code: M
ACGIH TLV: N/K (FP N) ACGIH TLV Code: M
ACGIH STEL: N/K (FP N) ACGIH STEL Code: M
EPA Reporting Quantity:
DOT Reporting Quantity:
Ozone Depleting Chemical:

Section 3 - Hazards Identification, Including Emergency Overview
ETHYLENE, GASEOUS - C2H4

Health Hazards Acute & Chronic:
ACUTE: MOST SIGNIFICANT HAZ ASSOC W/PROD IS INHAL OF OXYGEN-DEFICIENT ATMS. SYMPS OF OXYGEN DEFICIENCY INCL RESP DFCLTY, RINGING IN EARS, HDCH, SHORTNESS OF BREATH, WHEEZING, HDCH, DIZZ, INDIGESTION, NAUS, &, AT HIGH CONCS, UNCON/DEATH MAY OCCUR. AFTER OVEREXP, SKIN MAY HAVE BLUE COLOR. CONT W/CRYOGENIC LIQ/RAPIDLY EXPANDING GASES (WHICH ARE RELEASED UNDER HIGH PRESS) MAY CAUSE FROTSBT. SYMPS OF F ROSTBT INCL CHANGE IN SKIN COLOR TO WHITE/GRAYISH-YELLOW. PAIN AFTER CONT W/LIQ CAN QUICKLY SUBSIDE. CHRONIC: THERE ARE CURRENTLY NO KNOWN ADVERSE HLTH EFTS ASSOC W/CHRONIC EXPOS TO COMPONENTS OF THIS COMPRESSED GAS.

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Signs & Symptoms of Overexposure:
INHAL: EXPOS TO EXTREMELY HIGH CONCS (20%) CAN CAUSE ANESTH EFTS. HIGH CONCS OF THIS GAS CAN CAUSE OXYGEN-DEFICIENT ENVIRON. INDIVIDUALS BRTHG SUCH ATM MAY EXPERIENCE SYMPS WHICH INCL HDCH, RINGING IN EARS, DIZZ, DROW, UNCON, NAUS, VOMIT, & DEPRESS OF ALL SENSES. 12-16% OXYGEN: BRTHG & PULSE RATE INCRD, MUSC COORD SLIGHTLY DISTURBED. 10-14% OXYGEN: EMOTIONAL UPSET, ABNORM FATG, DISTURBED RESP. 6-1 0% OXYGEN: NAUS & VOMIT, COLLAPSE/LOSS OF CONSCIOUSNESS. BELOW 6% OXYGEN: CONVULSIVE MOVEMENTS, POSS RESP COLLAPSE, & DEATH. (TOX INFO)

Medical Conditions Aggravated by Exposure:
ACUTE OR CHRONIC RESPIRATORY CONDITIONS MAY BE AGGRAVATED BY OVEREXPOSURE TO THE COMPONENTS OF THIS PRODUCT.

LD50 LC50 Mixture: LC50 (INHALATION, MOUSE): 96 PPH.

Route of Entry Indicators:
Inhalation: YES
Skin: NO
Ingestion: NO

Carcenogenicity Indicators
NTP: NO
IARC: NO
OSHA: NO

Carcinogenicity Explanation: ETHYLENE IS NOT FOUND ON THE FOLLOWING LISTS: FEDERAL OSHA Z LIST, NTP, CAL/OSHA, AND THEREFORE IS NOT CONSIDERED TO BE, OR SUSPECTED TO BE A CANCER-CAUSING AGENT BY THESE AGENCIES. ETHYLENE IS LISTED AS AN IARC GROUP 3 COMPOUND (NOT CLASSIFIABLE IN TERMS OF HUMAN CARCINOGENICITY).

Section 4 - First Aid Measures
ETHYLENE, GASEOUS - C2H4

First Aid:
RESCUERS SHOULD NOT ATTEMPT TO RETRIEVE VICTIMS W/OUT ADEQ PERS PROT EQUIP. AT MIN, SCBA & FIRE-RETARDANT PERS PROT EQUIP SHOULD BE WORN. ADEQ FIRE PROT MUST BE PROVIDED DURING RESCUE SITUATIONS. INHA L: REMOVE TO FRESH AIR IMMED. TRAINED PERS SHOULD ADMIN SUPP OXYGEN &/OR CPR, IF NEC. ONLY TRAINED PERS SHOULD ADMIN SUPP OXYGEN. SKIN: PLACE FROSTBITTEN PART IN WARM WATER. DO NOT USE HOT WATER. IF W ARM WATER NOT AVAIL/IMPRACTICAL TO USE, WRAP AFFECTED PARTS GENTLY IN BLANKETS. ALTERNATIVELY, IF FINGERS/HANDS ARE FROSTBITTEN,

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PLACE IN ARMPIT. ENCOURAGE VICTIM TO GENTLY EXERCISE AFFECTED PARTS WHI LE BEING WARMED. (SUP DAT)

Section 5 - Fire Fighting Measures
ETHYLENE, GASEOUS - C2H4

Fire Fighting Procedures:
WEAR NIOSH APPRVD SCBA & FULL PROT EQUIP (FP N). BEST FIRE-FIGHT TECHNIQUE MAY BE SIMPLY TO LET BURNING GAS ESCAPE FROM PRESSURIZED CYL, TANK CAR/PIPELINE. STOP LEAK BEFORE EXTING FIRE. IF FIRE IS EXT INGUISHED BEFORE LEAK IS SEALED, STILL-LEAKING GAS COULD EXPLO RE-IGNITE W/OUT WARNING & CAUSE EXTENSIVE (SARA REGS)

Unusual Fire or Explosion Hazard:
WHEN INVOLVED IN FIRE, GAS WILL DECOMPOSE & PRDCE TOX GASES INCL CARBON MONOXIDE & CARBON DIOXIDE. EXTREME EXPLO HAZ EXISTS IN WHICH GAS HAS BEEN RELEASED, BUT MATL HAS NOT YET IGNITED. DANGER! FIRES IMPINGING (DIRECT FLAME) ON OUTSIDE SURF OF UNPROT PRESS STOR VESSELS OF THIS PROD CAN BE VERY DANGEROUS. (FED REGS)

Extinguishing Media:
EXTINGUISH FIRES OF THIS GAS BY SHUTTING-OFF THE SOURCE OF THE GAS. USE WATER SPRAY TO COOL FIRE-EXPOSED CONTAINERS, STRUCTURES, AND EQUIPMENT.

Flash Point: Flash Point Text: FLAMMABLE GAS

Auto-ignition Temperature: = 490.C, 914.F
Auto-ignition Temperature Text:
Lower Limit(s): 2.7%
Upper Limit(s): 36%

Section 6 - Accidental Release Measures
ETHYLENE, GASEOUS - C2H4

Spill Release Procedures:
UNCONTROLLED RELEASES SHOULD BE RESPONDED TO BY TRAINED PERS USING PRE-PLANNED PROC. PROPER PROT EQUIP SHOULD BE USED. IN CASE OF SPILL, CLEAR AFFECTED AREA, PROTECT PEOPLE, & RESPOND W/TRAINED PERS. ADEQ FIRE PROT MUST BE PROVIDED. MIN PERS PROT EQUIP SHOULD BE LEVEL B: FIRE-RETARDANT PROT CLTHG, MECHANICALLY-RESIST GLOVES & SCBA. USE ONLY NON-SPKG TOOLS & EQUIP. (WASTE DISP METH)

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Section 7 - Handling and Storage
ETHYLENE, GASEOUS - C2H4

Handling and Storage Precautions:

Other Precautions:

Section 8 - Exposure Controls & Personal Protection
ETHYLENE, GASEOUS - C2H4

Respiratory Protection:
MAINTAIN OXYGEN LEVELS ABOVE 19.5% IN WORKPLACE. USE NIOSH APPROVED SUPPLIED-AIR RESPIRATORY PROTECTION IF OXYGEN LEVELS ARE BELOW 19.5% OR DURING EMERGENCY RESPONSE TO A RELEASE OF PRODUCT. IF RESPIR ATORY PROTECTION IS REQUIRED, FOLLOW THE REQUIREMENTS OF THE FEDERAL OSHA RESPIRATORY PROTECTION STANDARD (29 CFR 1910.134), OR EQUIVALENT STATE STANDARDS.

Ventilation:
LOCAL EXHAUST VENT IS PREFERRED; IT PREVENTS ETHYLENE DISPERSION INTO WORK PLACE BY ELIMINATING IT AT ITS SOURCE. CONTACT NEHC FOR MORE COMPLETE INFO (FP N).

Protective Gloves:
MECH-RESIST FOR CYLS. LOW-TEMP PROT GLOVES (KEVLAR) FOR CONTRS OF LIQ ETHYLENE.

Eye Protection: ANSI APPROVED CHEMICAL WORKERS GOGGLES (FP N).

Other Protective Equipment: ANSI APPRVD EMER EYEWASH & DELUGE SHOWER (FP N). BODY PROT APPROP FOR TASK. TRANSFER OF LGE QTYS UNDER PRESS MAY REQ PROT EQUIP APPROP AGAINST SPLASHES OF LIQ PROD, AS WELL AS FIRE RETARDANT ITEMS.

Work Hygienic Practices: AVOID GETTING PROD IN YOU. DO NOT EAT/DRINK WHILE HNDLG CHEMS. BE AWARE OF ANY SIGNS OF DIZZ/FATG; DUE TO OXYGEN DEFICIENCY, EXPOS TO FATAL CONCS COULD OCCUR W/OUT ANY SIGNIFICANT WARNING SYMPS.

Supplemental Health & Safety Information: FIRST AID PROC: SEEK IMMED MED ATTN. VICTIMS MUST BE TAKEN FOR MED ATTN. RESCUERS SHOULD BE TAKEN FOR MED ATTN, IF NEC. TAKE COPY OF LABEL & MSDS TO MD/OTHER HLTH PROFESSIONAL W/VICTIMS. EYES: FLUSH W /POTABLE

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WATER FOR AT LEAST 15 MINS. SEE MD (FP N). INGEST: CALL MD IMMED (FP N). (OTHER INFO)

Section 9 - Physical & Chemical Properties
ETHYLENE, GASEOUS - C2H4

HCC:
NRC/State License Number:
Net Property Weight for Ammo:
Boiling Point: = 68.3C, 155.F Boiling Point Text:
Melting/Freezing Point: = -168.7C, -272.F Melting/Freezing Text:
Decomposition Point: Decomposition Text: N/P
Vapor Pressure: N/A Vapor Density: 0.98 AIR=1
Percent Volatile Organic Content:
Specific Gravity: N/A
Volatile Organic Content Pounds per Gallon:
pH: N/A
Volatile Organic Content Grams per Liter:
Viscosity: N/P
Evaporation Weight and Reference: N/A
Solubility in Water: SOLUBLE
Appearance and Odor: COLORLESS GAS W/SWEET ODOR. COLORLESS CRYOGENIC LIQ W/SWEET ODOR.
Percent Volatiles by Volume: N/P
Corrosion Rate: N/P

Section 10 - Stability & Reactivity Data
ETHYLENE, GASEOUS - C2H4

Stability Indicator: YES

Materials to Avoid:
ETHYLENE MAY REACT VIOLENTLY WITH THE FOLLOWING MATERIALS: STRONG OXIDIZERS (E.G., CHLORINE, BROMINE PENTAFLUORIDE, OXYGEN, OXYGEN DIFLUORIDE, AND NITROGEN TRIFLUORIDE); ALUMINUM CHLORIDE, ORGANIC PEROXIDES, NITROGEN DIOXID

Stability Condition to Avoid:
CONTACT WITH INCOMPATIBLE MATERIALS AND EXPOSURE TO HEAT, SPARKS AND OTHER SOURCES OF IGNITION.

Hazardous Decomposition Products:
WHEN INGITED IN THE PRESENCE OF OXYGEN, THIS GAS WILL DECOMPOSE TO PRODUCE CARBON MONOXIDE AND CARBON DIOXIDE.

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Hazardous Polymerization Indicator: YES

Conditions to Avoid Polymerization:
HIGH TEMPERATURES AND PRESSURES.

Section 11 - Toxicological Information
ETHYLENE, GASEOUS - C2H4

Toxicological Information:
HLTH HAZS: DOGS EXPOSED TO 1.4% ETHYLENE WERE ANESTHETIZED IN 2-8.2 MINS. LCLO (INHAL, HUMAN)=950000 PPM/5 MINS. IRRIT OF PROD: PROD IS NOT IRRIT; HOWEVER, CONT W/RAPIDLY EXPANDING GASES CAN CAUSE FRO STBT TO EXPOSED TISS. SENSIT OF PROD: ETHYLENE IS NOT KNOWN TO CAUSE SENSIT IN HUMANS. REPRO TOX FOR HUMANS: ETHYLENE: NO EFTS HAVE BEEN DESCRIBED FOR MUTAGENICITY, TERATOGENICITY, EMBRYOTOX & REPRO T OX. EFTS OF OVEREXP: CONT W/CRYOGENIC LIQ/RAPIDLY EXPANDING GASES (WHICH ARE RELEASED UNDER HIGH PRESS) MAY CAUSE FROSTBT. SYMPS OF FROSTBT INCL CHANGE IN SKIN COLOR TO WHITE/GRAYISH-YELLOW. PAIN AFTE R CONT W/LIQ CAN QUICKLY SUBSIDE.

Section 12 - Ecological Information
ETHYLENE, GASEOUS - C2H4

Ecological Information:
ENVIRON STABILITY: THIS GAS WILL BE DISSIPATED RAPIDLY IN WELL-VENTILATED AREAS. ANY ADVERSE EFT ON ANIMALS WOULD BE RELATED TO OXYGEN DEFICIENT ENVIRONS. NO ADVERSE EFT IS ANTIC TO OCCUR TO PLANT-LIF E, EXCEPT FOR FROST PRDCED IN PRESENCE OF RAPIDLY EXPANDING GASES. EFT OF CHEM ON AQUATIC LIFE: NO EVIDENCE IS CURRENTLY AVAIL. OTHER PREC: CYLS SHOULD BE STORE UPRIGHT & FIRMLY SECURED TO PVNT FALLIN G/BEING KNOCKED OVER. CYLS CAN BE STORED IN OPEN, BUT SHOULD BE PROTECTED AGAINST EXTREMES OF WEATHER & FROM DAMPNESS OF GROUND TO PVNT RUSTING. CONT NEHC FOR MORE COMPLETE INFO (FP N).

Section 13 - Disposal Considerations
ETHYLENE, GASEOUS - C2H4

Waste Disposal Methods:
MUST BE I/A/W APPROP FED, STATE, & LOC REGS. RETURN CYLS W/ANY RESIDUAL PROD TO MFR. DO NOT DISPOSE OF LOCALLY. SPILL PROC: LOCATE & SEAL SOURCE OF LEAK. PROT PERS ATTEMPTING SHUT-OFF W/WATER SPRAY. A LLOW GAS TO DISSIPATE. MONITOR SURROUNDING AREA FOR OXYGEN & COMBUST GAS LEVELS. CONT NEHC FOR MORE COMPLETE INFO (FP N).

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Section 14 - MSDS Transport Information
ETHYLENE, GASEOUS - C2H4

Transport Information:
HAZ AS DEFINED BY 49 CFR 172.101 BY U.S. DEPARTMENT OF TRANSPORTATION. FOR ETHYLENE GAS: PROPER SHIPPING NAME: ETHYLENE, COMPRESSED; HAZ CLASS # & DESCRIPTION: 2.1 (FLAMM GAS); UN IDENTIFICATION #: UN 1962; PACKING GRP: N/A; DOT LABEL REQUIRED: FLAMM GAS; NORTH AMERICAN EMER RESPONSE GUIDEBOOK # (1996): 116P. FOR LIQUIFIED ETHYLENE: PROPER SHIPPING NAME: ETHYLENE, REFRIGERATED LIQ; HAZ CLASS # & D ESCRIPTION: 2.1 (FLAMM GAS); UN IDENTIFICATION #: UN 1038; PACKING GRP: N/A; DOT LABEL REQUIRED: FLAMM GAS; NORTH AMERICAN EMER RESPONSE GUIDEBOOK # (1996): 115. ETHYLENE NOT CLASSIFIED AS MARINE POLL UTANT. CONT NECH FOR MORE INFO (FP N).

Section 15 - Regulatory Information
ETHYLENE, GASEOUS - C2H4

SARA Title III Information:
THIS PROD IS SUBJECT TO REPORTING REQS OF SECTIONS 302, 304 & 313 OF TITLE III OF SUPERFUND AMENDMENTS & REAUTHORIZATION ACT, AS FOLLOWS: ETHYLENE: SARA 302/304: NO; SARA 313: YES. SARA TPQ: N/A. FIRE FIGHT PROC: DMG, INJURY/FATALITY. IN THIS CASE, INCR VENT (IN ENCLSD AREAS) TO PVNT FLAMM MIXT FORM. FOR LGE RELEASES, CONSIDER EVACUATION. NORTH AMERICAN EMER RESPONSE GUIDEBOOK (GUIDE # 115) RECS 0.5 MILES. OTHER INFO FOR PRE-PLANNING CAN BE FOUND IN AMERICAN PETRO INSTITUTE PUBLICATIONS 2510 & 2510A, NORTH AMERICAN EMER RESPONSE GUIDEBOOK, & DOT EMER RESPONSE GUIDEBOOK.

Federal Regulatory Information:
TSCA INVENTORY STATUS: ETHYLENE IS LISTED ON TSCA INVENTORY. CERCLA RQ: N/A. ETHYLENE IS SUBJECT TO REPORTING REQS OF SECTION 112(R) OF CLEAN AIR ACT. THRESHOLD QTY FOR THIS GAS IS 10,000 LBS. DEPENDI NG ON SPECIFIC OPERATIONS INVOLVING USEOF THIS PROD, REGS OF PROCESS SFTY MANAGEMENT OF HIGHLY HAZ CHEMS MAY BE APPLIC (29 CFR 1910.119). EXPLO HAZ: DIRECT FLAME EXPOS ON CYL WALL CAN CAUSE EXPLO EITH ER BY BLEVE (BOILING LIQ EXPANDING VAP EXPLO)/BY EXOTHERMIC DECOMP. THIS IS A CATASTROPHIC FAILURE O F VESSEL RELEASING CONTENTS INTO MASSIVE FIREBALL & EXPLO. CONT NEHC FOR MORE COMPLETE INFO (FP N).

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State Regulatory Information:
ETHYLENE IS COVERED UNDER SPECIFIC STATE REGS, AS DENOTED BELOW: ALASKA-DESIGNATED TOX & HAZ SUBSTANCES; CALIFORNIA-PEL FOR CHEM CONTAMS; FLORIDA-SUBSTANCE LIST; ILLINOIS-TOX SUBSTANCE LIST; KANSAS-SE CTION 302/313 LIST; MASSACHUSETTS-SUBSTANCE LIST; MINNESOTA-LIST OF HAZ SUBSTANCES; MISSOURI-EMPLOYER INFO/TOX SUBSTANCE LIST; NEW JERSEY-RIGHT TO KNOW HAZ SUBSTANCE LIST; PEENSYLVANIA-HAZ SUBSTANCE L IST; RHODE ISLAND-HAZ SUBSTANCE LIST. CALIFORNIA PROPOSITION 65: ETHYLENE IS NOT ON CALIFORNIA PROPO SITION 65 LISTS.

Section 16 - Other Information
ETHYLENE, GASEOUS - C2H4

Other Information:
PROD USE: FOR GEN ANALYTICAL/SYNTHETIC CHEM USES. NFPA RATING: HLTH=1; FLAMM=4; REACTIVITY=2. HMIS RATING: HLTH=1 (BLUE); FLAMM=4 (RED); REACTIVITY=2 (YELLOW); PROT EQUIP=B. SUP DAT: NOTE TO MD: ADMIN OXYGEN, IF NEC; TREAT SYMPS; REDUCE/ELIMINATE EXPOS. PHYSICAL/CHEM PROPERTIES: ODOR THRESHOLD: 700 MG/M3 (DETECTION); EXPANSION RATIO: 489 (CRYOGENIC); SPECIFIC VOL: 13.6 FT3/LB. HOW TO DETECT SUBSTA NCE (WARNING PROPERTIES): THERE ARE NOT DISTINCT WARNING PROPERTIES. IN TERMS OF LEAK DETECTION, FITTINGS & JOINTS CAN BE PAINTED W/SOAP SOLN TO DETECT LEAKS, WHICH WILL BE INDICATED BY BUBBLE FORM.

HAZCOM Label Information

Product Identification: ETHYLENE, GASEOUS - C2H4
CAGE: 0MN39
Assigned Individual: N
Company Name: AIRGAS INC
Company PO Box:
Company Street Address1: 100 MATSONFORD RD SUITE 550
Company Street Address2: WAYNE, PA 19087 US
Health Emergency Telephone: 800-424-9300 (CHEMTREC)
Label Required Indicator: Y
Date Label Reviewed: 12/30/1999
Status Code: A
Manufacturer's Label Number:
Date of Label:
Year Procured: N/K
Organization Code: F
Chronic Hazard Indicator: N
Eye Protection Indicator: YES
Skin Protection Indicator: YES
Respiratory Protection Indicator: YES

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Signal Word: DANGER
Health Hazard: Moderate
Contact Hazard: Moderate
Fire Hazard: Severe
Reactivity Hazard: None

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2.4 This solution is being completed.

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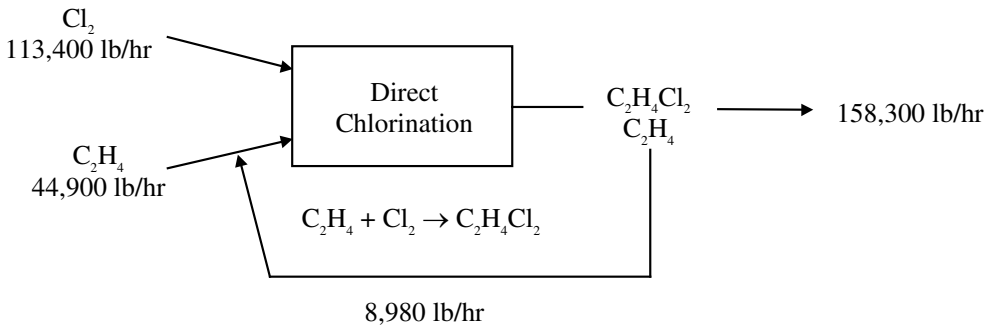
2.5 a. Principal disadvantage – the boiling point temperature of HCl product is too low. Refrigeration at lower temperatures is necessary to condense the overhead vapor to produce reflux. The power requirements for refrigeration are very high. Alternatively, the HCl can be recovered by scrubbing the effluent gases from the pyrolysis furnace with water at low pressure. The product stream from the scrubber, which is concentrated in vinyl chloride and dichloroethane, would also contain water, which would have to be recovered from this mixture.

b. No – the vapor to be condensed from the direct chlorination reactor is at 90°C, whereas the bottoms from the first distillation column is at 93°C. To use the heat of condensation from the vapor stream, reduce the pressure of the first distillation column such that the bubble-point temperature of the bottoms is reduced to 85°C, for example. The disadvantage of this approach is that the boiling point of the overhead vapor from the first column would be reduced from –26.2°C, requiring somewhat higher refrigeration costs.

c.



d. As the quality of the feed approaches unity (saturated liquid), the reflux ratio in the tower is reduced. Consequently, less refrigeration is required at –26.2°C. While refrigeration is required to cool the feed to its bubble point at 6°C, refrigeration at higher temperatures is less costly. The disadvantage, however, is that two separate sources of refrigeration become necessary, which may substantially increase the capital costs of refrigeration equipment.

e. A shell-and-tube heat exchanger would be used to exchange heat between the two streams. As the effluent gases from the pyrolysis furnace are cooled, chemical equilibrium favors carbon deposition; that is, the formation of solid carbon deposits, which could potentially foul the tubes of the exchanger, reducing the rate of heat transfer, and requiring periodic shut-downs to remove the carbon. Another factor is the high concentration of corrosive HCl, which could require the periodic replacement of corroded tubes.

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f. The trays permit condensed $C_2H_4Cl_2$ to scrub impurities from the vapor product.

g. Through the use heat integration as considered in (b) and (e). For the latter, it would be important to determine the rate of carbon deposition, in the laboratory or pilot plant, as discussed in the section on *Checking the Key Assumptions in Process Synthesis*.

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2.6 a. As discussed in Section 6.7, and illustrated with Example 6.11, it is normally far less costly to pump a liquid rather than compress a gas. Following this heuristic (Heuristic 43, Table 6.2), process 2 is preferred.

b. A partial condenser is used when the overhead vapor contains chemical species that normally exist pure in the vapor phase; e.g., CH_4, H_2, CO_2, and HCl. When a partial condenser is used such that a vapor product is removed in the distillate, and the reflux stream is condensed at its dew-point temperature. Total condensers require that the entire overhead vapor stream be condensed at, or below, its bubble-point temperature, which is normally very low because these light gaseous species are present.

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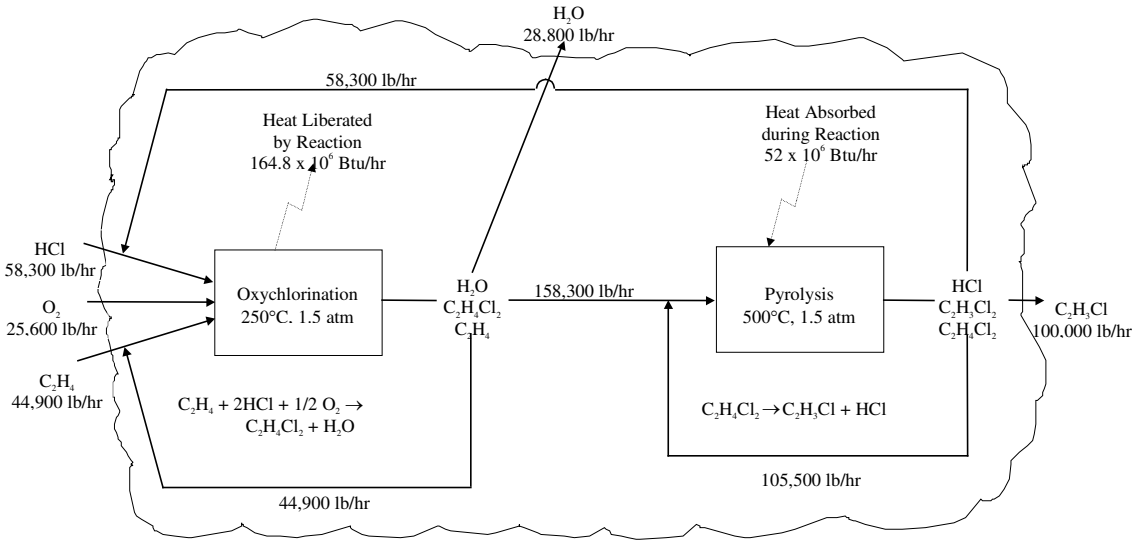
2.7 For Reaction Path 4, which involves the oxychlorination reaction, one flowsheet that shows a potential distribution of chemicals follows. Note that the molar ratio of C_2H_4/HCl entering the oxychlorination reaction is set at unity to promote complete conversion of HCl.



Using ASPEN PLUS, with the feed chemicals at 25°C and a mole ratio of C_2H_4/HCl entering the oxychlorination reactors at unity, the adiabatic exit temperature is 1,007°C, far higher than 250°C at which the reaction is to be carried out. Several methods of heat removal are possible, as discussed in Section 6.5. In the flowsheet below, fixed-bed reactors in series are shown with intercoolers. The details of this configuration can be determined using a process simulator. The possibilities for providing heat needed elsewhere in the flowsheet should be examined in the process integration step. Furthermore, a partial condenser is shown following the last stage of the fixed-bed reactor. At this stage in process synthesis, it is assumed that the condenser can be cooled with cooling water such that its effluent leaves at 35°C. It is further assumed that the effluent can be separated in a decanter into a vapor phase containing nearly pure C_2H_4, a nearly pure water phase, and an organic phase containing nearly pure $C_2H_4Cl_2$. This assumption would be checked using a simulator, combined with experimental VLLE data from a laboratory or pilot plant. The remainder of the flowsheet, involving the processing of $C_2H_4Cl_2$ is unchanged from that in Figure 2.6. Of course, alternate configurations are possible for this portion of the flowsheet.

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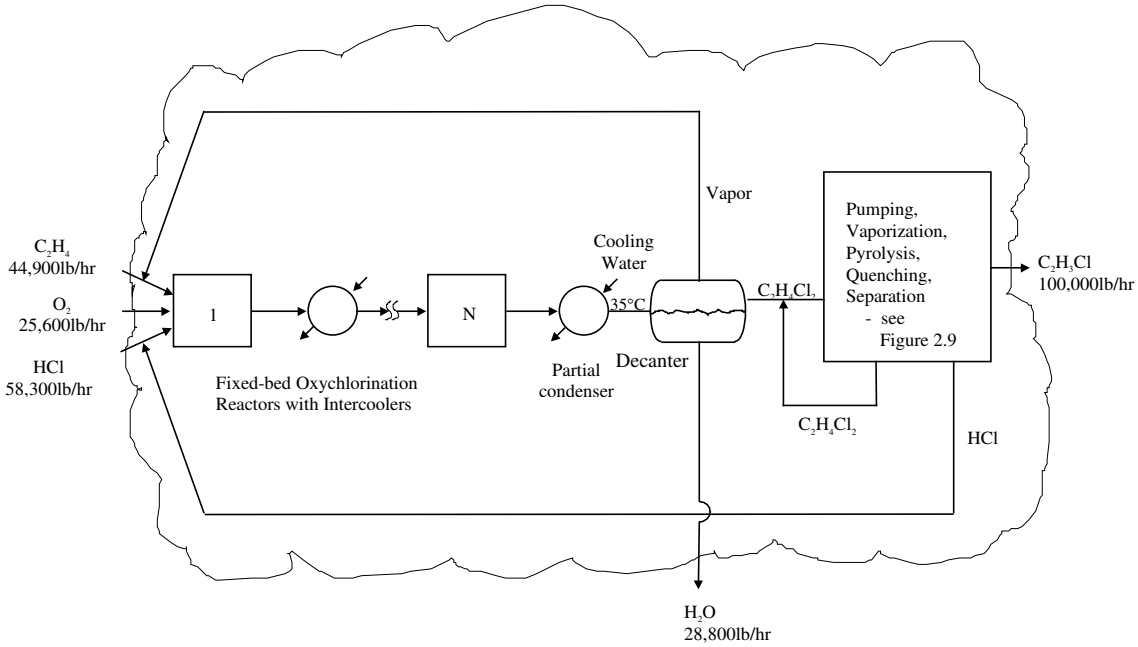

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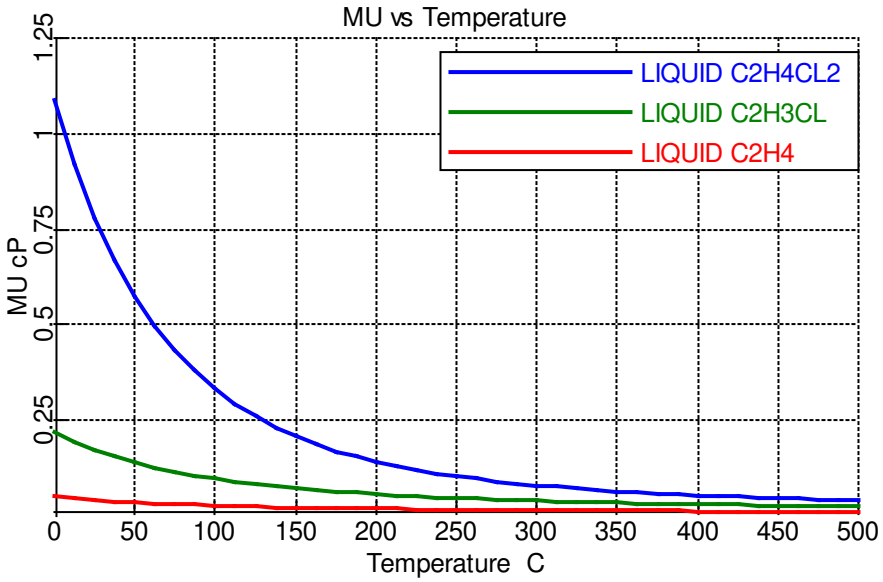
2.8 The detailed database for the vinyl chloride process requires transport data for estimating pressure drops and heat transfer coefficients. The following table, taken from Woods (*Data for Process Design and Engineering Practice*, Prentice-Hall, 1995) provides typical viscosity and thermal conductivity data at 25°C unless indicated.

	μ, kPa-s		k, kW/1,000K	
	Liquid	Vapor	Liquid	Vapor
Chlorine	0.496	10.9	163	6.9
HCl	0.58 (-100°C)	14.5	421 (-100°C)	14
Ethylene	0.162	6.04	192	6.44
Vinyl chloride	0.43 (-50°C)	11	114	11
1,1-dichloroethane	0.453	9.38	113	9.5

In addition, a source of molecular diffusion coefficients is needed for the calculation of mass-transfer rates, as well as a source of surface tensions to estimate flooding velocities. When data are not available, estimation methods are available. For example, viscosity, thermal conductivity, and surface tension can be estimated for the pure species as a function of temperature using ASPEN PLUS, as illustrated below:



Kinetic data are needed to size the direct chlorination and pyrolysis reactors. A search of the literature is needed. If data are not found, laboratory or pilot plant data are needed.

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For the vinyl chloride process in Figures 2.6 and 2.17, as discussed in the Section 2.3, data are needed on the rate of carbon deposition when cooling the pyrolysis effluent from 500 - 170°C. These will most likely be taken in laboratory or pilot plant experiments.

For vapor-liquid equilibria of mixtures involving HCl, C_2H_3Cl, and $C_2H_4Cl_2$, experimental data are needed to determine the interaction coefficients for estimation of liquid-phase activity coefficients. These are needed for bubble-point calculations and for estimating the number of stages and reflux ratio of the distillation column to recover HCl.

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2.9 a. Growth time = $\dfrac{3\times10^6 - c_i \dfrac{\text{cell}}{\text{mL}}}{0.39\times10^6 \dfrac{\text{cell}}{\text{mL-day}}} = 3 \text{ day}$

$$3\times10^6 - c_i = 3\times0.39\times10^6 = 1.17\times10^6$$

$$c_i = 3\times10^6 - 1.17\times10^6 = 1.83\times10^6 \frac{\text{cell}}{\text{mL}}$$

$$c_i = 1.83\times10^6 \frac{\text{cell}}{\text{mL}} = \frac{300\text{L}}{V}\times3\times10^6 \frac{\text{cell}}{\text{mL}}$$

$$V = \frac{300\text{L}\times(3\times10^6)}{1.83\times10^6} = 492 \text{ L}$$

Recommended reactor volume (~20% larger) = $492\times1.2 \cong 600$ L

b. From patent – O_2 consumed = $0.2\times10^{-12} \dfrac{\text{mol } O_2}{\text{cell-hr}}$

For cultivator 3:

$$1.61\times10^6 \frac{\text{cell}}{\text{mL}}\times4{,}000{,}000 \text{ mL}\times0.2\times10^{-12} \frac{\text{mol } O_2}{\text{cell-hr}}\times$$
$$7 \text{ day}\times\frac{24 \text{ hr}}{\text{day}} = 216.4 \text{ mol}\times\frac{0.032 \text{ kg}}{\text{mol}} = 6.924 \text{ kg}$$

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2.10 This solution has not been completed.

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