Week 13: Cryogenic processes

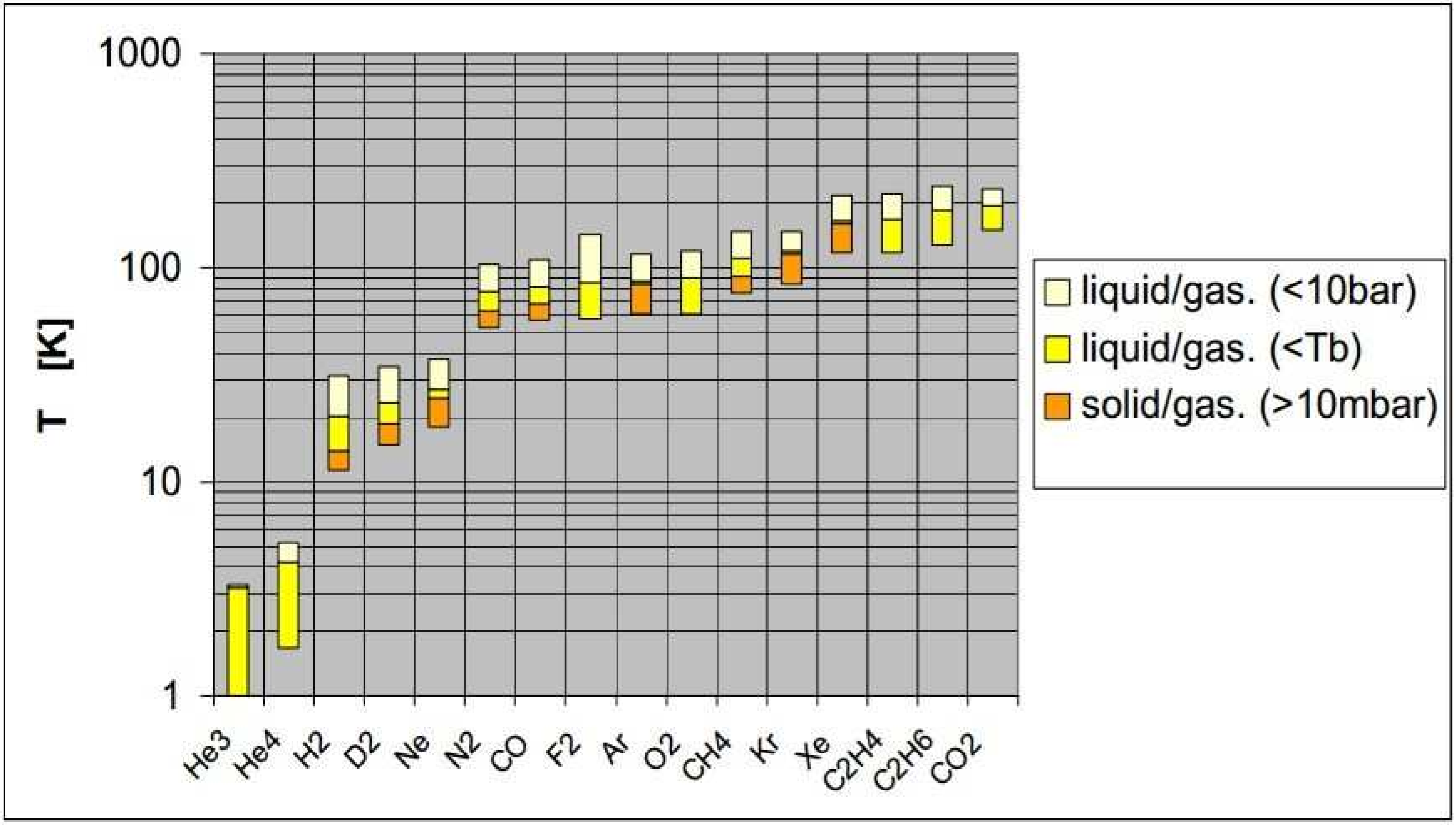
Mainly processes below -150 C

(123 K)

Cryogenic properties of some gases

Gas	Boiling point C	Melting point C
He	-268.9	-272.2
H2	-252.7	-259.1
N2	-195.8	-209.86
Ar	-185.7	-189.2
O2	-183.0	-218.4
CH4	-161.4	-182.6

Refrigerants - ranges



Refrigerant	He^3	He^4	H_2	D_2	Ne	N_2	CO [illegible]rbon Monoxide	F_2 Fluorine
Temperatures [K]		liq						liq
2-phase equilibrium at 10 mbar	0.97	1.67	11.4	15	18.1	53	57	58
triple point			13.9	18.7	24.559	63.148	68.09	53.6
boiling point at 1.01325bar	3.19	4.22	20.3	23.6	27.097	77.313	81.624	85.24
2-phase equilibrium at 10 bar			31.36	34.7	37.531	103.641	108.959	
critical point	3.33	5.2	33.19	38.3	44.49	126.19	132.8	144.41

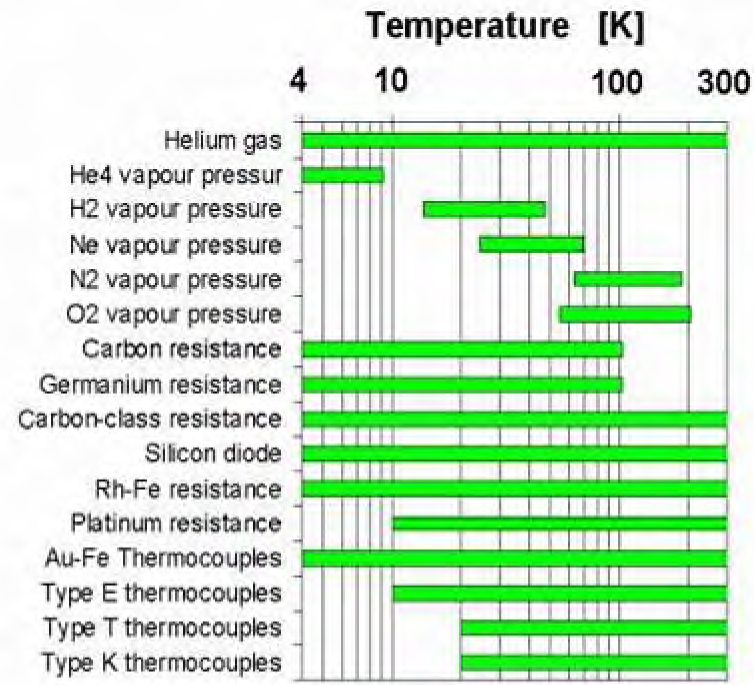
Refrigerant	Ar Argon	O_2 Oxygen	CH_4 Methane	Kr Krypton	Xe Xenon	C_2H_4 Ethylene	C_2H_6 Ethane	CO_2 Carbon
Temperatures [K]		liq				liq	liq	
2-phase equilibrium at 10 mbar	60.7	61.3	76.1	84.3	117.3	117.6	127.8	151.2
triple point	83.82	54.361	90.67	115.94	161.36			
boiling point at 1.01325bar	87.281	90.191	111.685	119.765	165.038	169.242	184.548	194.65
2-phase equilibrium at 10 bar	116.55	119.623	149.198	149.198	218.612	221.25	241.9	233.038
critical point	150.66	154.58	190.56	109.43	289.73	282.35	305.33	

Instrumentation - temperature measurement

- Primary thermometers
  - gas thermometer
  - vapour thermometer
- Secondary thermometers
  - metallic resistances
  - non-metallic resistances
  - thermocouples

  - others: capacitance t,; resonance t.; inductance t.

- Precision factors
  - sensitivity (e.g. Ω/K)
  - reproducability (factors - installation, self heating, ageing)
  - magnet field dependence



PT 100

Silicon diode

Refrigeration

And the Joule-Thompson effect:

Isoenthalpic fast reduction of pressure

Joule Thomson coefficient

- The Joule-Thomson coefficient is a measure of the temperature of a gas with decreased
- pressure at constant enthalpy.
- **μ = (dT/dP) at constant enthalpy**

- If the coefficient is positive you get cooling
- If the coefficient is negative you have to

precool the gas below the inversion temp.

Some inversion temperatures at atmospheric pressure

- Nitrogen 621 K = 348 C
- Oxygen 764 K = 491 C
- Hydrogen 205 K = -68 C
- Helium 51 K = -222 C

- A variety of other numbers may be found

Inversion curve for various gases

Note: The maximum T to begin hydrogen liquefaction is 202 K at 0 atm.

Since expansion must begin at a higher pressure, it is usually started below 100 K.

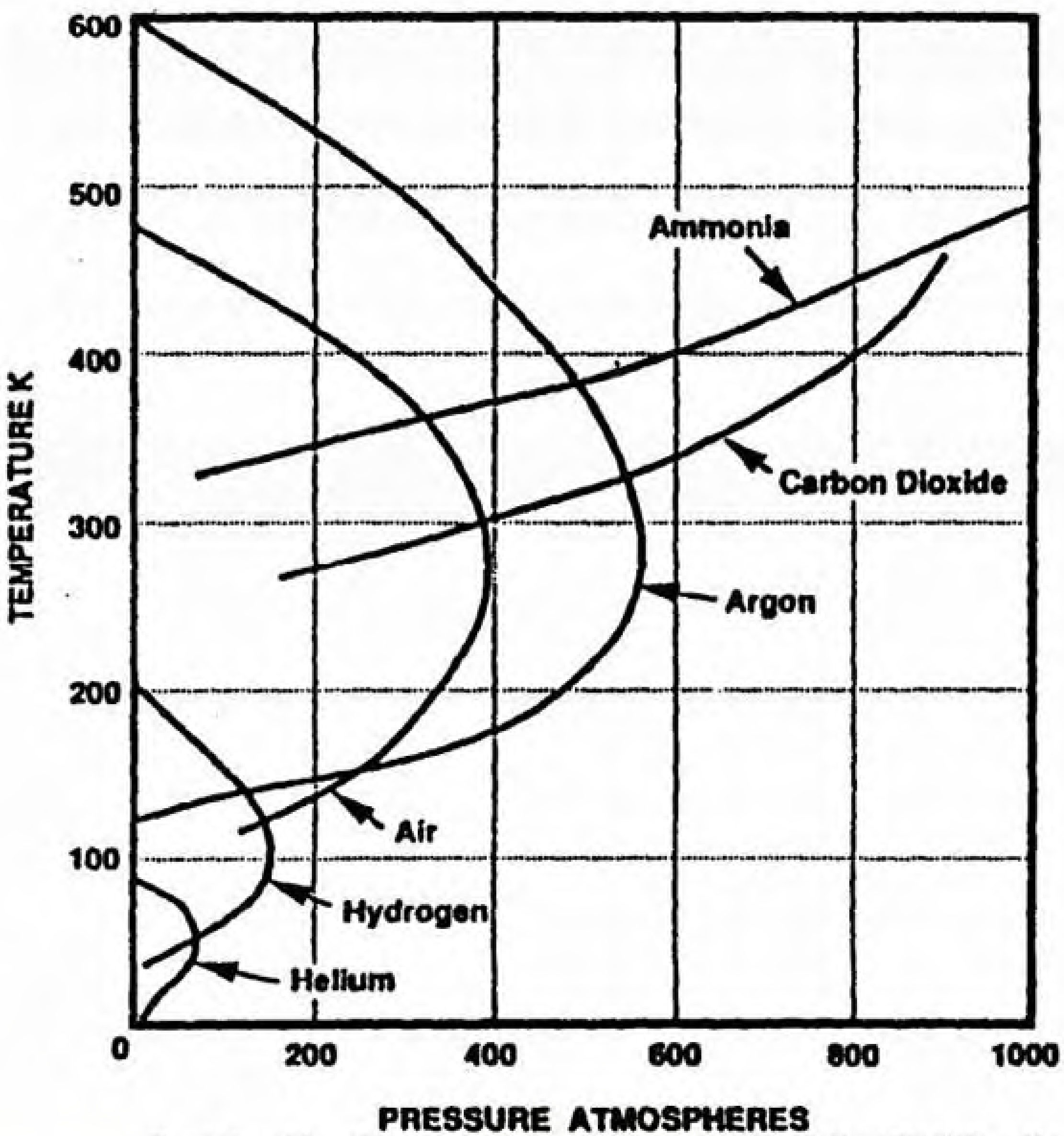


Figure adapted from *Cryogenic Engineering* by Thomas M. Flynn, Dekker:NY (1997), p. 284

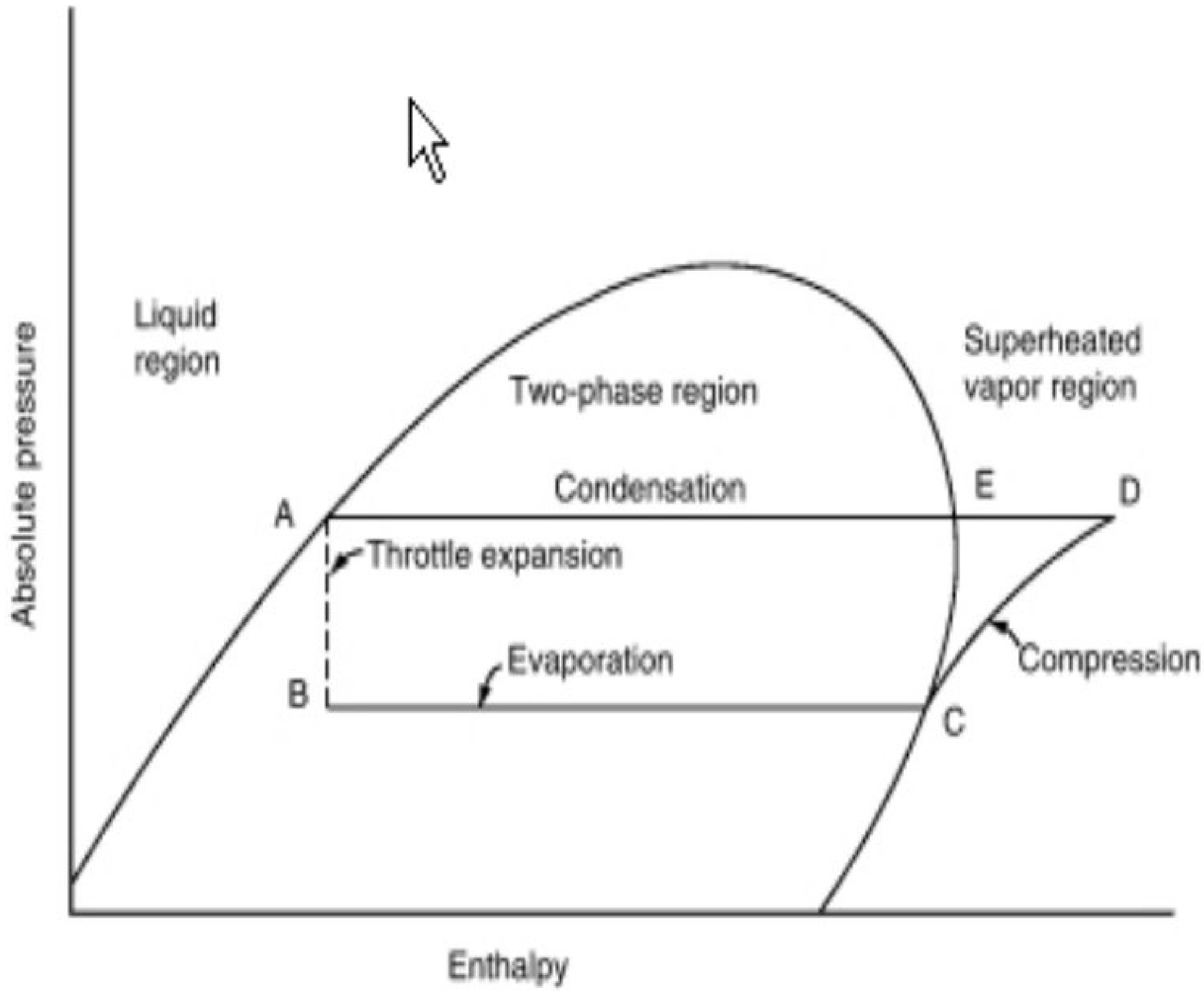
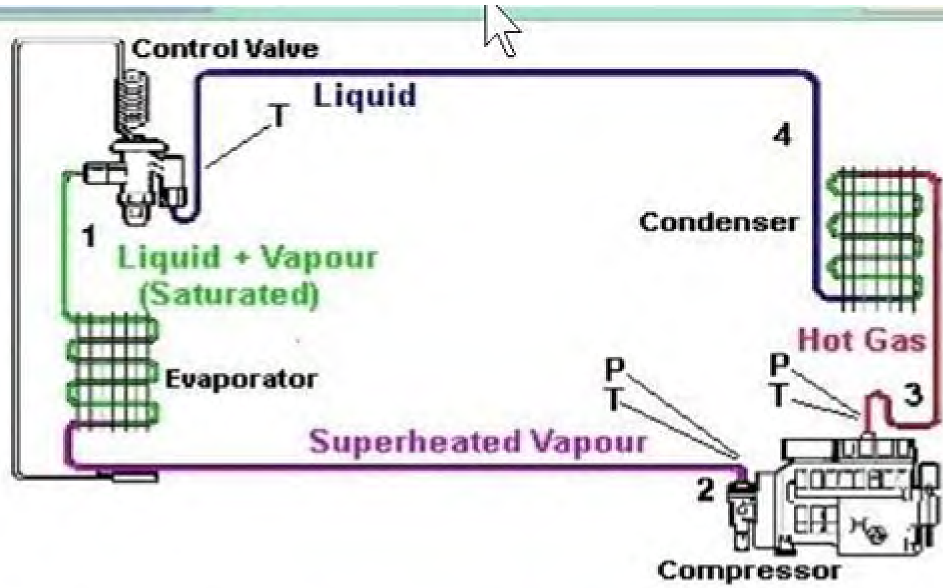
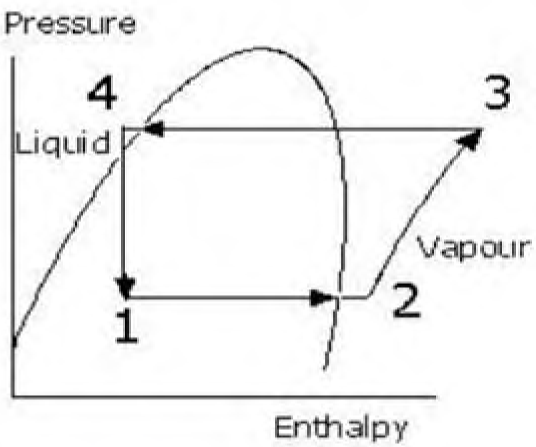
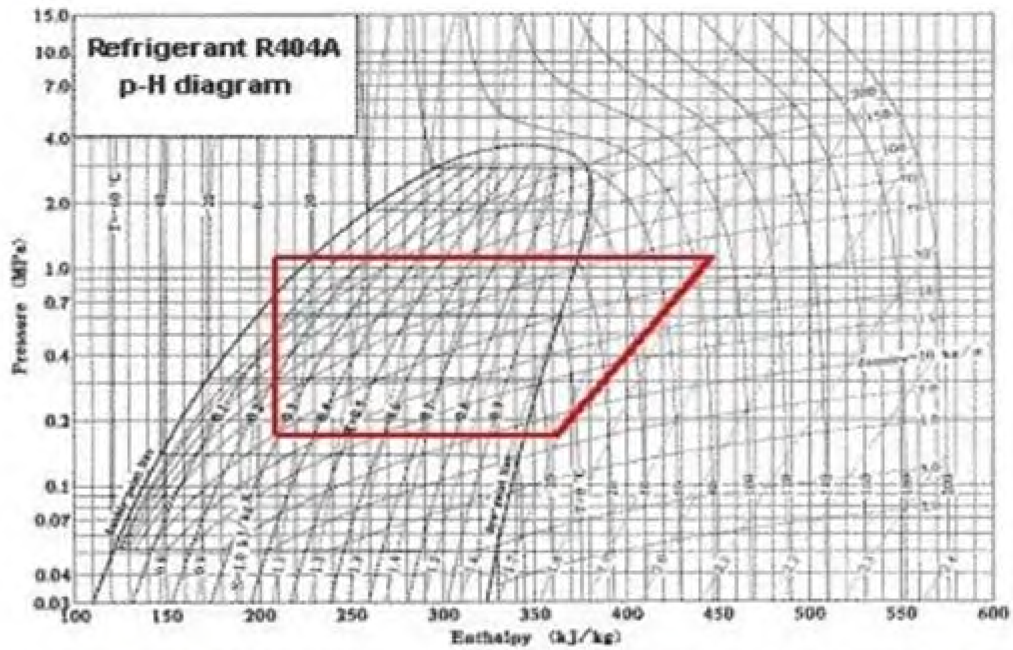


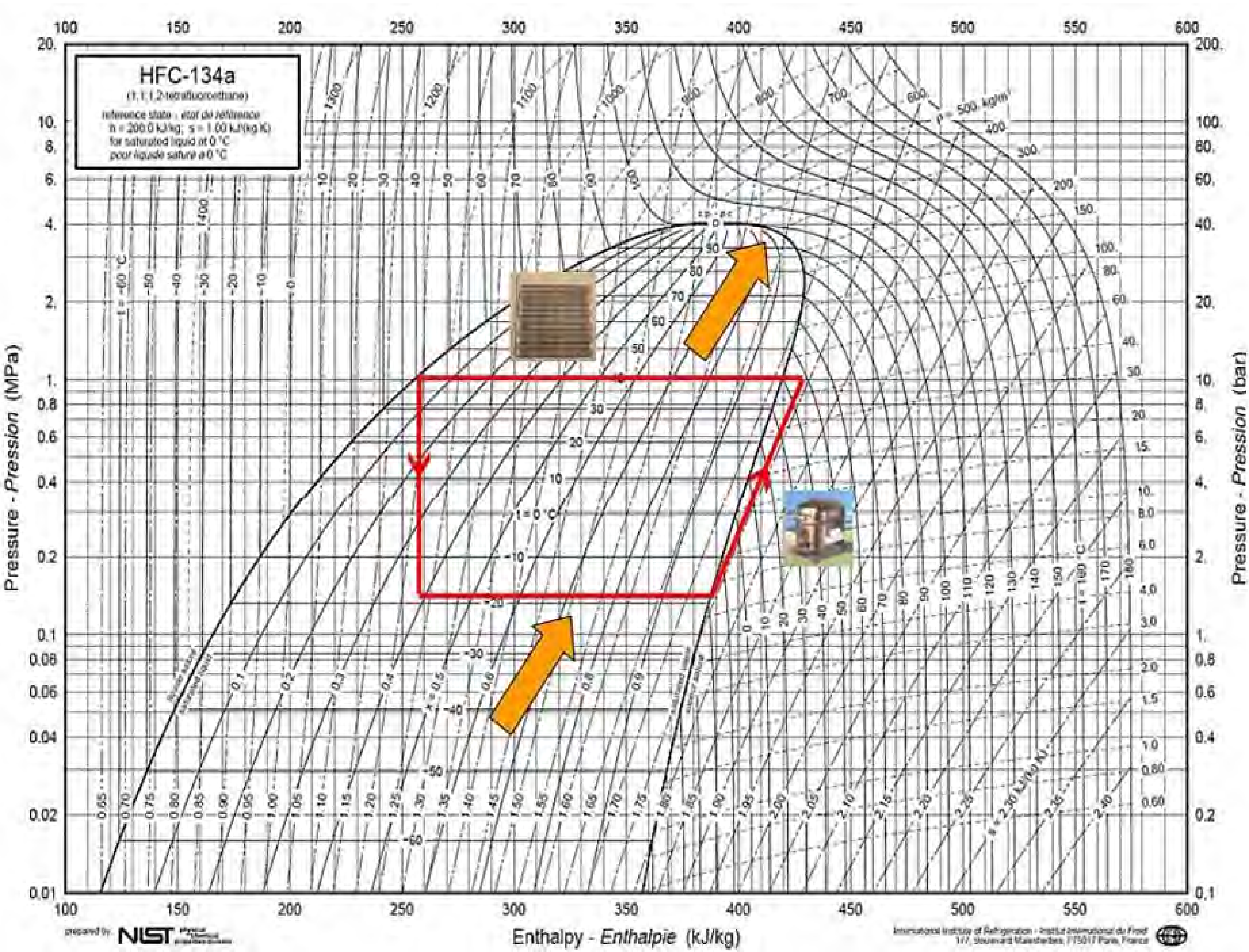
FIGURE 1.4 Mollier or pressure–enthalpy diagram used in vapor compression systems employing condensation by recompression followed by throttle expansion, evaporation. (Courtesy of F.G. Kerry, Inc., 2006. With permission.)



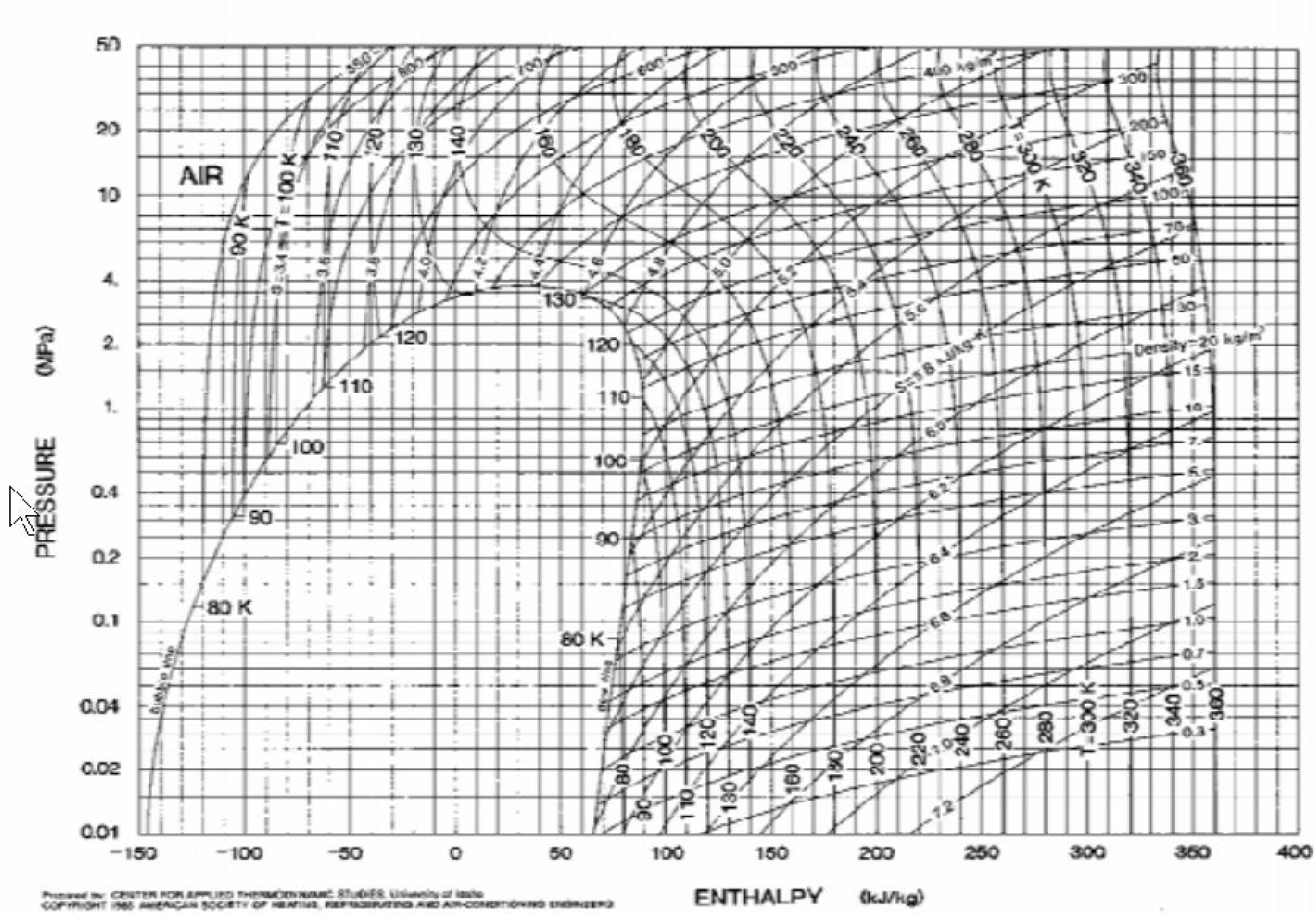
The Vapour Compression Cycle, Practical Circuit and P-h Charts






HFC-134a
(1,1,1,2-tetrafluoroethane)
Pressure - Pression (MPa)
Pressure - Pression (bar)
Enthalpy - Enthalpie (kJ/kg)

Works for air



Does not work so well for hydrogen and helium

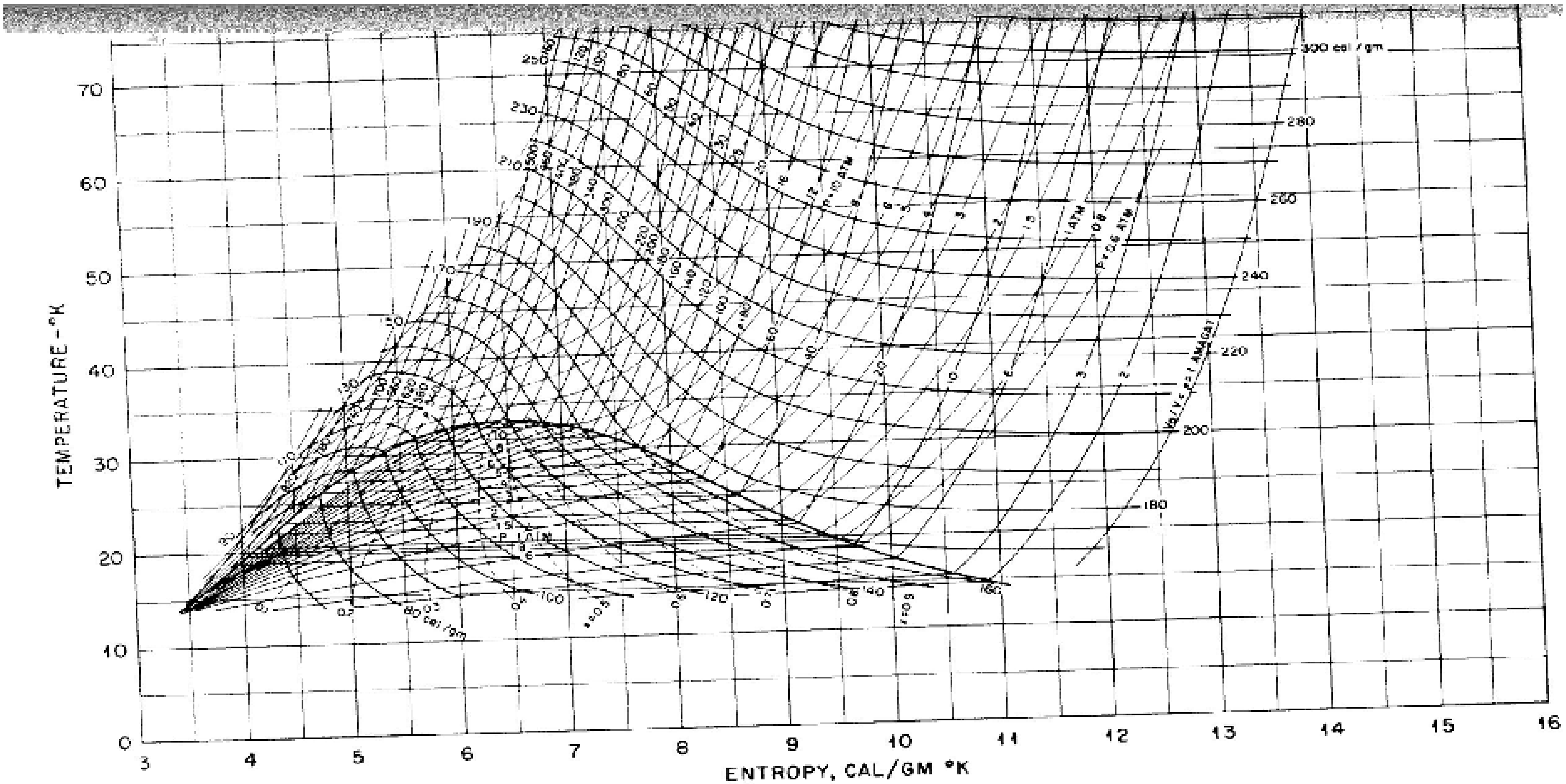


FIGURE 9.16. Temperature-entropy diagram for hydrogen [31].

Special for cryogenic systems

- Hardness and tensile strength are different
- Very good insulation is required
- Good heat integration is a must
- Cold box makes maintenance expensive
- Heat exchangers are a separate class
- Unusual thermodynamic behaviour.

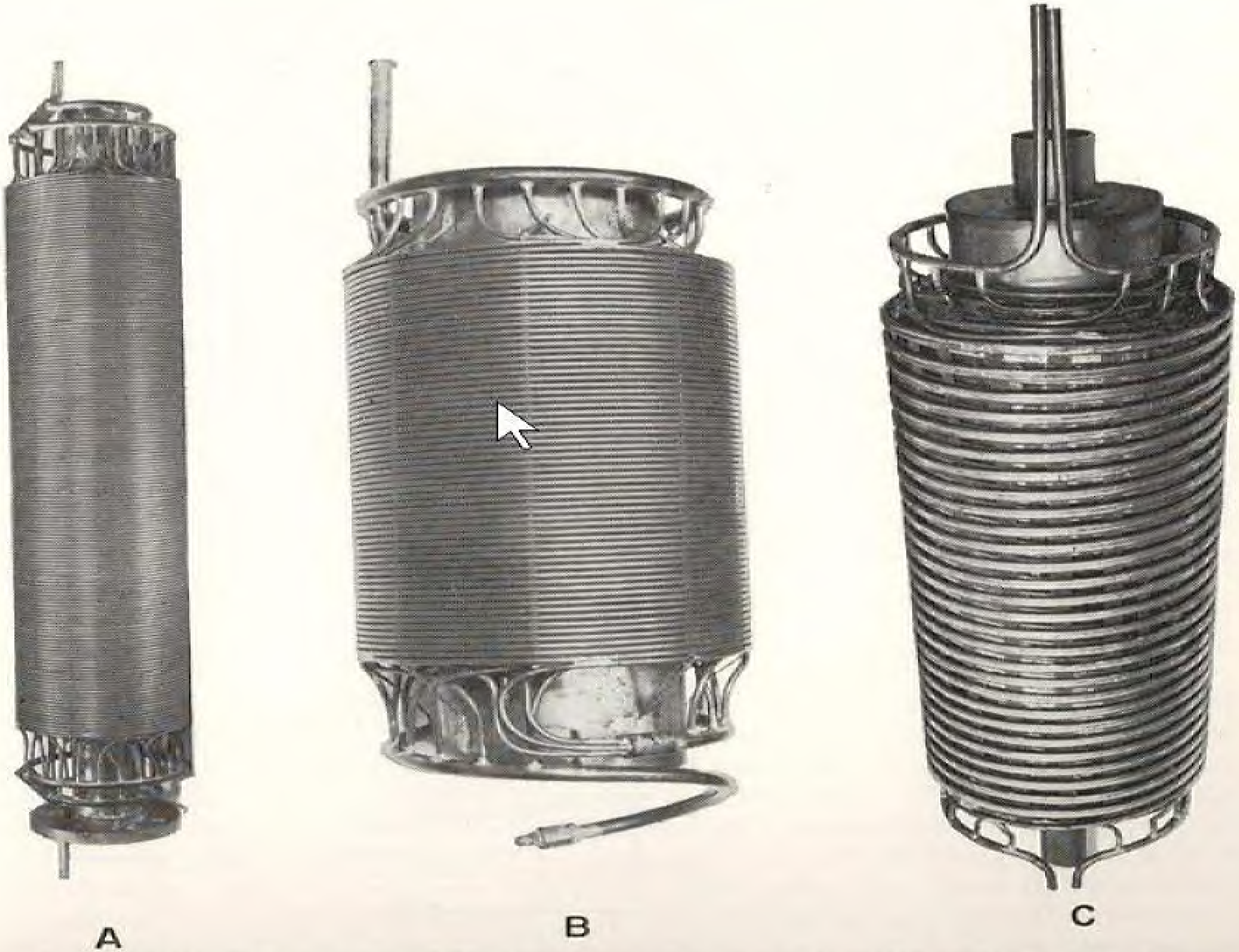
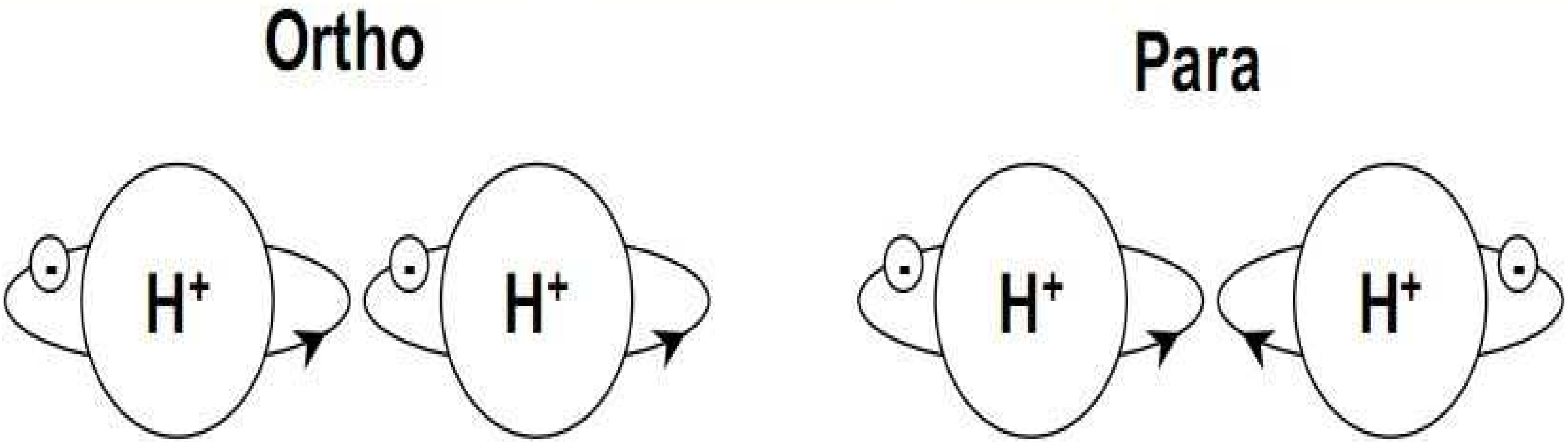


FIGURE 2.24. Three types of heat exchangers used in the NBS hydrogen liquefier.

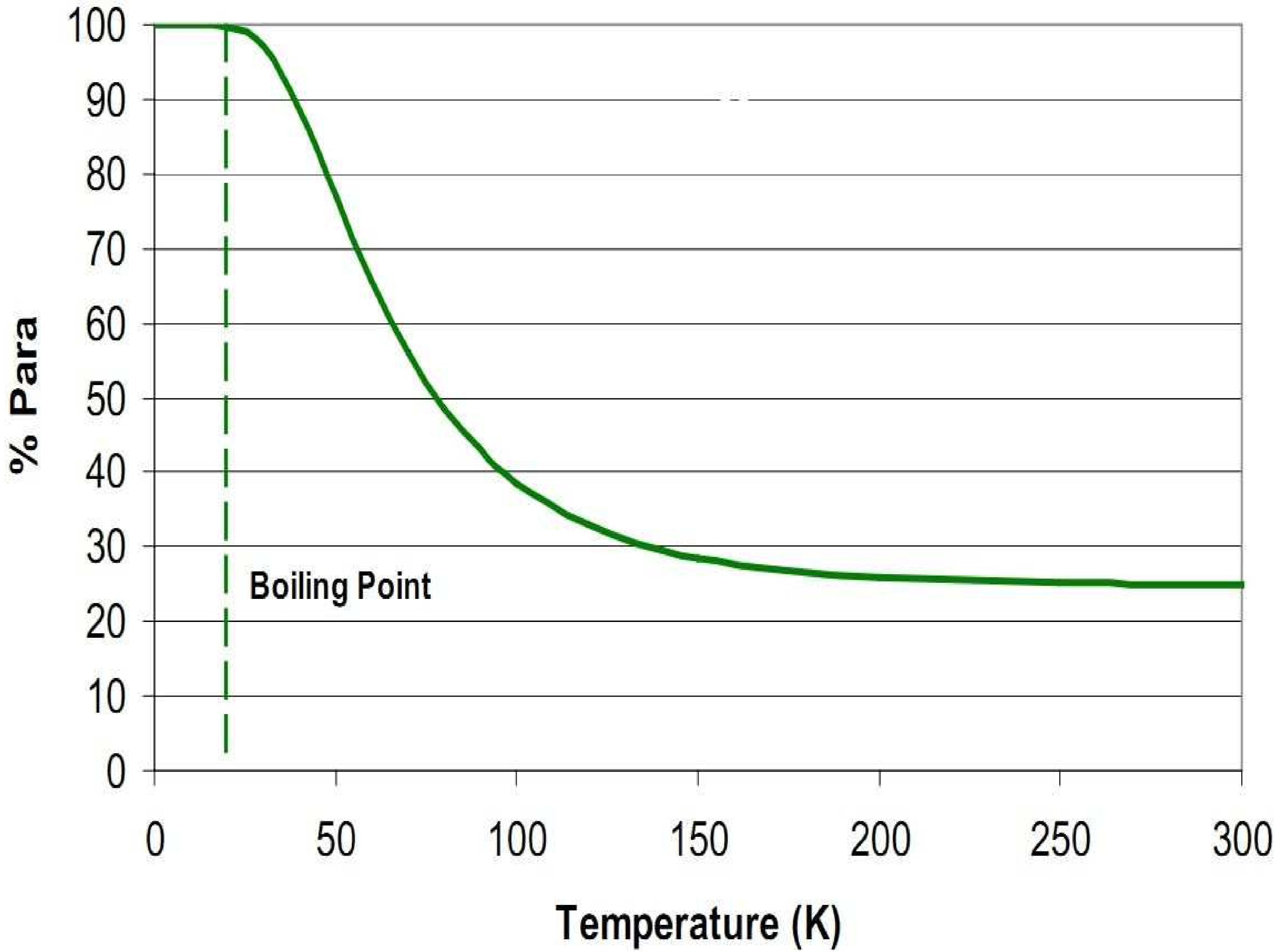
Unusual properties

OF HYDROGEN AND HELIUM



- Normal Hydrogen is 75% Ortho, 25% Para
- Liquid Hydrogen is 0.2% Ortho, 99.8% Para

- Heat of Conversion from Normal to Para is 0.146 kWh_{th}/kg
- Heat of Liquefaction is 0.123 kWh_{th}/kg
- Conversion can cause Vaporization



100
90
80
70
60
50
40
30
20
10
0
% Para
Boiling Point
0
50
100
150
200
250
300
Temperature (K)

Particularities of Hydrogen

- exists in two molecular spin states:

  orthohydrogen and parahydrogen

- equilibrium depends on temperature

  300K 75% ortho 25% para
  20.4K 0.2% ortho 99.8% para

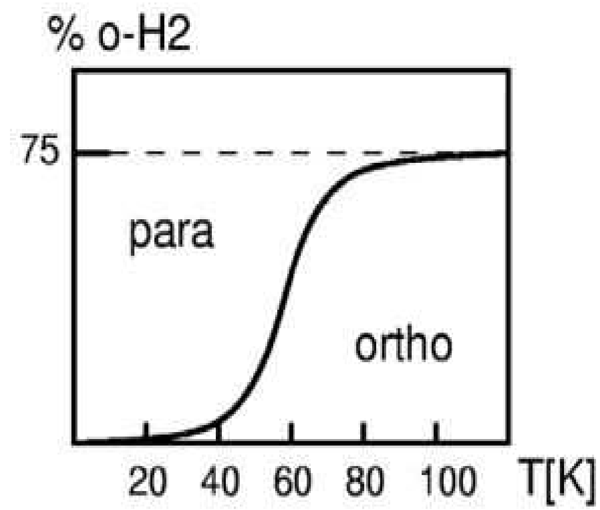
- conversion is slow (days) and exotherm

  Q_{conv} = -703 kJ/kg_{ortho}

  or 527 $kJ/kg_{n\text{-}H2}$ > evaporation enthalpy of 447kJ/kg

- specific heat and thermal conductivity of ortho- and parahydrogen are significantly different

- forms slush



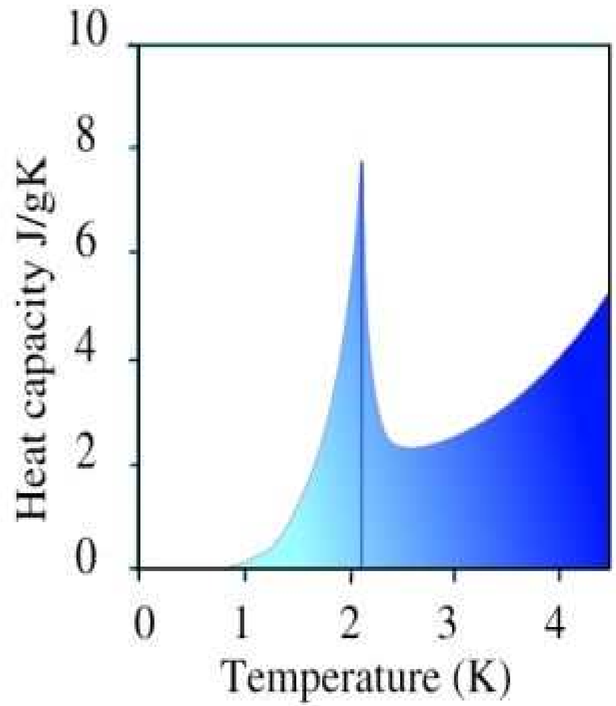
Particularities of Helium

- transition to a superfluid phase below the λ-point (2.17K)

  effects:

  - viscosity decreases by several orders of magnitude
  - creeps up the wall
  - thermomechanic (fountain) effect
  - heat conductivity increases by several orders of magnitude
  - second sound

  due to the two-fluid character



Helium II

- Liquid helium below the Lambda temperature (T_l = 2.172 K) behaves as a Non-Newtonian fluid. It can flow through narrow gaps or capillaries without any viscous dissipation. It also has unusually high thermal conductivity.
- Other strange properties of superfluid include the Rollin film, mechanocaloric effect and fountain effect.

Major cryogenic processes

- Separation of air
- Production of LOX*, liquid nitrogen, argon
- Separation of helium from natural gas
- Liquification of hydrogen
- Production of LNG**
- * liquid oxygen
- ** liquified natural gas

Air Separation Processes

- Cryogenic distillation (For large scale)
- Pressure Swing adsorption using molecular sieves
- Using ion transport membranes

somewhat different
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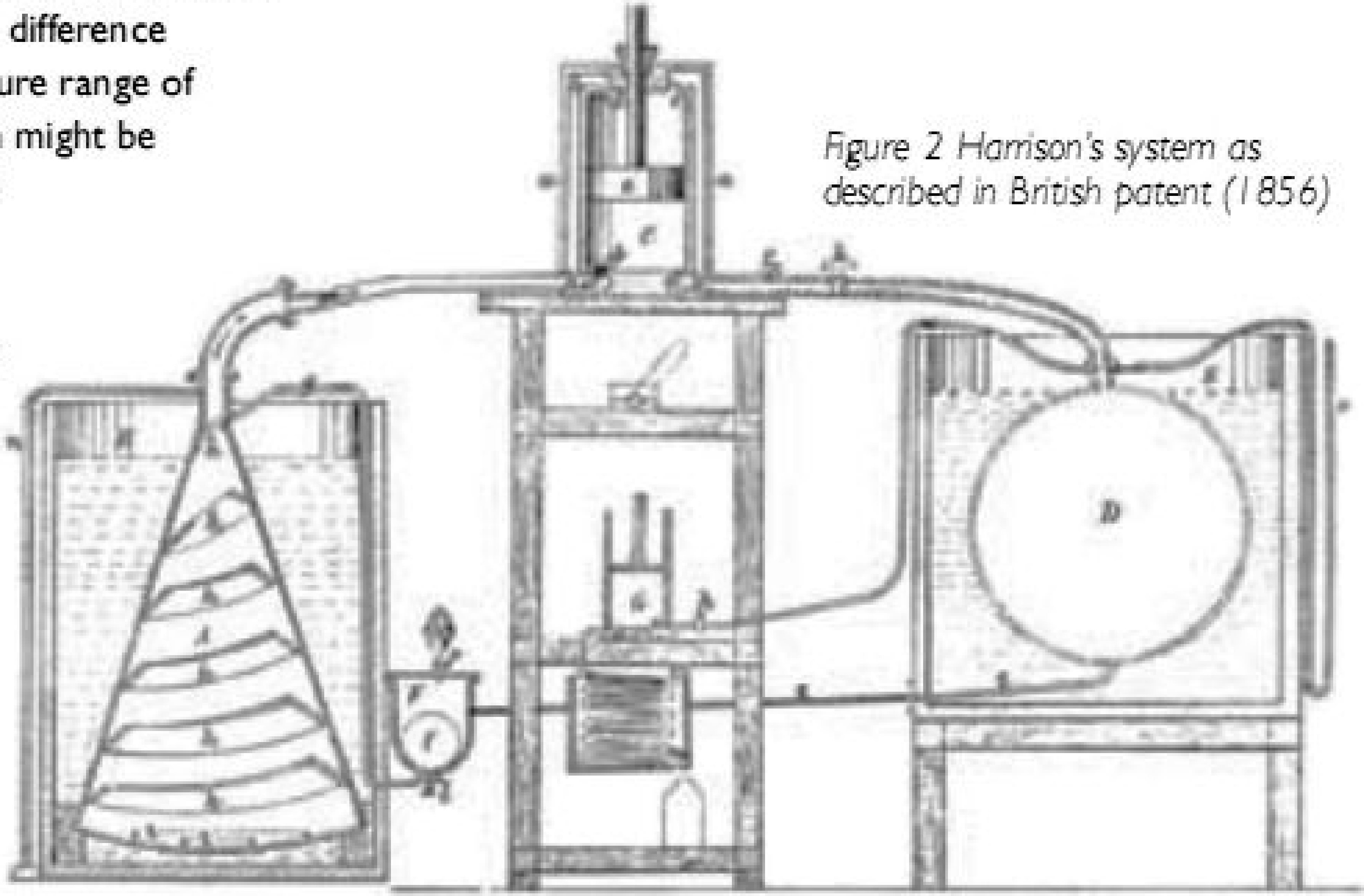
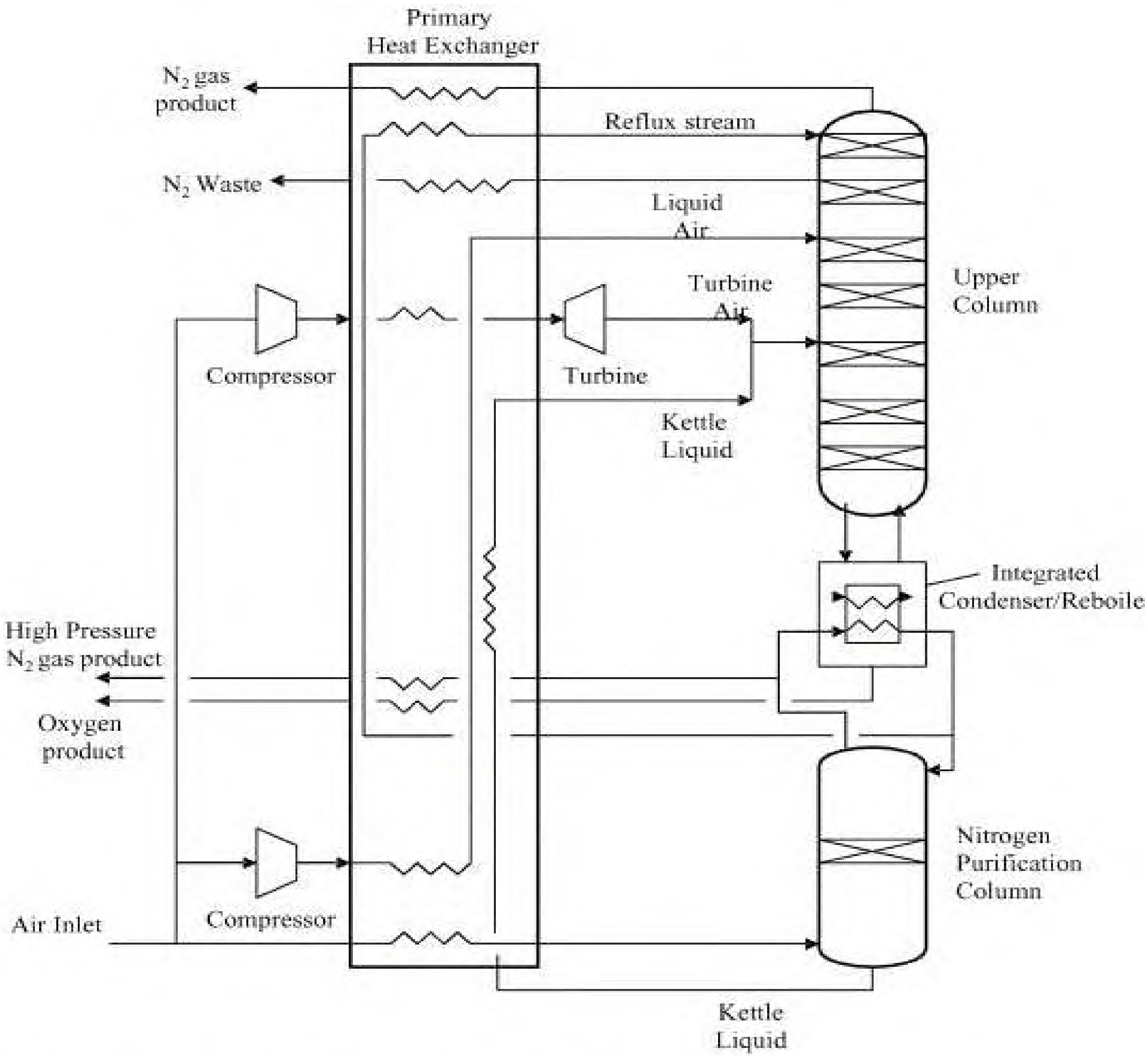


Figure 2 Harrison's system as described in British patent (1856)



[redacted]. Schematic diagram of a typical double column air separation plant.

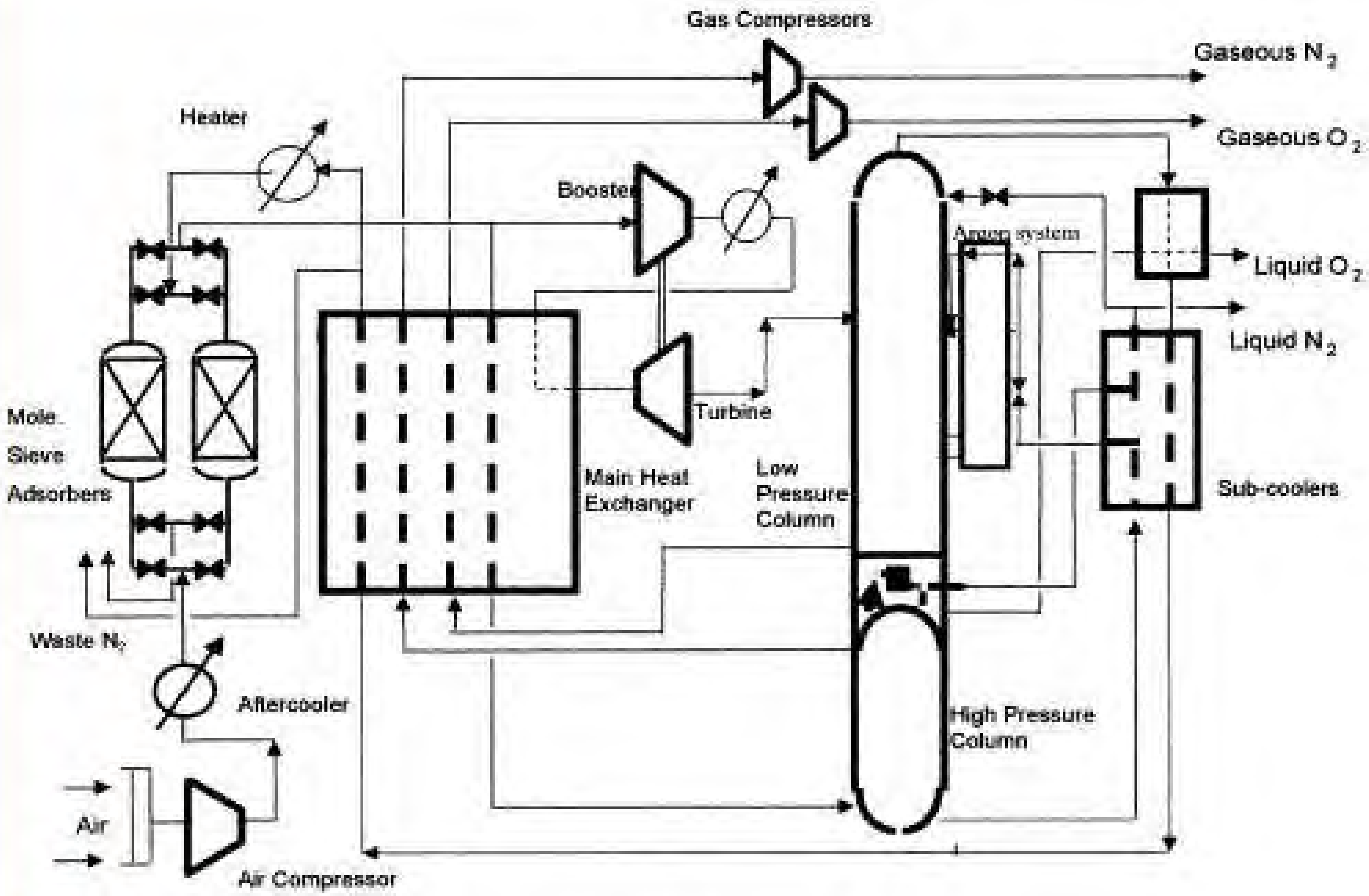


Fig. 1. Simplified flowsheet of low pressure air separation plant.

Fig. 1. Schéma simplifié d'une installation de séparation d'air à basse pression

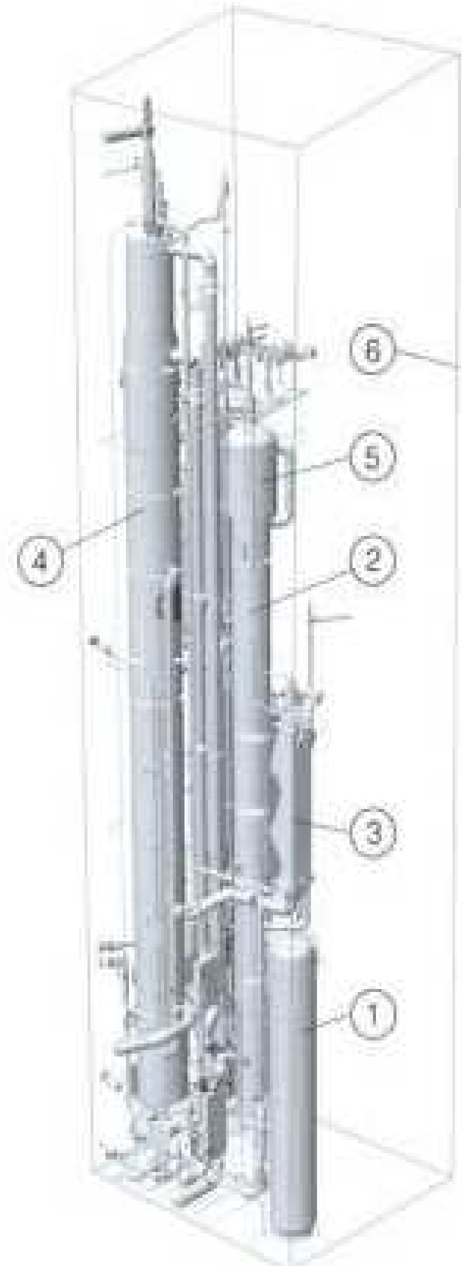


Fig. 2.17 3D-view of the Coldbox.
(1) Rectification column (pressure section);
(2) Second section of the crude argon column;
(3) Main condenser/evaporator;
(4) Rectification column (low-pressure section);
(5) Crude argon condenser;
(6) Coldbox shell.

Design

Do not trust computers absolutely

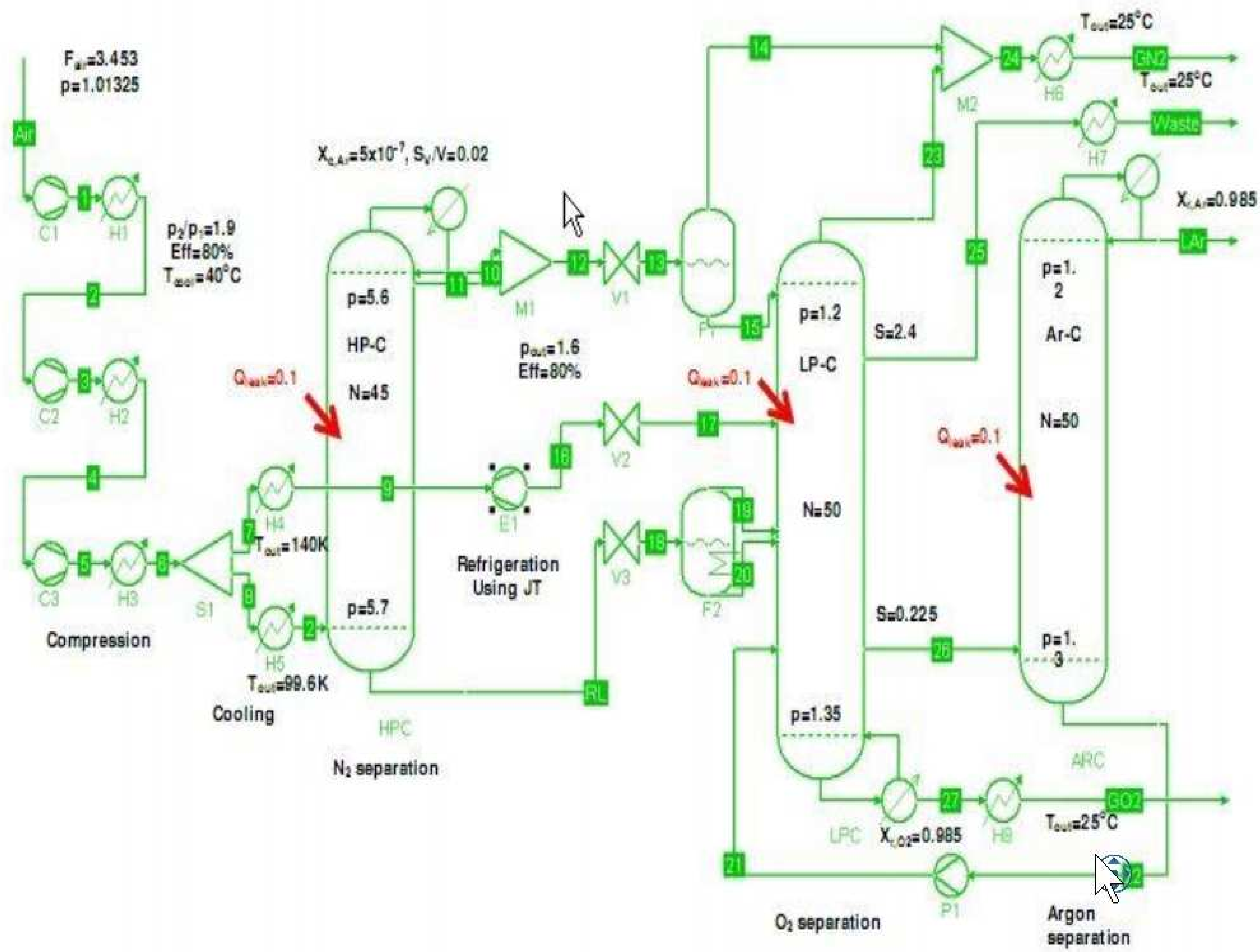


Figure 3: ASU in COCO showing plant specifications

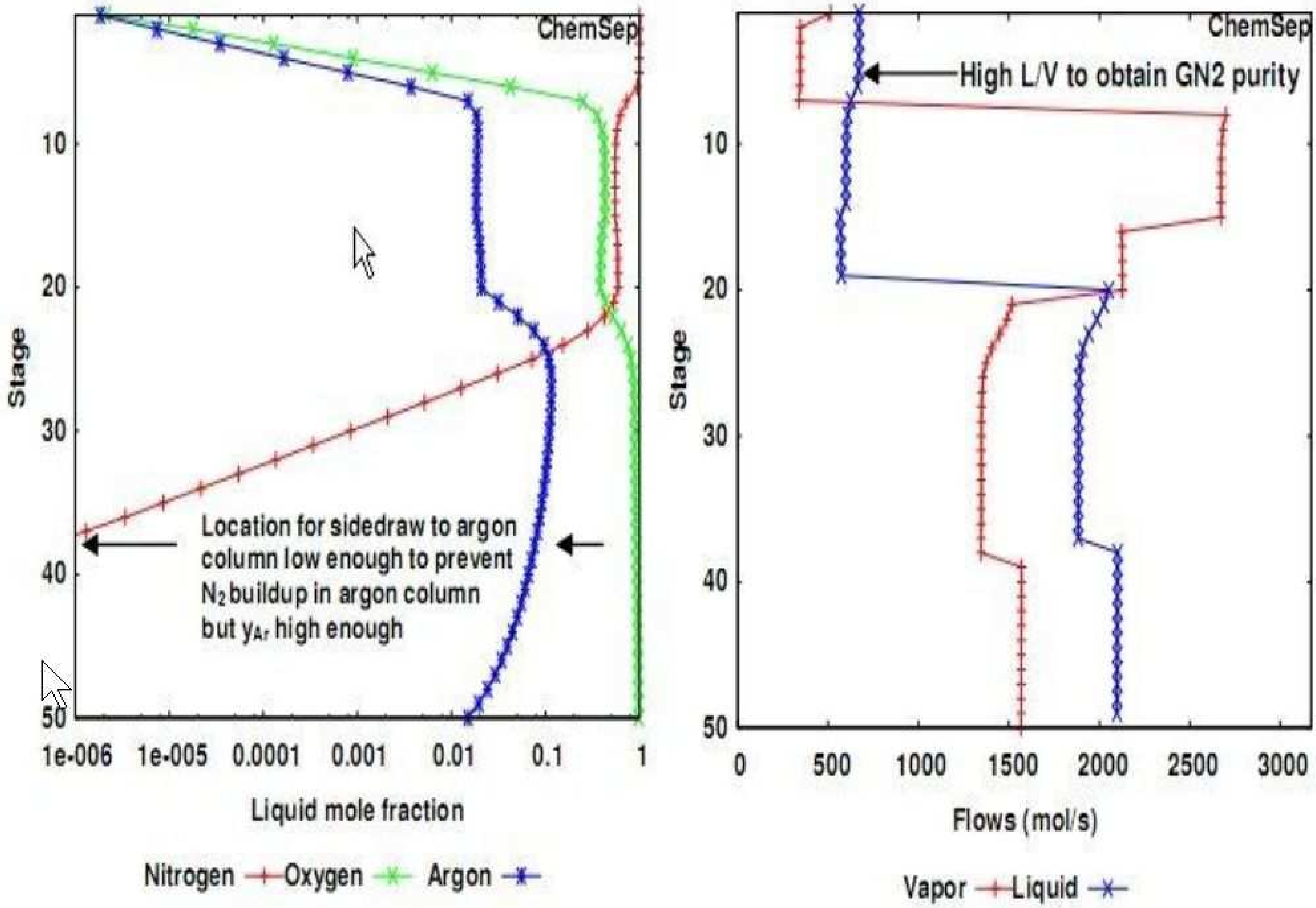


Figure 6: Composition and flow profiles in the low pressure column in ASU.

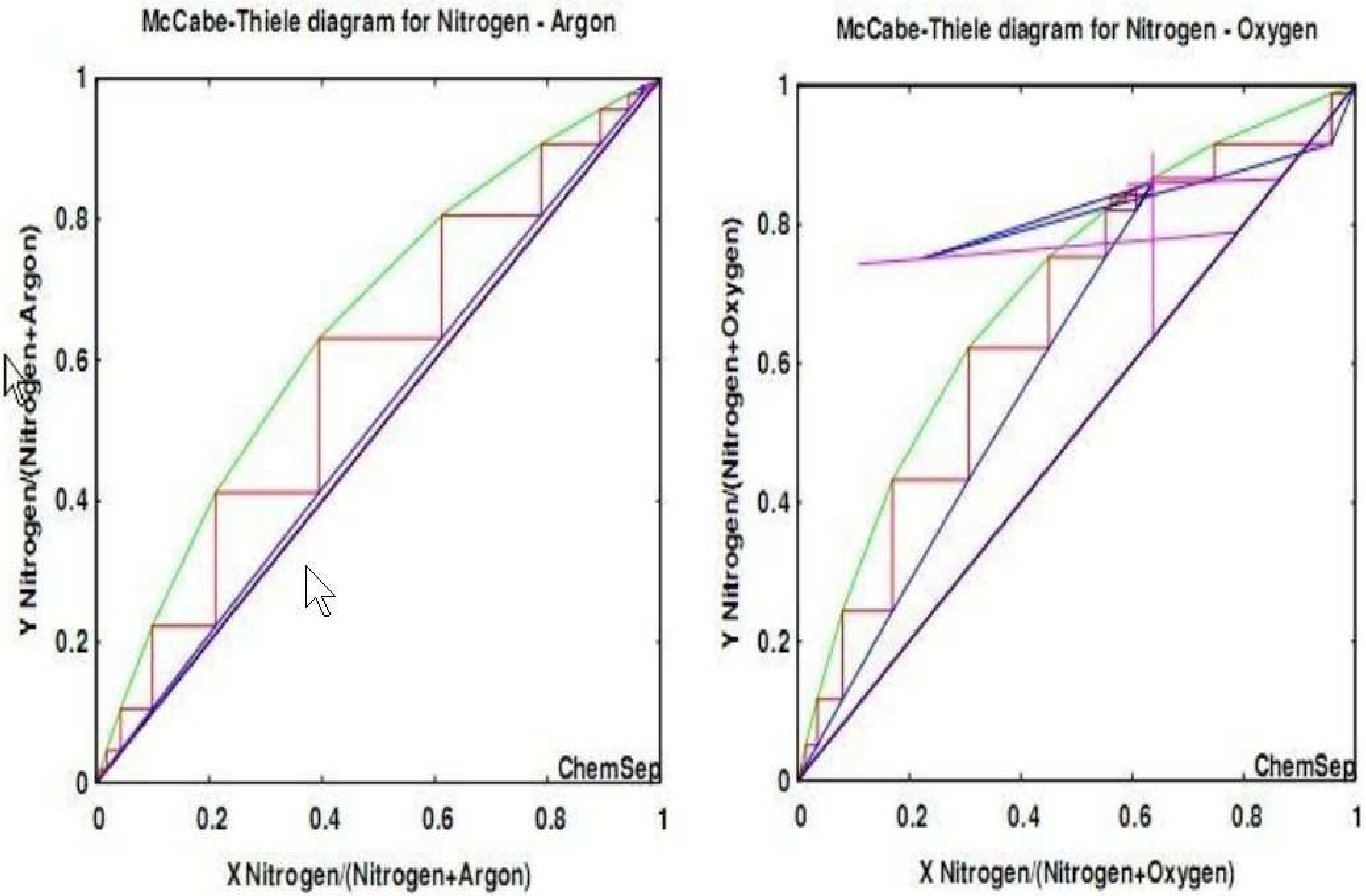


Figure 7: McCabe-Thiele diagrams for low pressure column in ASU.

$$L_{j-1}x_{i,j-1} - (V_j + W_j)y_{i,j} - (L_j + U_j)x_{i,j} + V_{j+1}y_{i,j+1} + F_j z_{i,j} = 0$$

$$y_{i,j} - K_{i,j}x_{i,j} = 0$$

$$\sum_{i=1}^{m} y_{i,j} - 1.0 = 0$$

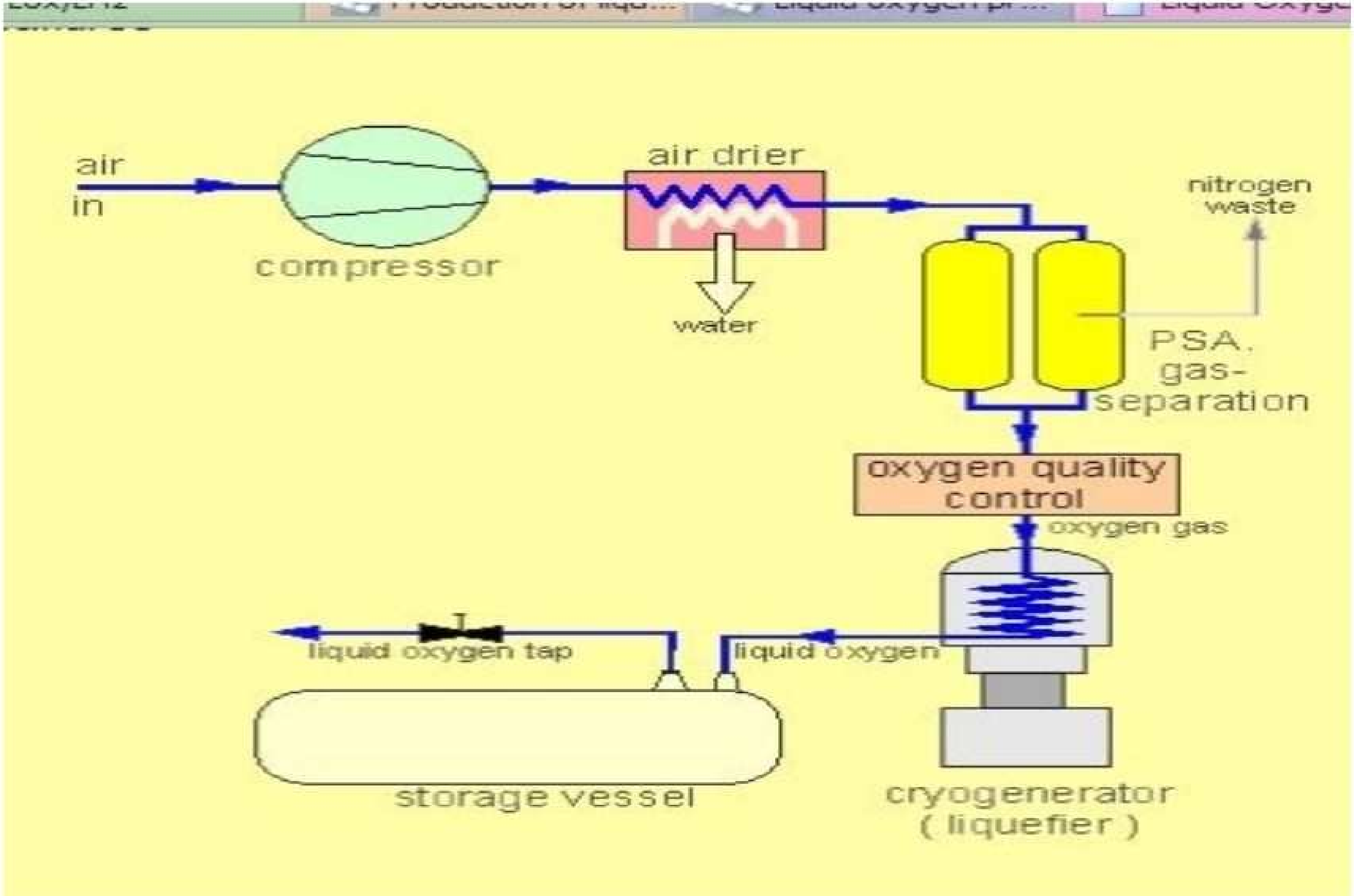
$$\sum_{i=1}^{m} x_{i,j} - 1.0 = 0$$

$$L_{j-1}h_{j-1} - (V_j + W_j)H_j - (L_j + U_j)h_j + V_{j+1}H_{j+1} + F_j H_{F,j} - Q_j = 0$$

Non Cryogenic processes

FOR AIR SEPARATION

Pressure swing adsorption



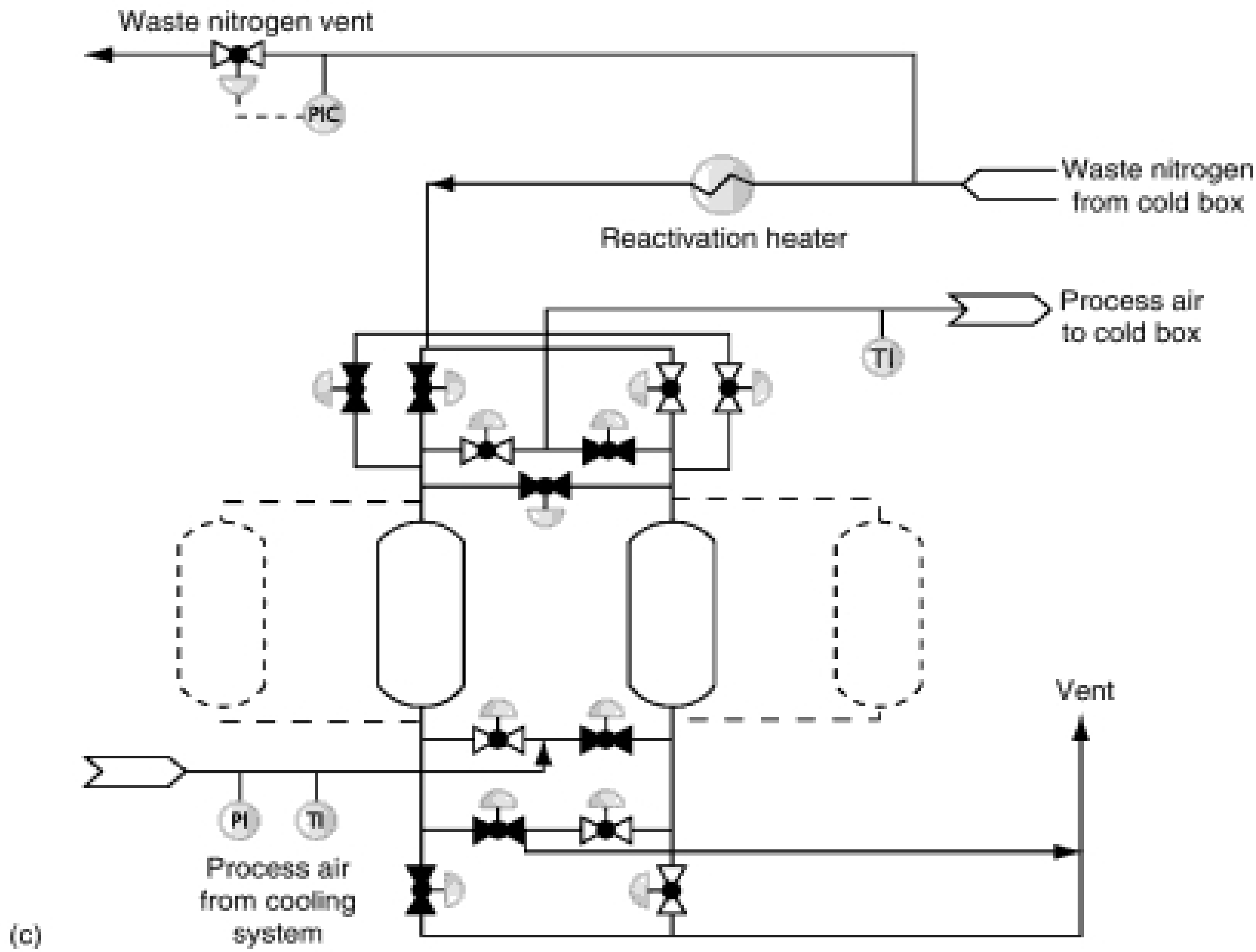
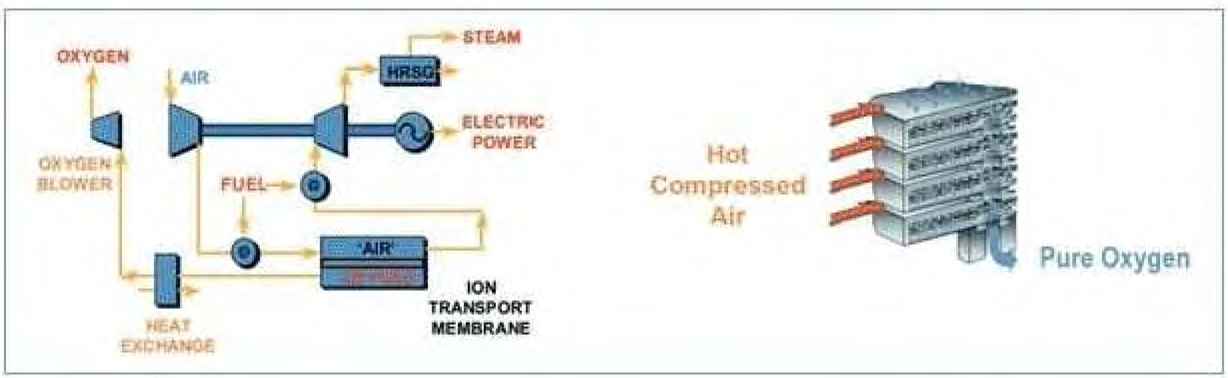


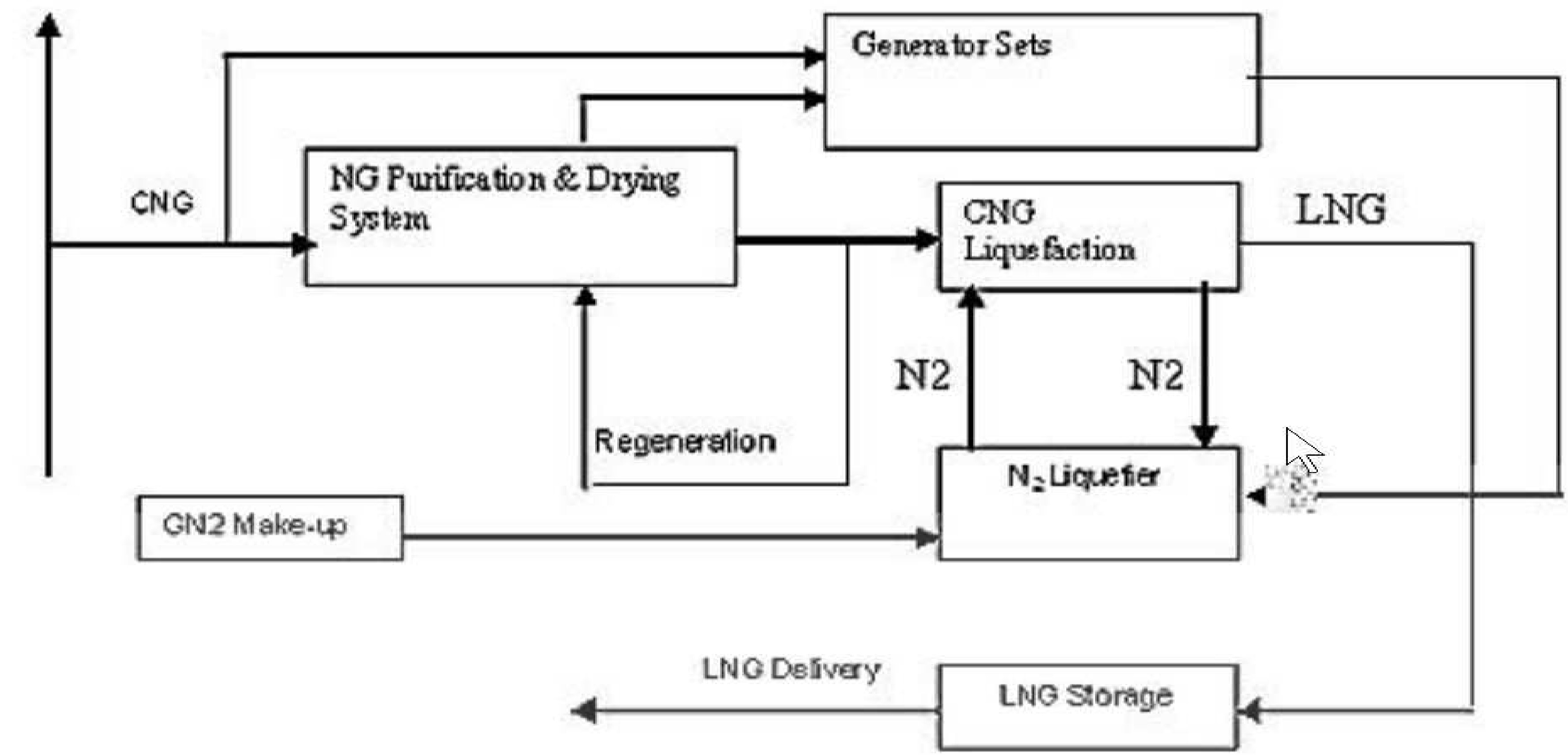
FIGURE 5.4 (continued) (c) Basic adsorber unit of vertical vessels with possible option for multiple vessels. (Courtesy of F.G. Kerry, Inc. With permission.)

Membrane separation



Other cryogenic processes

LNG



CLNG plants offered by Cryonorm Projects have following features:

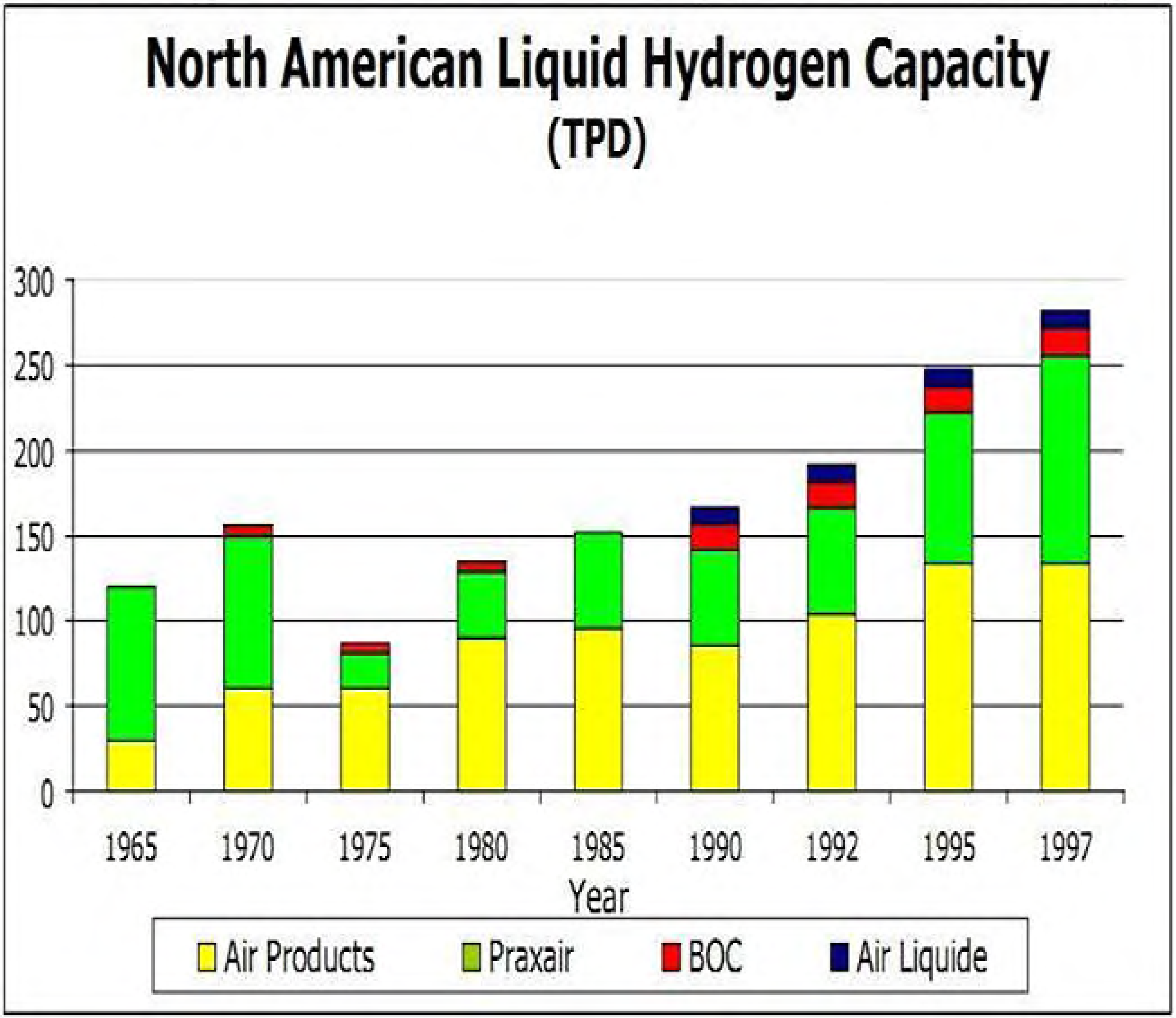
air products' baseload LNG projects

Location		Initial Start-up	Trains	LNG Rundown Per Train (MTA)	Process
Abu Dhabi		1977	2	1.7	C_3MR
		1994	1	2.6	C_3MR
Algeria	GL1Z	1977	6	1.3	C_3MR
	GL2Z	1981	6	1.4	C_3MR
	Skikda	2009	1	4.5	C_3MR/SplitMR™
Australia		1989-1993	3	2.5	C_3MR
Brunei		1972	5	1.3	C_3MR
Egypt		2004	1	5.0	C_3MR/SplitMR™
Indonesia	Bontang	1977-1997	7	2.6	C_3MR
		1999	1	3.0	C_3MR
	Arun	1978-1986	6	2.0	C_3MR
	Tangguh	2007	2	4.0	C_3MR/SplitMR™
Libya		1970	4	0.8	SMR
Malaysia	Satu	1982	3	2.5	C_3MR
	Dua	1995	3	2.8	C_3MR
	Tiga	2003	2	3.8	C_3MR
Nigeria		1999-2002	3	3.2	C_3MR
		2005-2007	3	3.7	C_3MR
Oman		2000-2005	3	3.3	C_3MR
Peru		2009	1	4.0	C_3MR/SplitMR™
Qatar	Qatargas	1996-1998	3	2.5	C_3MR
	Qatargas 2	2008	2	7.8	AP-X®
	Qatargas 3 & 4	2009	2	7.8	AP-X®
	RasGas	1999	2	3.3	C_3MR
	RasGas II	2003-2007	3	4.7	C_3MR/SplitMR™
	RasGas 3	2008	2	7.8	AP-X®
Yemen		2009	2	3.4	C_3MR/SplitMR™
Total			79		

Hydrogen

There are 10 hydrogen liquefaction plants in North America

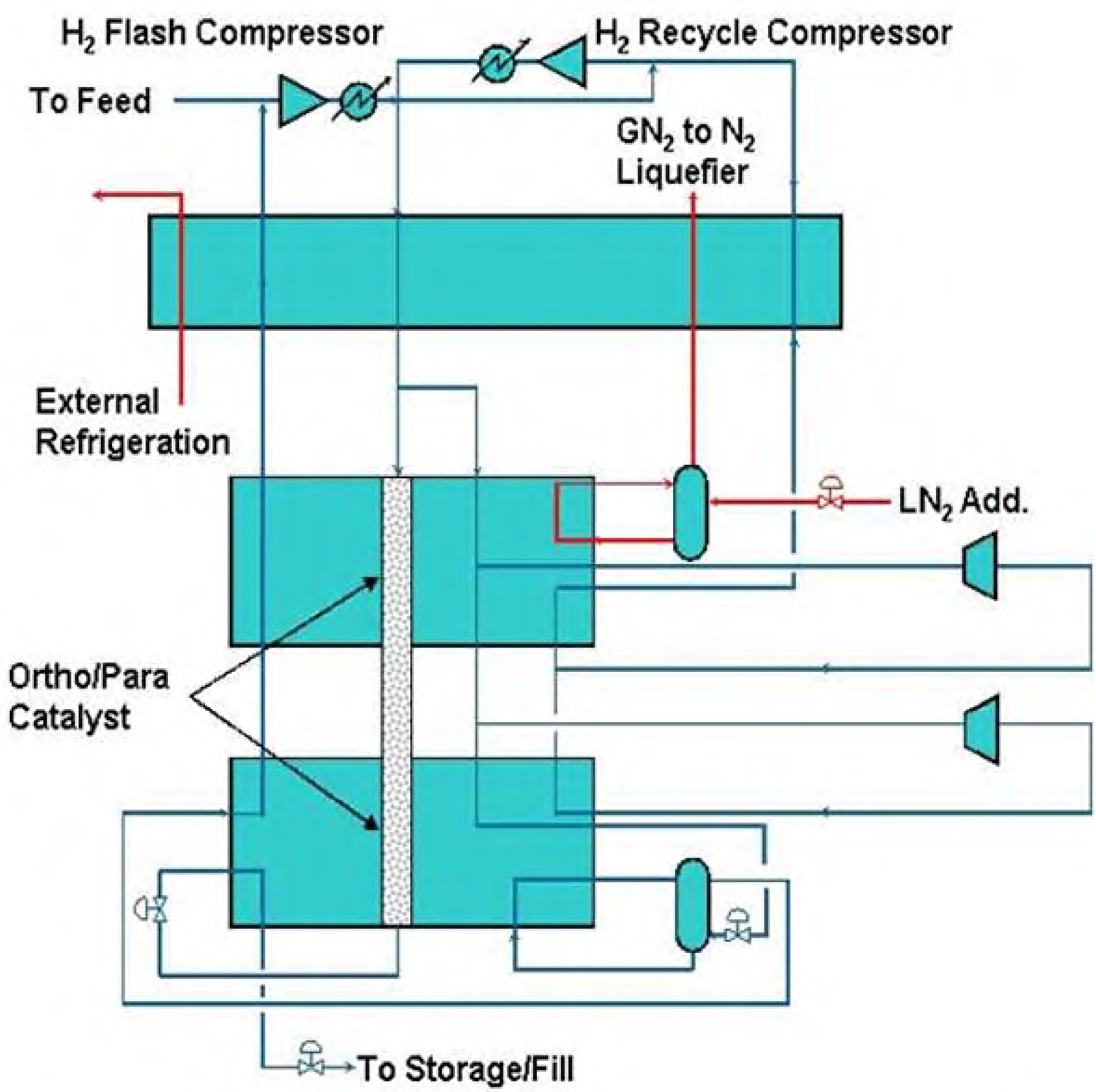
- Train size ranges from 6 to 35 TPD (5,400 to 32,000 kg/day)



Continent/Country	Location	Operated by	Capacity (TPD)	Commissioned in	Still in operation
America					
Canada	Sarnia	Air Products	30	1982	Yes
Canada	Montreal	Air Liquide Canada Inc.	10	1986	Yes
Canada	Becancour	Air Liquide	12	1988	Yes
Canada	Magog, Quebec	BOC	15	1989	Yes
Canada	Montreal	BOC	14	1990	Yes
French Guyane	Kourou	Air Liquide	5	1990	Yes
USA	Painsville	Air Products	3[a]	1957	No
USA	West Palm Beach	Air Products	3.2[a]	1957	No
USA	West Palm Beach	Air Products	27[a]	1959	No
USA	Mississippi	Air Products	32.7[a]	1960	No
USA	Ontario	Praxair	20	1962	Yes
USA	Sacramento	Union Carbide, Linde Div.	54[a]	1964	No
USA	New Orleans	Air Products	34	1977	Yes
USA	New Orleans	Air Products	34	1978	Yes
USA	Niagara Falls	Praxair	18	1981	Yes
USA	Sacramento	Air Products	6	1986	Yes
USA	Niagara Falls	Praxair	18	1989	Yes
USA	Pace	Air Products	30	1994	Yes
USA	McIntosh	Praxair	24	1995	Yes
USA	East Chicago, IN	Praxair	30	1997	Yes
Subtotal			300		
Europe					
France	Lille	Air Liquide	10	1987	Yes
Germany	Ingolstadt	Linde	4.4	1991	Yes
Germany	Leuna	Linde	5	2008	Yes
Netherlands	Rosenburg	Air Products	5	1987	Yes
Subtotal			24.4		
Asia					
China	Beijing	CALT	0.6	1995	Yes
India	Mahendragiri	ISRO	0.3	1992	Yes
India	India	Asiatic Oxygen	1.2	–	Yes
India	Saggonda	Andhra Sugars	1.2	2004	Yes
Japan	Amagasaki	Iwatani	1.2[a]	1978	No
Japan	Tashiro	MHI	0.6[a]	1984	No
Japan	Akita Prefecture	Tashiro	0.7	1985	Yes
Japan	Oita	Pacific Hydrogen	1.4	1986	Yes
Japan	Tane-Ga-Shima	Japan Liquid Hydrogen	1.4	1986	Yes
Japan	Minamitane	Japan Liquid Hydrogen	2.2	1987	Yes
Japan	Kimitsu	Air Products	0.3	2003	Yes
Japan	Osaka	Iwatani (Hydro Edge)	11.3	2006	Yes
Japan	Tokyo	Iwatani, built by Linde	10	2008	Yes
Subtotal			30.6		

Hydrogen Liquefaction Existing Process Flow Diagram

- Existing process is highly integrated with air separation
- Liquid nitrogen typically used as a coolant in the process



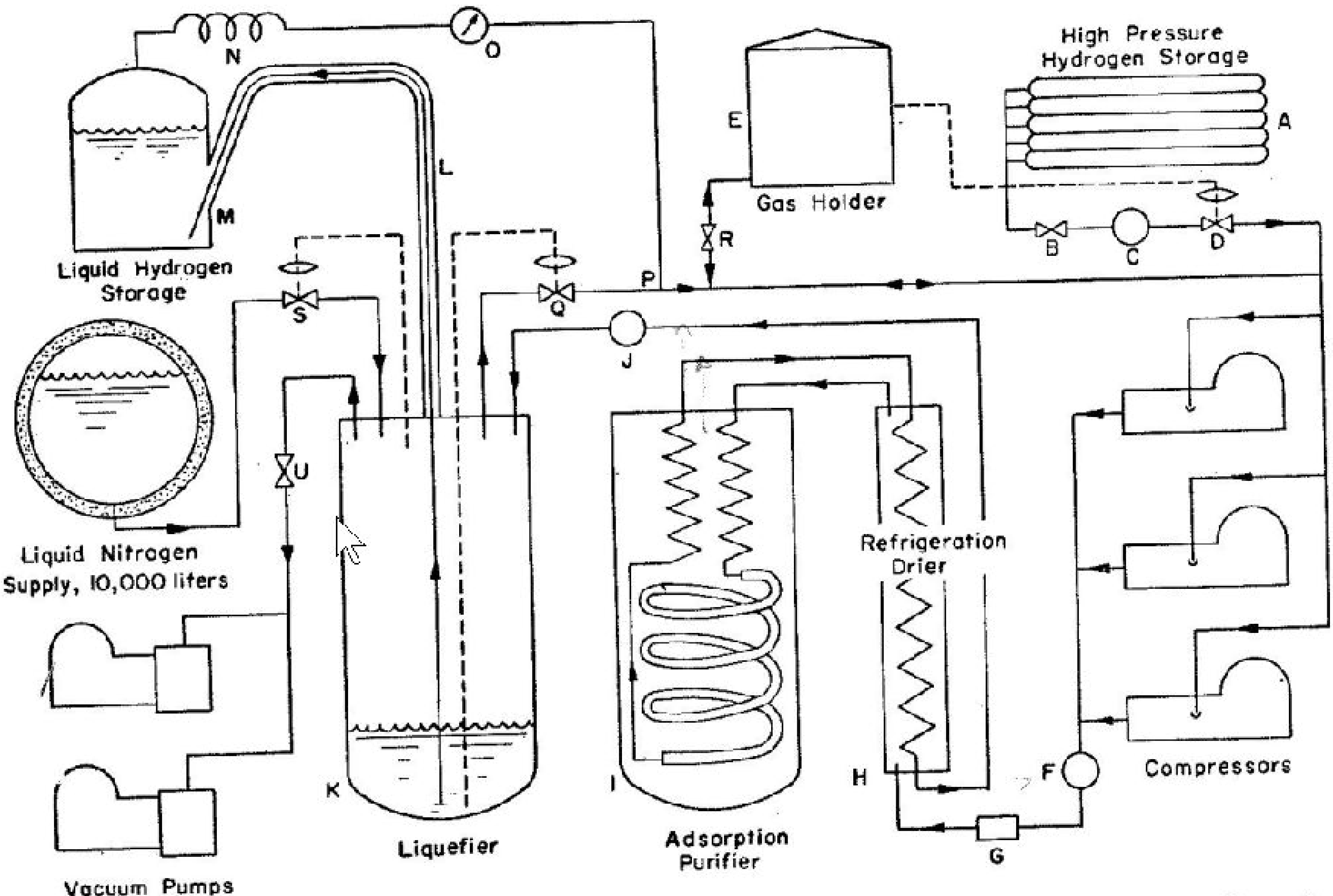
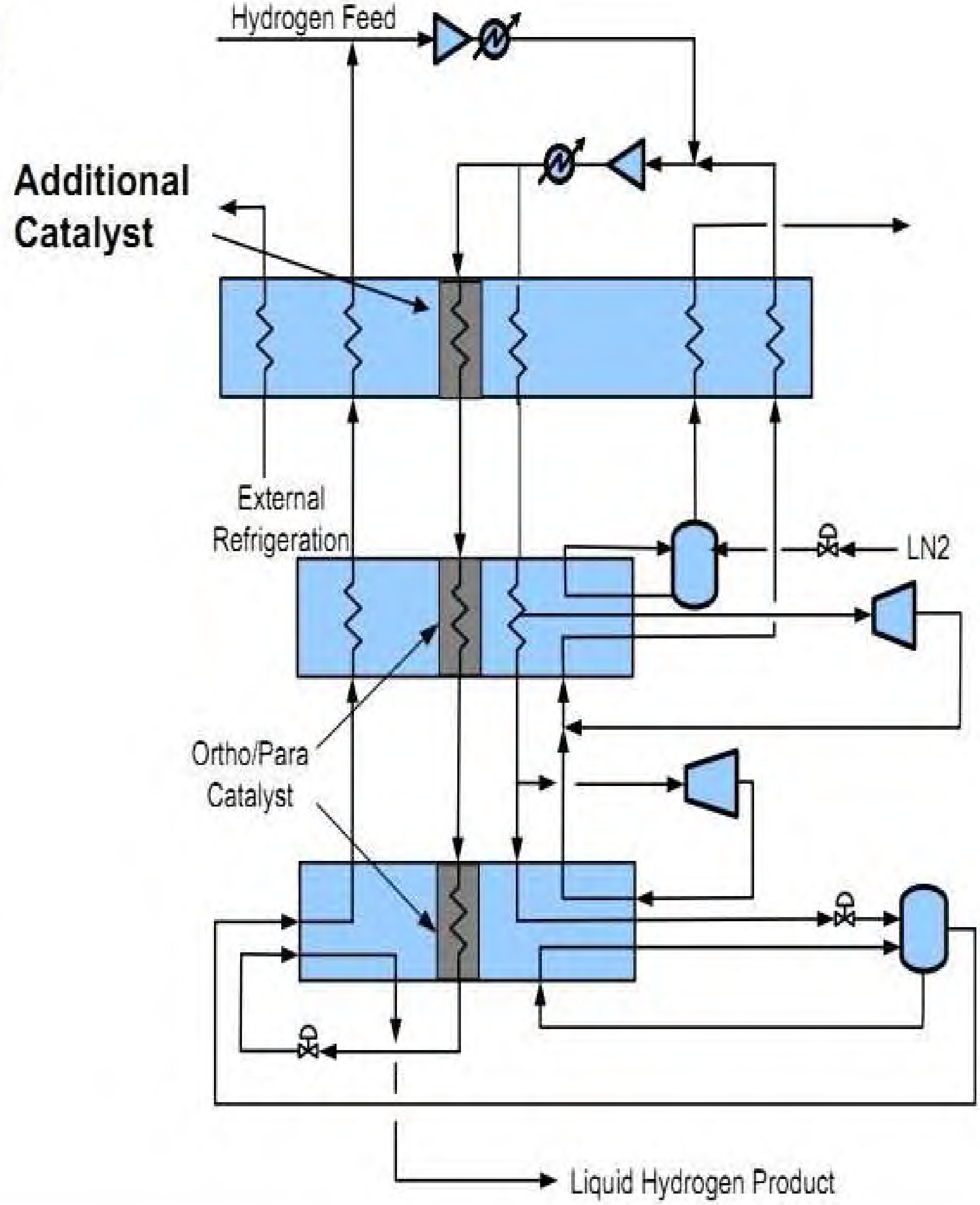


FIGURE 2.22. Flow diagram showing the major components of the hydrogen liquefier of the National Bureau of Standards Cryogenic Engineering Laboratory.

- Cooling load is moved from 2nd heat exchanger to 1st heat exchanger
- External refrigeration increases by 17%
- LN2 requirement decreases by 11%
- Overall power consumption decreases by 2.4%
- Recycle flow is reduced



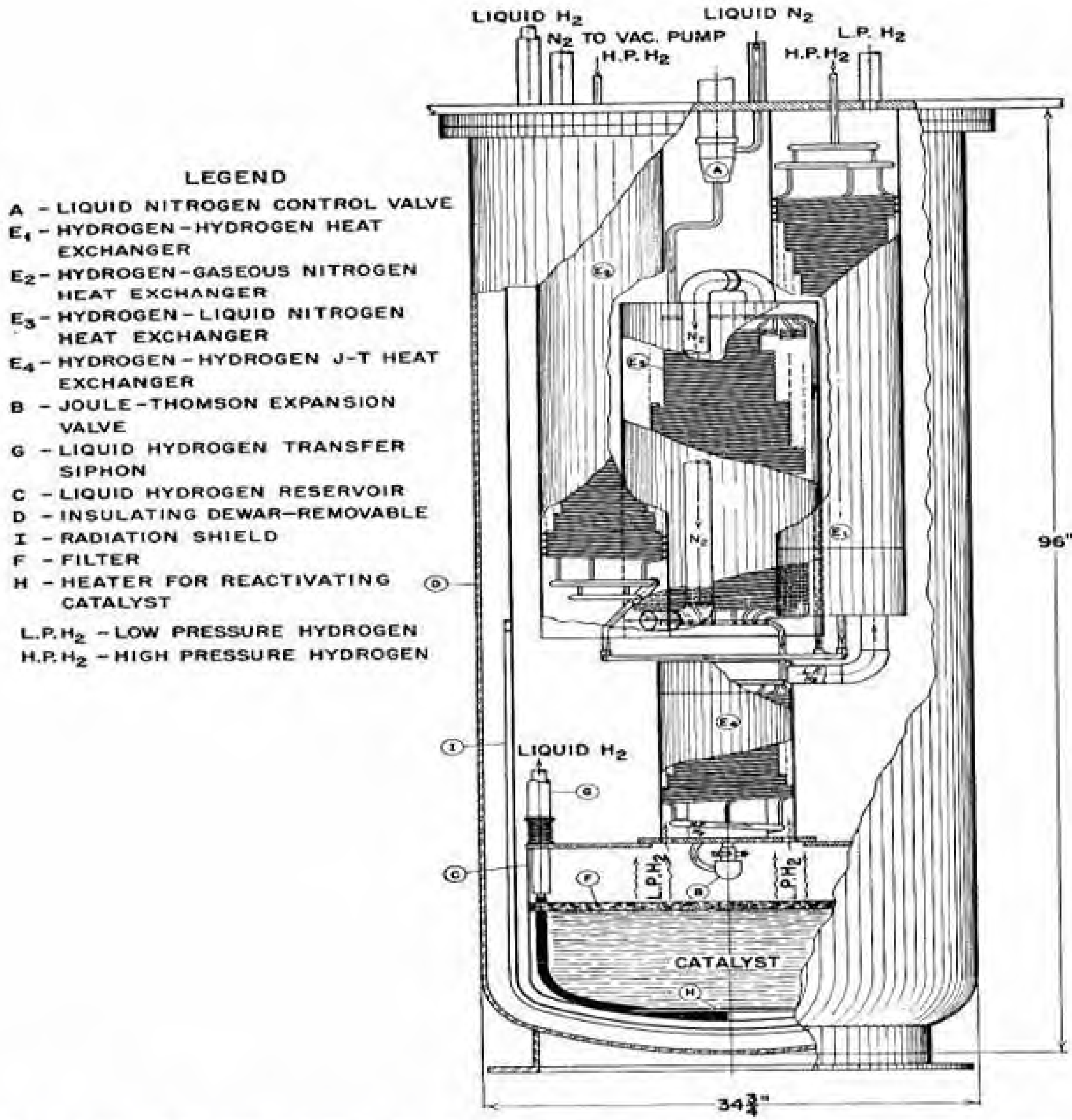
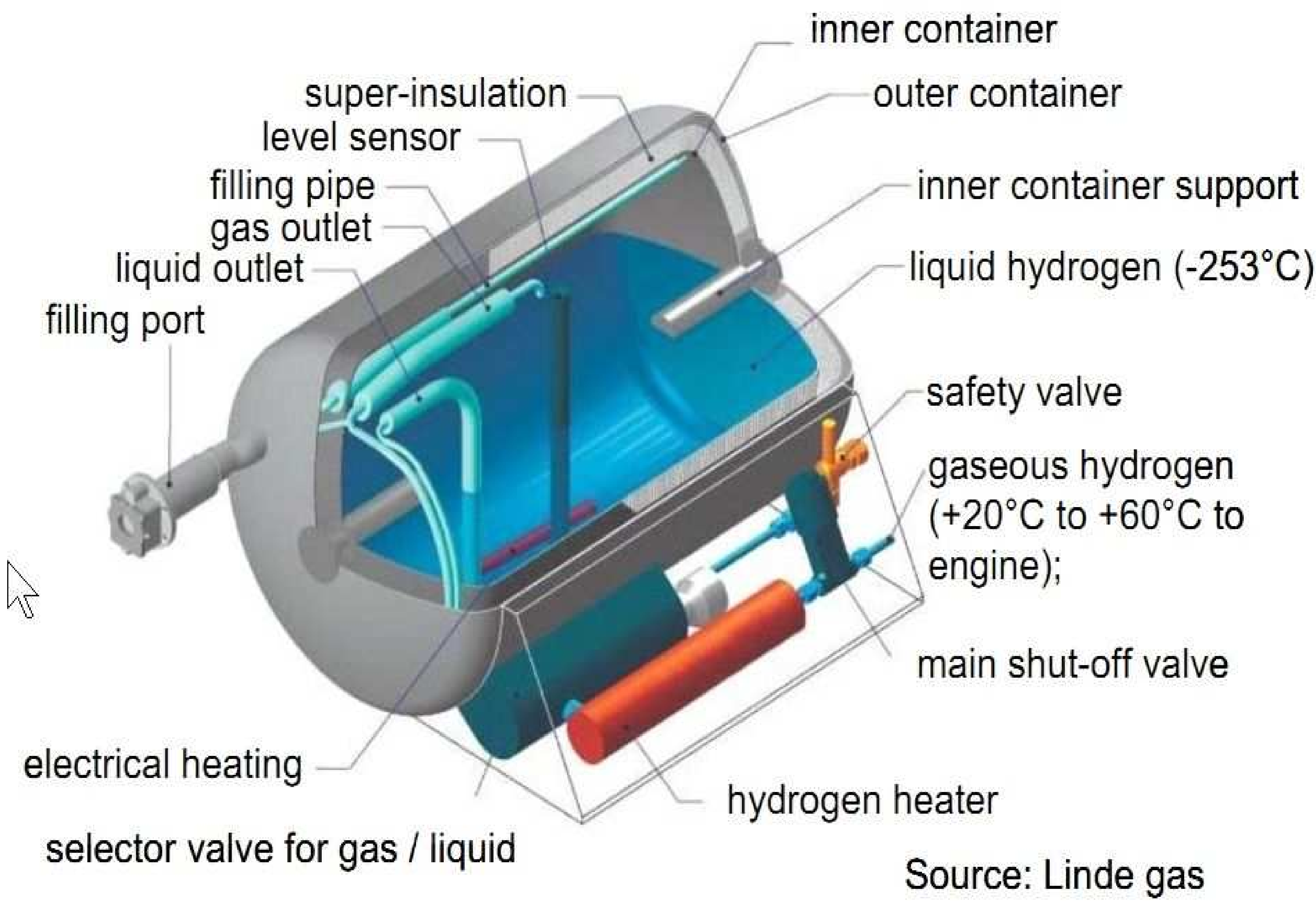


FIGURE 2.23. Cut-away assembly of the hydrogen liquefier proper, showing the arrangement of parts.



Tank system for storing cryogenic liquid hydrogen at -253 °C

Helium

[All values are in metric tons (t) helium content unless otherwise noted]

Last modification: December 1, 2010

Year	Production	Shipments	Imports	Exports	Stocks	Apparent consumption	Unit value ($/t)	Unit value (98$/t)	World production
1985	4,780	9,030	0	2,100	178,000	6,920	7,970	12,100	9,750
1986	4,770	9,310	0	2,070	173,000	7,230	7,970	11,900	10,000
1987	9,240	10,500	0	2,370	172,000	8,130	7,970	11,400	11,600
1988	10,700	12,100	0	3,110	171,000	8,970	7,970	11,000	13,300
1989	11,200	13,500	0	3,740	165,000	9,780	7,970	10,500	14,800
1990	17,800	14,400	0	4,180	162,000	10,200	7,970	9,950	15,600
1991	14,600	14,900	0	4,590	161,000	10,300	7,990	9,560	15,900
1992	15,600	16,000	0	5,200	161,000	10,800	11,700	13,600	16,900
1993	16,800	16,200	0	4,740	162,000	11,400	11,700	13,200	16,900
1994	19,000	16,900	0	4,230	164,000	12,800	11,700	12,900	17,900
1995	17,100	16,300	0	4,690	164,000	11,600	11,700	12,500	18,800
1996	17,400	16,000	0	3,860	166,000	12,200	11,700	12,200	18,800
1997	19,600	18,100	24	4,990	167,000	13,100	11,700	11,900	23,400
1998	19,300	19,000	40	4,710	163,000	14,300	11,700	11,700	22,700
1999	19,300	19,800	0	4,540	166,000	15,200	11,700	11,400	22,900
2000	16,600	21,500	0	6,260	161,000	15,200	10,500	9,940	19,800
2001	14,700	22,300	0	7,280	153,000	15,100	10,650	9,840	17,900
2002	14,800	21,500	0	6,690	147,000	14,800	11,000	9,960	18,500
2003	14,700	20,700	0	7,000	141,000	13,700	11,200	9,920	24,400
2004	14,600	22,000	0	7,600	133,000	14,000	11,500	9,920	26,100
2005	12,900	22,500	0	8,700	124,000	13,800	11,500	9,600	27,100
2006	13,400	23,200	0	10,500	114,000	12,700	12,000	9,700	28,100
2007	13,000	23,300	0	10,900	103,000	12,400	12,400	9,750	28,900
2008	13,500	22,000	0	11,800	86,500	10,200	12,800	9,690	29,500
2009	13,200	20,000	0	12,000	79,100	8,000	12,900	9,800	24,900

World Production and Reserves:

	Production		Reserves[8]
	2011	2012[e]	
United States (extracted from natural gas)	71	75	4,000
United States (from Cliffside Field)	59	60	([9])
Algeria	20	20	1,800
Canada	NA	NA	NA
China	NA	NA	NA
Poland	3	3	30
Qatar	13	15	NA
Russia	6	—	1,700
Other countries	NA	NA	NA
World total (rounded)	172	173	NA

Helium from natural gas

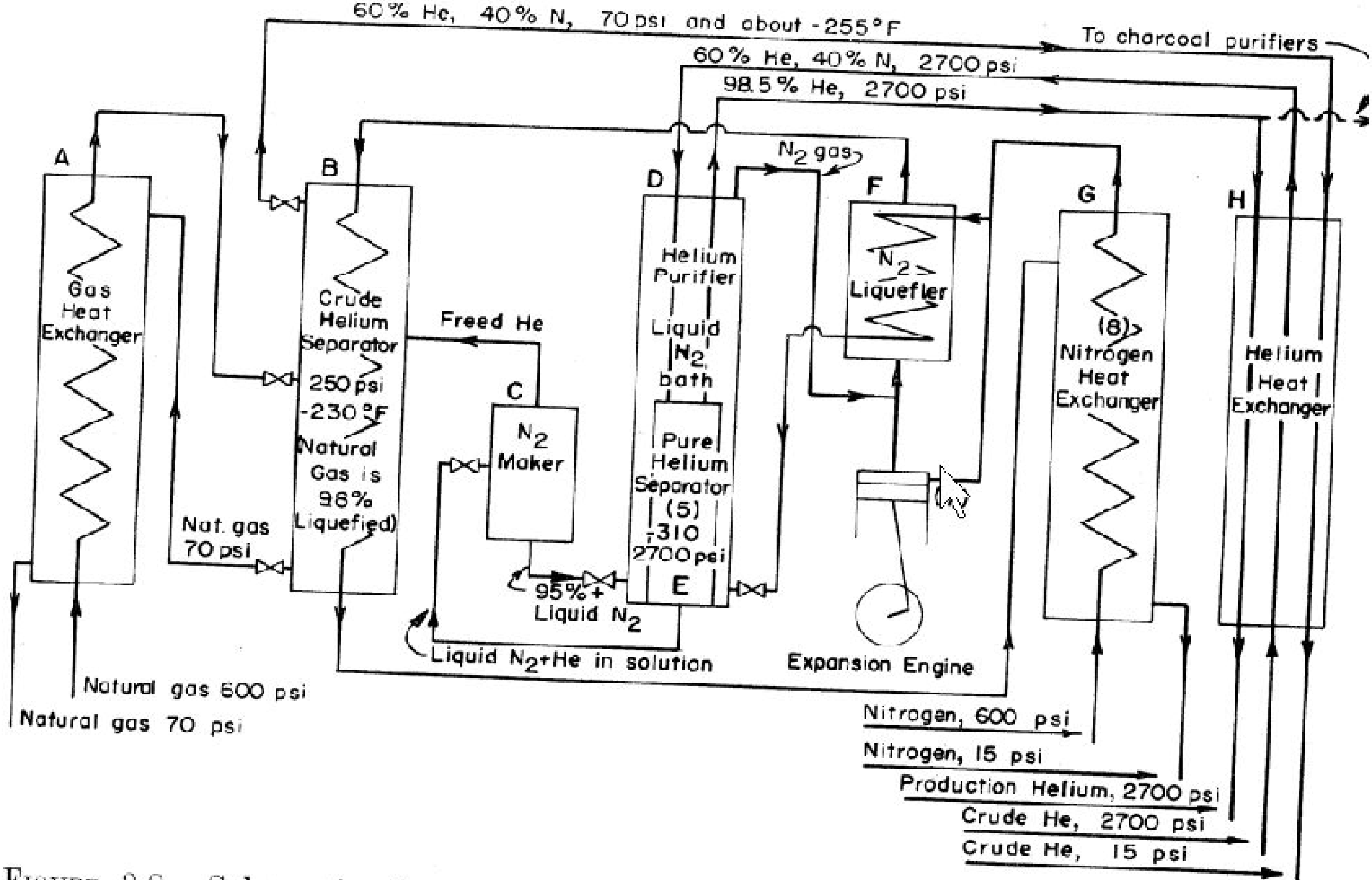


FIGURE 3.8. Schematic diagram of a helium separation plant of the United States Bureau of Mines.

New PSA process

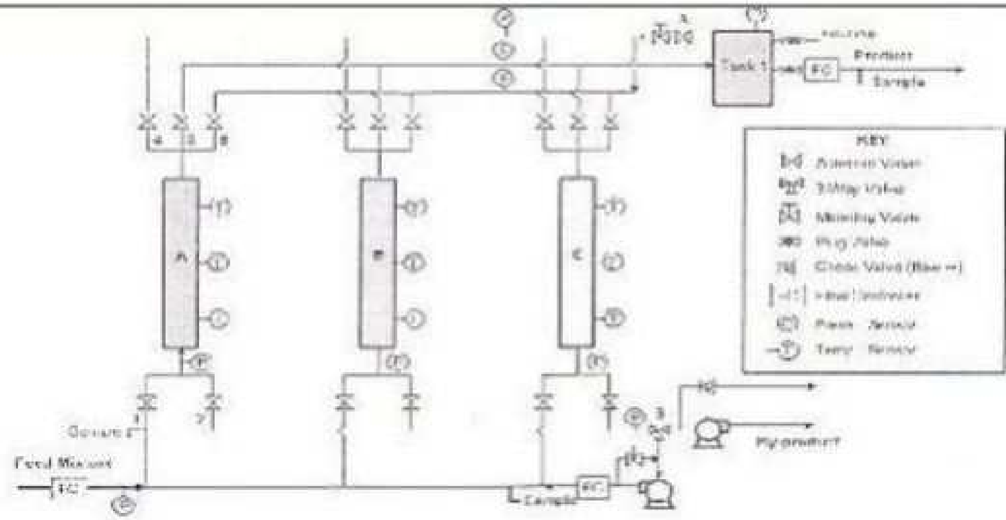


Figure 4. Schematic flowsheet of P&I diagram of each stage.

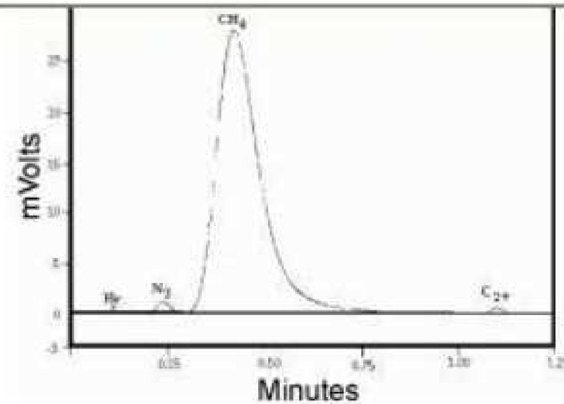


Figure 6. Composition of the stage I product gas as also feed of stage II.

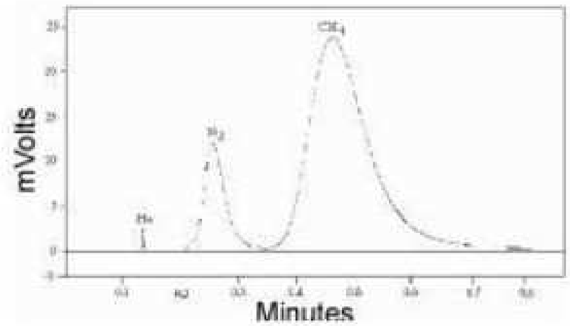
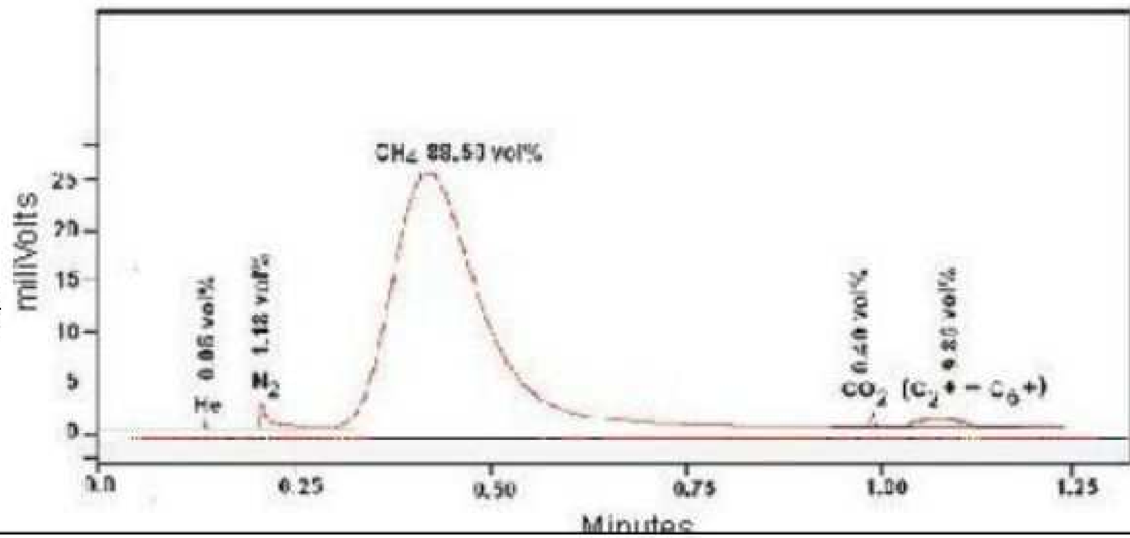


Figure 7. Composition of the stage II product gas as also feed of stage III.



the GCS Kuthalam site. It is observed that the major constituent of the feed stream is methane, while helium content

Helium liquification

Helium liquification

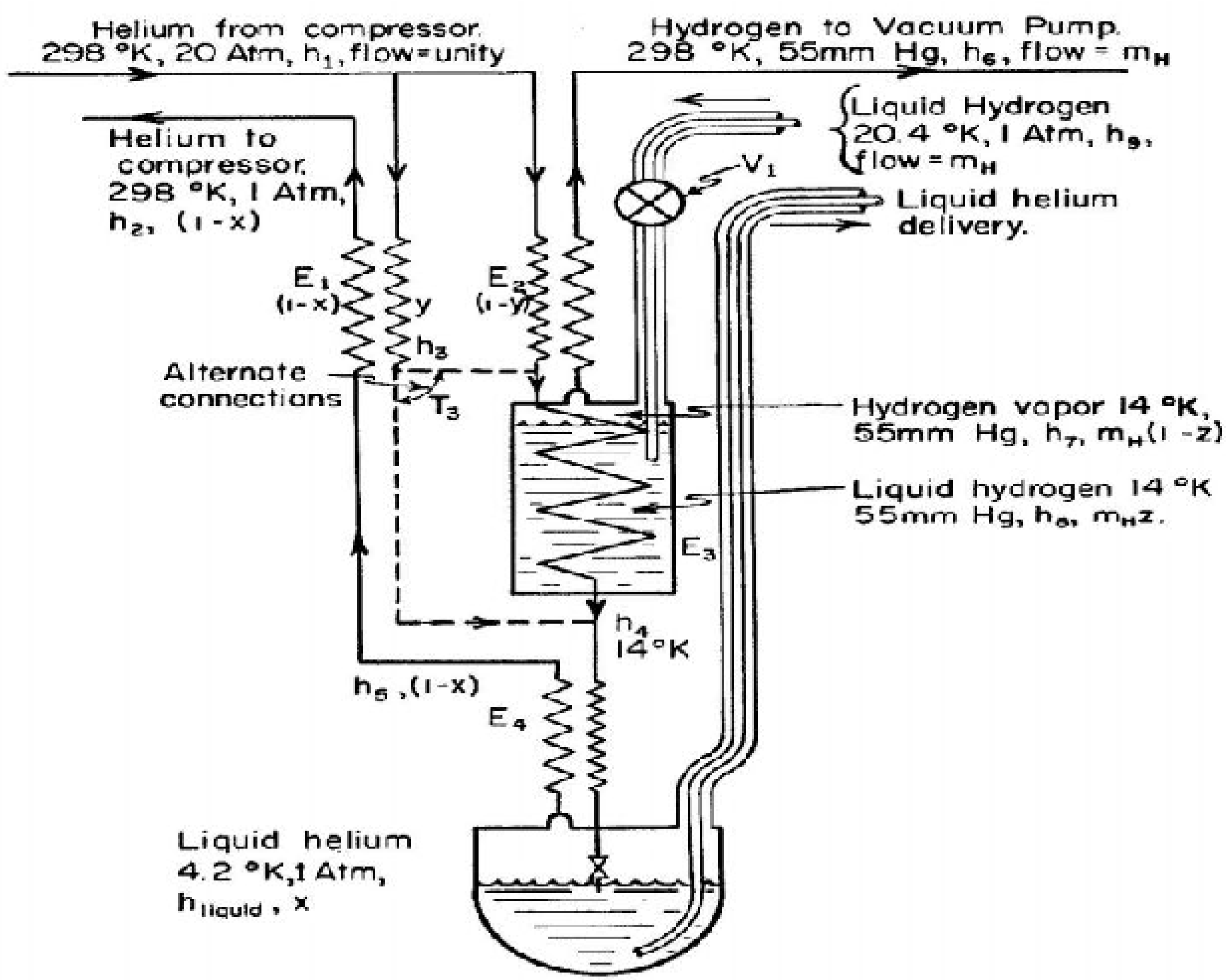
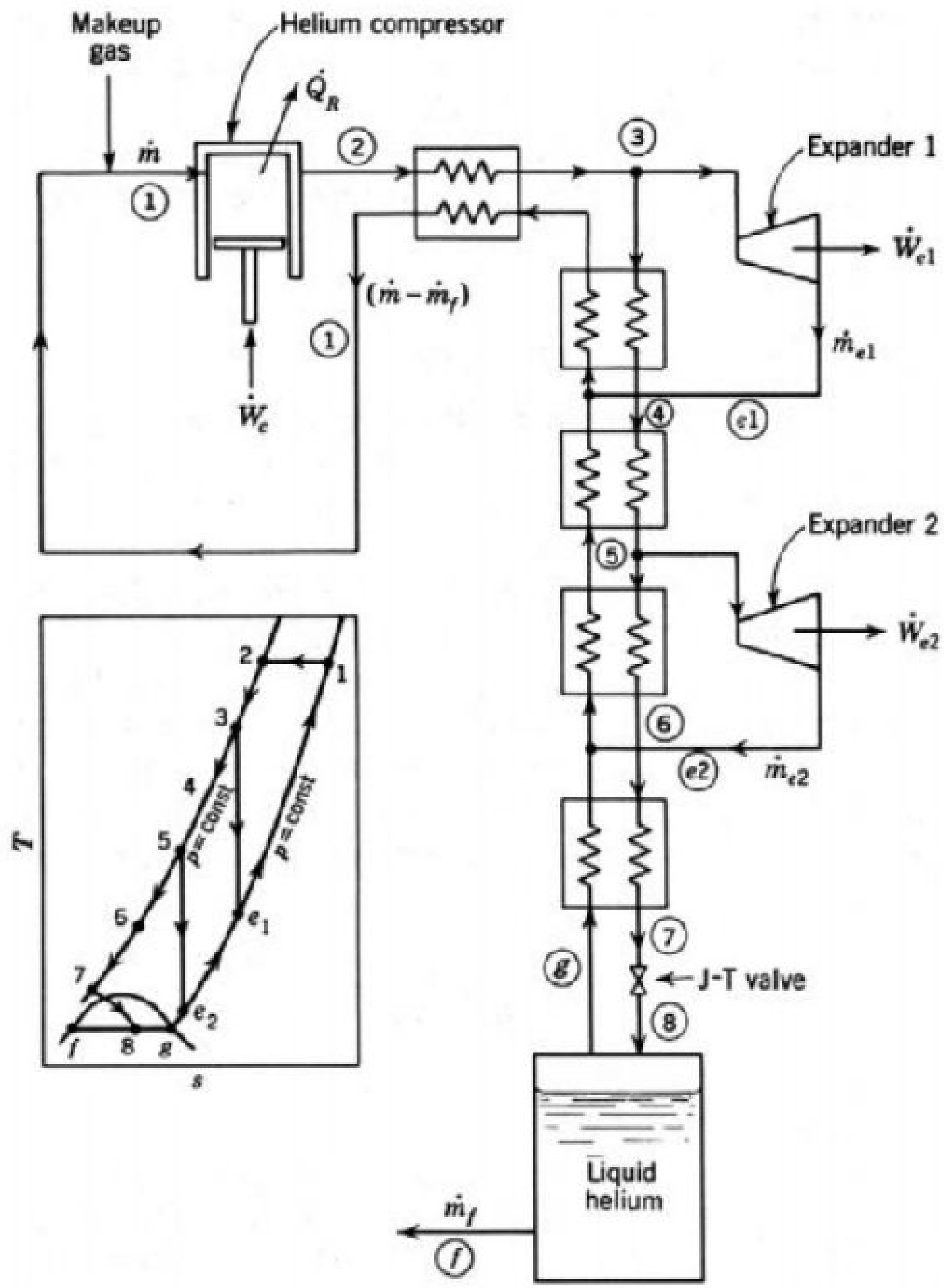


FIGURE 2.28. Joule-Thomson helium-helium liquefier.


Makeup gas
Helium compressor
Expander 1
Expander 2
J-T valve
Liquid helium
T
s
p = const
p = const

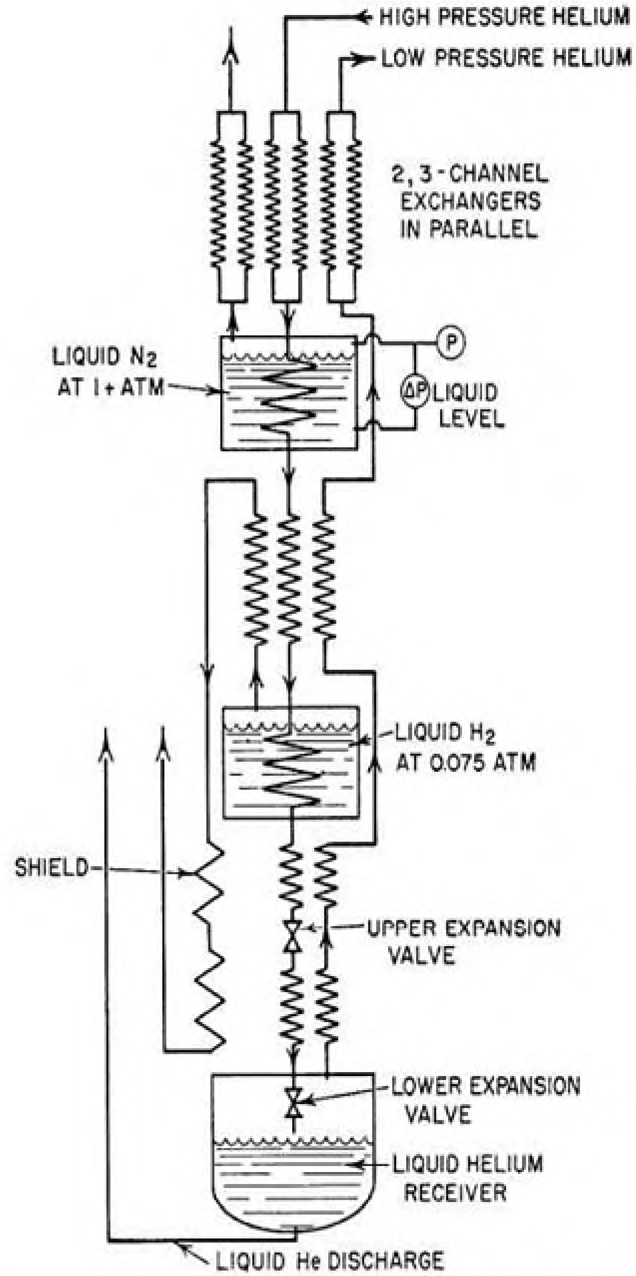


FIGURE 2.30. Flow diagram of a helium liquefier used at National Bureau of Standards Cryogenic Engineering Laboratory.

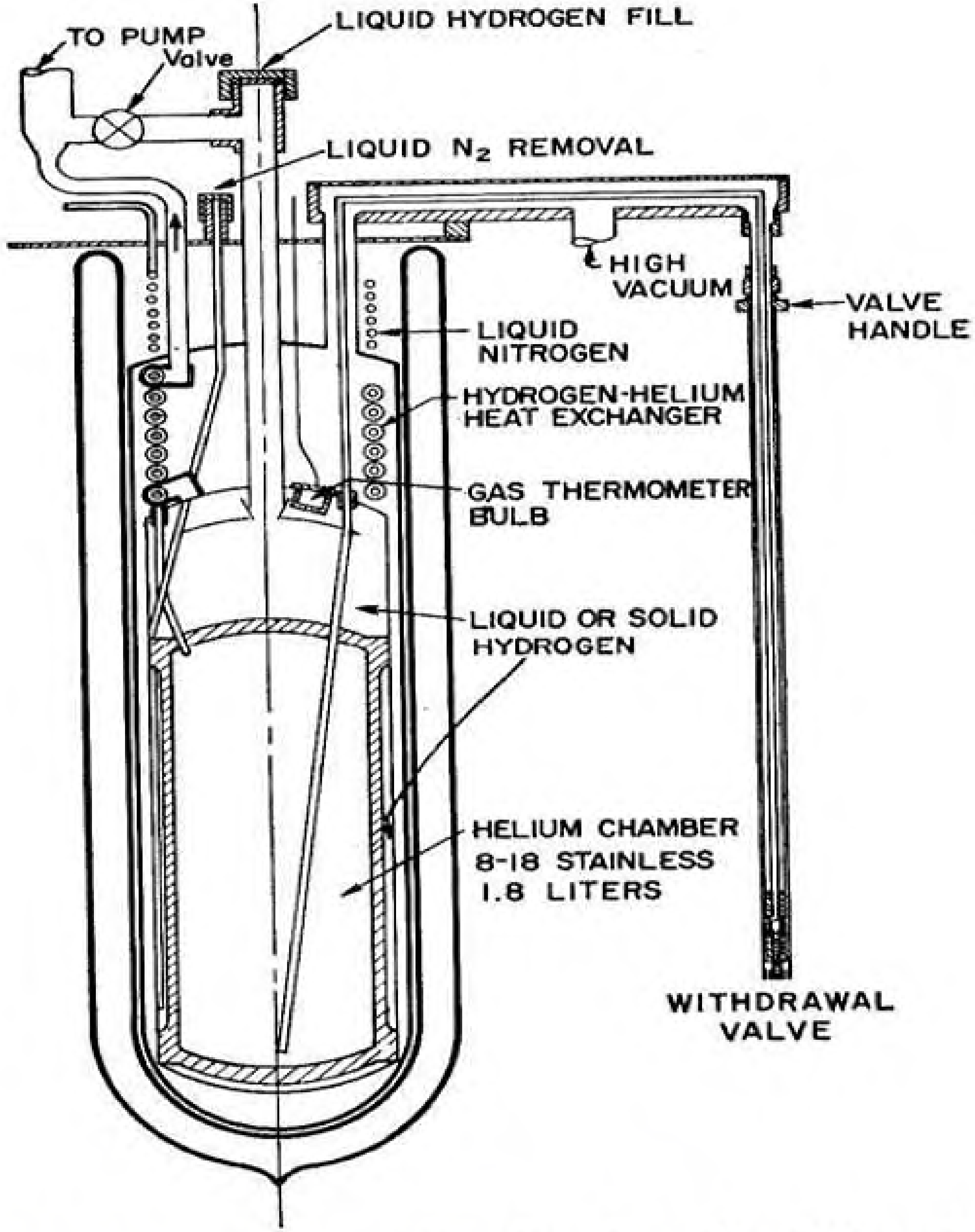


FIGURE 2.33. Simon-type helium liquefier with withdrawal siphon.