# **Refrigeration and Liquefaction**

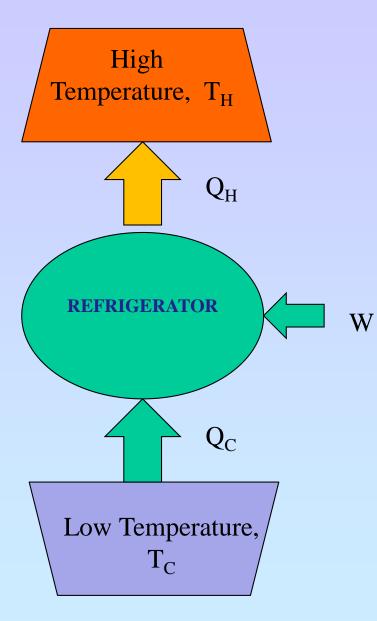
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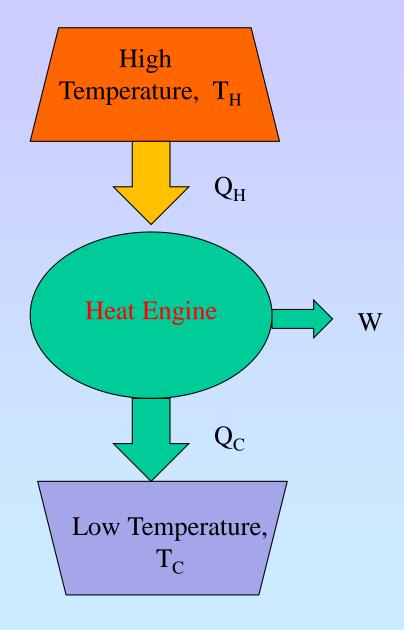


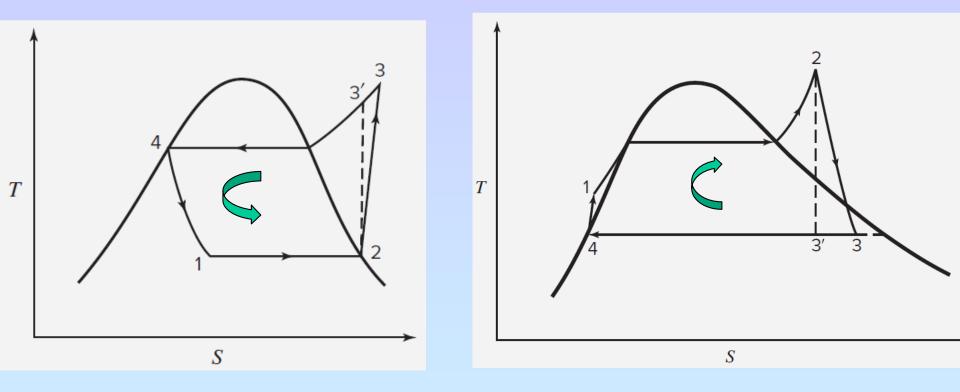
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## Refrigeration and liquefaction

- Refrigeration Cooling of an object and maintenance of its temperature below that of surroundings
- Application
  - Air conditioning of buildings, transportation, and preservation of foods and beverages
  - Manufacture of ice
  - Dehydration of gases
  - Petroleum industry include lubrication-oil purification
  - Low-temperature reactions
  - Separation of volatile hydrocarbons
- Continuous absorption of heat at a low temperature level, usually accomplished by evaporation of liquid in a steady-state flow process.







Heat Engine (e.g. Steam Power Plant)

Refrigerator

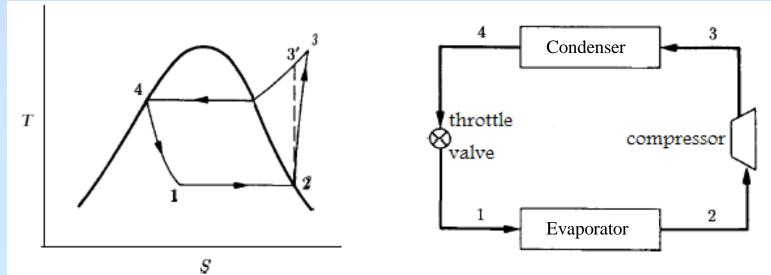
#### The Carnot Refrigerator

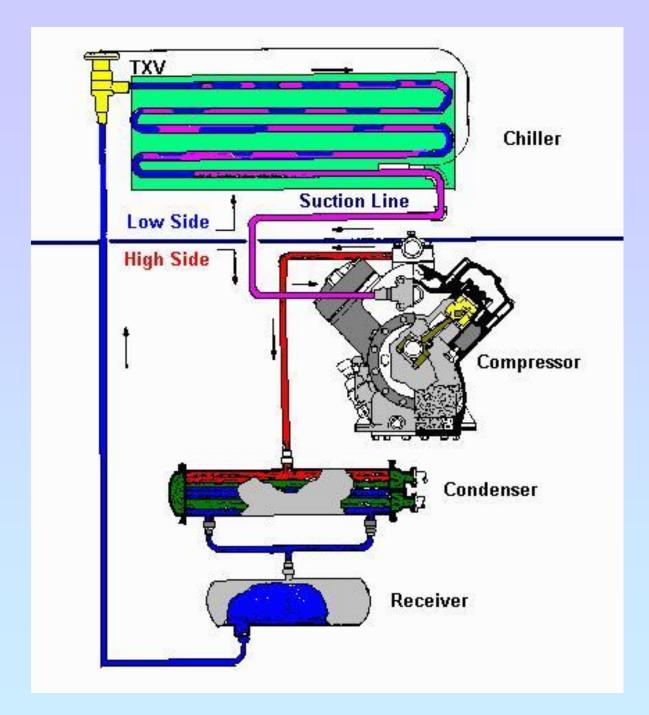
- The ideal refrigerator, like the ideal heat engine, operates on a Carnot cycle, consisting of two isothermal steps in which heat  $|Q_C|$  is absorbed at the lower temperature  $T_C$  and heat  $|Q_H|$  is rejected at the higher temperature  $T_H$  and two adiabatic steps.
- The coefficient of performance:

$\rho = \frac{heat \ absorbed \ at \ the \ lowe}{}$	r temperature $ Q_c $	$-  Q_c $	$\_T_{C}$
net work	-W	$ Q_{H}  -  Q_{C} $	$T_H - T_C$

### The vapor-compression cycle

- 1→2: liquid (absorb heat) evaporating at constant pressure
- $2 \rightarrow 3$ : isentropic compression to a higher pressure
- 3→4: cooled and condensed with rejection of heat at a higher temperature level
- $4 \rightarrow 1$ : expansion throttling process



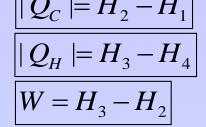


On the basis of a unit mass of fluid

The heat absorbed in the evaporator:  $||Q_C| = H_2 - H_1$ 

The heat rejected in the condenser:

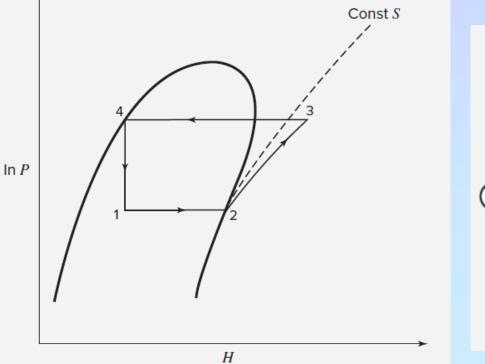
The work of compression:

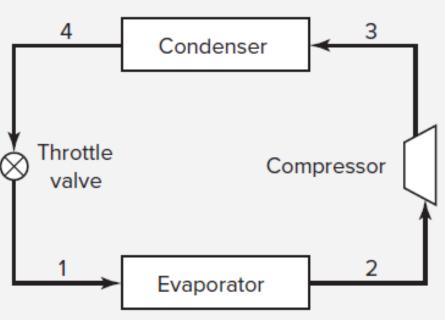


$$\omega = \frac{|Q_{C}|}{W} = \frac{H_{2} - H_{1}}{H_{3} - H_{2}}$$

Define the rate of circulation of refrigerant:

$$\dot{m} = \frac{|\dot{Q}_C|}{H_2 - H_1}$$





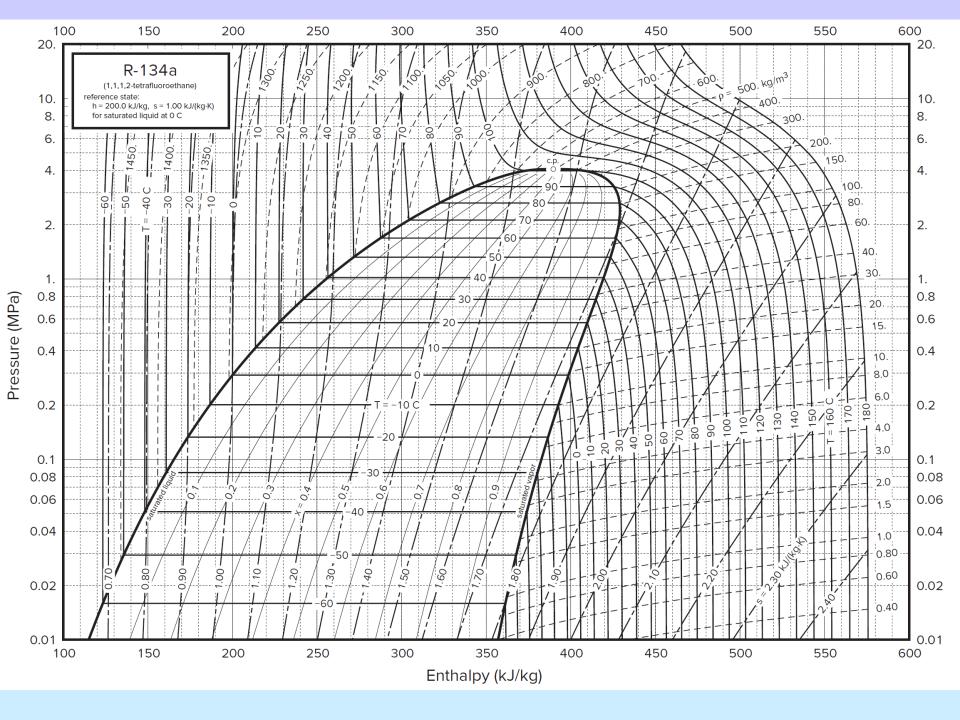


Table 9.1: Properties of Saturated 1,1,1,2-Tetrafluoroethane (R134A) <sup>†</sup>									
		Volume m <sup>3</sup> ·kg <sup>-1</sup>		Enthalpy kJ⋅kg <sup>−1</sup>		Entropy kJ·kg <sup>-1</sup> ·K <sup>-1</sup>			
<i>T</i> (°C)	P (bar)	$V^l$	$V^{\nu}$	$H^l$	$H^{\nu}$	$S^l$	S <sup>v</sup>		
-40	0.512	0.000705	0.361080	148.14	374.00	0.796	1.764		
-35	0.661	0.000713	0.284020	154.44	377.17	0.822	1.758		
-30	0.844	0.000720	0.225940	160.79	380.32	0.849	1.752		
-25	1.064	0.000728	0.181620	167.19	383.45	0.875	1.746		
-20	1.327	0.000736	0.147390	173.64	386.55	0.900	1.741		
-18	1.446	0.000740	0.135920	176.23	387.79	0.910	1.740		
-16	1.573	0.000743	0.125510	178.83	389.02	0.921	1.738		
-14	1.708	0.000746	0.116050	181.44	390.24	0.931	1.736		
-12	1.852	0.000750	0.107440	184.07	391.46	0.941	1.735		
-10	2.006	0.000754	0.099590	186.70	392.66	0.951	1.733		
-8	2.169	0.000757	0.092422	189.34	393.87	0.961	1.732		
-6	2.343	0.000761	0.085867	191.99	395.06	0.971	1.731		
-4	2.527	0.000765	0.079866	194.65	396.25	0.980	1.729		
-2	2.722	0.000768	0.074362	197.32	397.43	0.990	1.728		
0	2.928	0.000772	0.069309	200.00	398.60	1.000	1.727		
2 4	3.146	0.000776	0.064663	202.69	399.77	1.010	1.726		
	3.377	0.000780	0.060385	205.40	400.92	1.020	1.725		
6	3.620	0.000785	0.056443	208.11	402.06	1.029	1.724		
8	3.876	0.000789	0.052804	210.84	403.20	1.039	1.723		
10	4.146	0.000793	0.049442	213.58	404.32	1.049	1.722		
12	4.430	0.000797	0.046332	216.33	405.43	1.058	1.721		
14	4.729	0.000802	0.043451	219.09	406.53	1.068	1.720		
16	5.043	0.000807	0.040780	221.87	407.61	1.077	1.720		
18	5.372	0.000811	0.038301	224.66	408.69	1.087	1.719		
20	5.717	0.000816	0.035997	227.47	409.75	1.096	1.718		
22	6.079	0.000821	0.033854	230.29	410.79	1.106	1.717		
24	6.458	0.000826	0.031858	233.12	411.82	1.115	1.717		
26	6.854	0.000831	0.029998	235.97	412.84	1.125	1.716		
28	7.269	0.000837	0.028263	238.84	413.84	1.134	1.715		
30	7.702	0.000842	0.026642	241.72	414.82	1.144	1.715		
35	8.870	0.000857	0.023033	249.01	417.19	1.167	1.713		
40	10.166	0.000872	0.019966	256.41	419.43	1.191	1.711		
45	11.599	0.000889	0.017344	263.94	421.52	1.214	1.709		
50	13.179	0.000907	0.015089	271.62	423.44	1.238	1.70		
55	14.915	0.000927	0.013140	279.47	425.15	1.261	1.705		
60	16.818	0.000950	0.011444	287.50	426.63	1.285	1.702		
65	18.898	0.000975	0.009960	295.76	427.82	1.309	1.699		
70	21.168	0.001004	0.008653	304.28	428.65	1.333	1.696		
75	23.641	0.001037	0.007491	313.13	429.03	1.358	1.691		
80	26.332	0.001077	0.006448	322.39	428.81	1.384	1.685		

A refrigerated space is maintained at -20°C and cooling water is available at 21°C. Refrigeration capacity is 120.000 kJ/hr. The evaporator and condenser are of sufficient size that a 5°C minimum-temperature difference for heat transfer can be realized in each. The refrigerant is 1,1,1,2-tetrafluoreothane (HFC – 134a), for which data are given in Table 9.1 and Fig F.2 (App. F). (1) what is the value of  $\omega$  for a Carnot refrigerator? (2) Calculate  $\omega$  and  $\dot{\mathbf{m}}$  for the vapor-compression cycle of Fig 9.1 if the compressor efficiency is 0.80.

(1) Temperature difference =  $5^{\circ}$ C

The evaporator temperature is :

The condenser temperature is :

$$T_{\rm C} = -20^{\circ}{\rm C} - 5^{\circ}{\rm C} = -25^{\circ}{\rm C} = 248.15 \text{ K}$$
  
 $T_{\rm H} = 21^{\circ}{\rm C} + 5^{\circ}{\rm C} = 26^{\circ}{\rm C} =$ 

For a Carnot refrigerator:

$$\omega = \frac{T_c}{T_H - T_c} = \frac{248.15}{(299.15) - (248.15)} = 4.87$$

$$H_2 = 383.45 \frac{kJ}{kg} \qquad S_2 = 1.746 \frac{kJ}{kg.K}$$

At  $26^{\circ}$ C, HFC – 134a condenses at 6.854 bar

(2) At -25°C, HFC – 134a vaporizes at 1.064 bar:

$$H_4 = 235.97 \ \frac{kJ}{kg} = H_1$$

Compression step is reversible and adiabatic (isentropic) from 2 to 3':

$$S'_{3} = S_{2} = 1.746 \frac{kJ}{kg.K} \xrightarrow{\text{at 6.854 bar}} H'_{3} = 421.97 \frac{kJ}{kg}$$

$$(\Delta H)_{s} = H'_{3} - H_{2} = 38.52 \frac{kJ}{kg} \xrightarrow{\text{black}} H_{3} - H_{2} = (\Delta H)_{s} / \eta = 48.15 \frac{kJ}{kg}$$

$$\omega = \frac{H_{2} - H_{4}}{H_{3} - H_{2}} = 3.06$$

$$\dot{m} = \frac{|\dot{Q}_{c}|}{H_{2} - H_{1}} = \frac{120000}{383.45 - 235.97} = 814 \frac{kg}{hr}$$

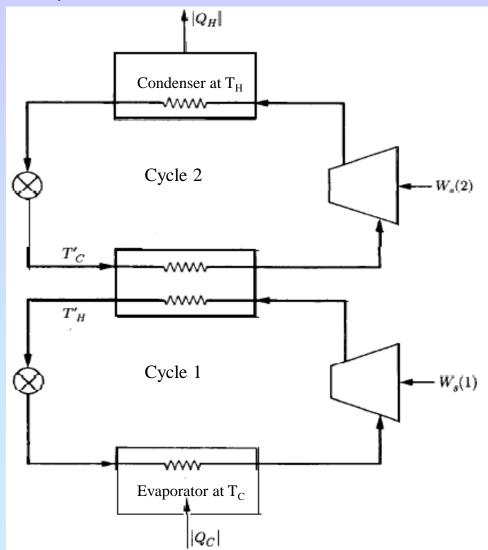
### The choice of refrigerant

- Dependence?
  - The efficiency of a Carnot heat engine is independent of the working medium of the engine.
  - The coefficient of performance of a Carnot refrigerator is independent of the refrigerant.
  - Vapor-compression cycle cause the coefficient of performance to dependent to some extent on the refrigerant.
- Other factors:
  - toxicity, flammability, cost, corrosion properties, vapor pressure in relation to temperature, etc.

- Two requirement:
  - The vapor pressure of the refrigerant at the evaporator temperature should be greater than atmospheric pressure to avoid air leaking.
  - The vapor pressure at the condenser temperature should not be unduly high, because of the initial cost and operating expense of high-pressure equipment.
- Refrigerants
  - Ammonia, methyl chloride, carbon dioxide, propane and other hydrocarbons
  - Halogenated hydrocarbons
    - common in 1930s (e.g.  $CCl_3F$ ,  $CCl_2F_2$ ) and now mostly end
    - stable molecules causing severe ozone depletion
    - replacements are certain hydrochlorofluorocarbons, less than fully halogenated hydrocarbons, and hydrofluorocarbons which contains no chlorine (e.g., CHCl<sub>2</sub>CF<sub>3</sub>, CF<sub>3</sub>CH<sub>2</sub>F).

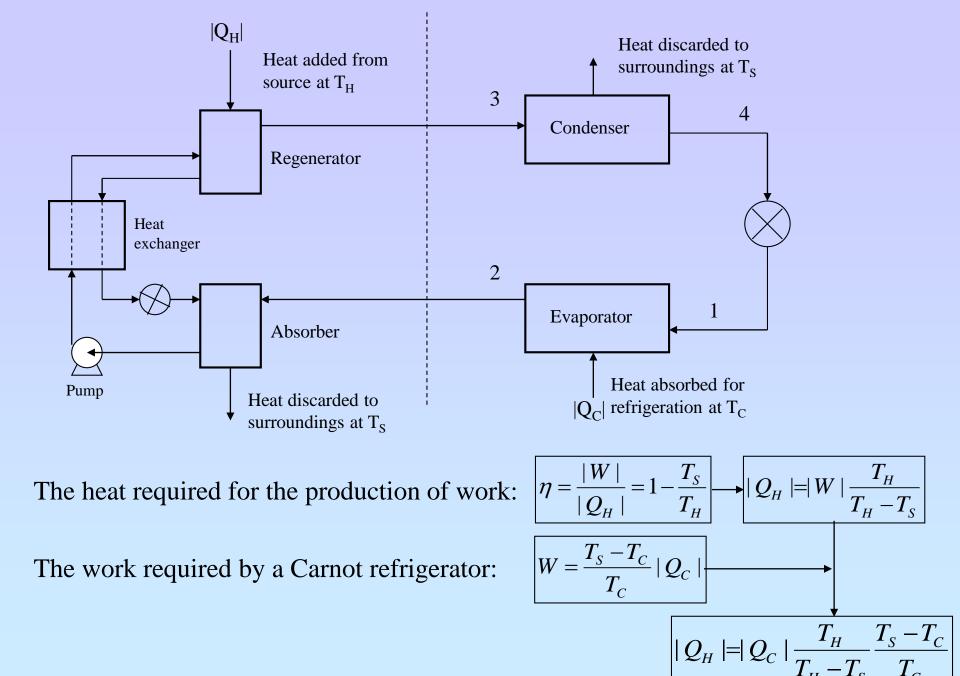
Two-state cascade: (with  $T_H$  fixed by the temperature of the surroundings, a lower limit is placed on the temperature level of refrigeration).

The two cycles operate so that the heat absorbed in the interchanger by the refrigerant of the higher-temperature cycle 2 serves to condense the refrigerant in the lower temperature cycle 1.



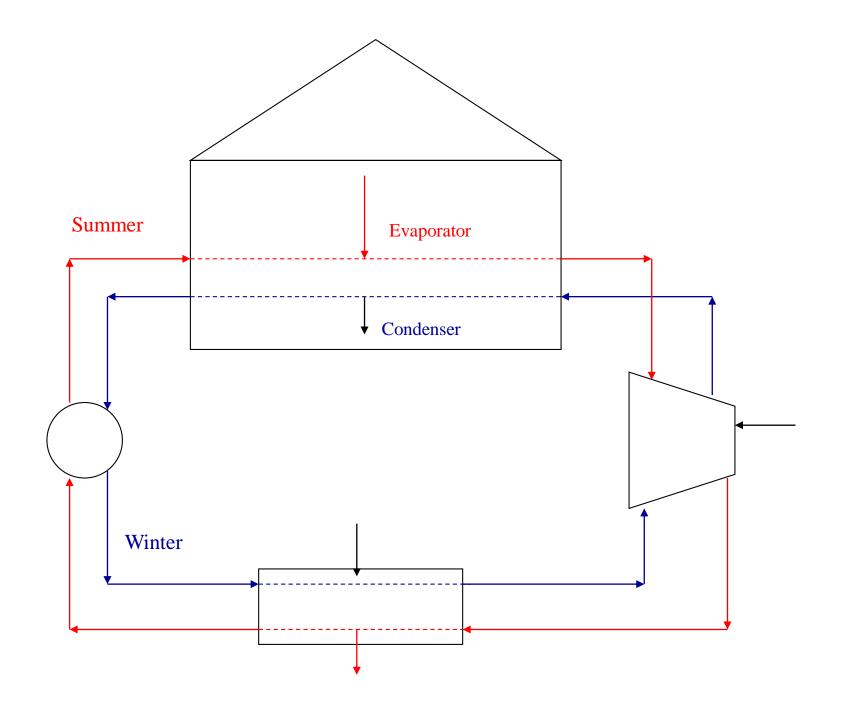
### Absorption refrigeration

- Absorption refrigeration: the direct use of heat as the energy source for refrigeration (not from an electric motor).
  - The essential difference between a vapor-compression and an absorption refrigerator is in the different means employed for compression.
  - The most commonly used absorption-refrigeration system operates with water as the refrigerant and a lithium bromide solution as the absorbent.
  - Low-pressure steam is the usual source of heat for the regenerator.



### The heat pump

- for heating houses in winter:
  - Refrigerant evaporates in coils placed underground or in the outside air; vapor compression is followed by condensation, heat being transferred to air or water, which is used to heat the building.
- and cooling them in summer:
  - The flow of refrigerant is reversed, and heat is absorbed from the building and rejected through underground coils or to the outside air.



A house has a winter heating requirement of 30 kJ/s and a summer cooling requirement of 60 kJ/s. Consider a heat-pump installation to maintain the house temperature at 20°C in winter and 25°C in summer. This requires circulation of the refrigerant through interior exchanger coils at 30°C in winter and 5°C in summer. Underground coils provide the heat source in winter and the heat sink in summer. For a year-round ground temperature of 15°C, the heat-transfer characteristics of the coils necessitate refrigerant temperatures of 10°C in winter and 25°C in summer. What are the minimum power requirements for winter heating and summer cooling?

The minimum power requirements are provided by a Carnot heat pump:

For winter heating, the heat absorbed in the ground coils:

$$Q_C \models Q_H \mid \frac{T_C}{T_H} = 30 \left(\frac{10 + 273.15}{30 + 273.15}\right) = 28.02 \frac{kJ}{s}$$

The power requirement:  $W = |Q_H| - |Q_C| = 30 - 28.02 = 1.98 \frac{kJ}{s}$ 

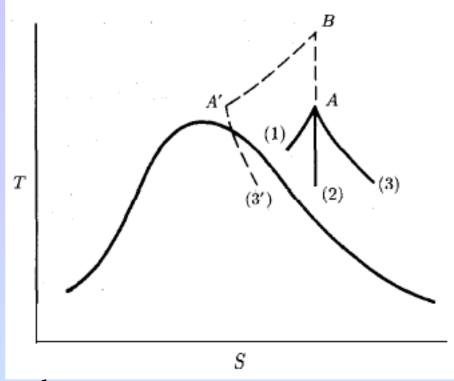
For summer cooling, the house coils are at the lower temperature  $T_C$ :

The power requirement:

$$\frac{F}{W} = |Q_C| \frac{T_H - T_C}{T_C} = 60 \frac{(25 + 273.15) - (5 + 273.15)}{5 + 273.15} = 4.13 \frac{kJ}{s}$$

### Liquefaction processes

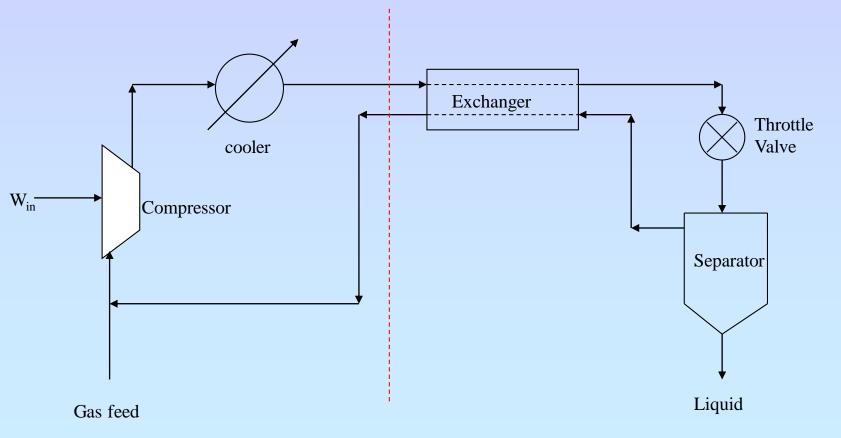
- Common use for:
  - Liquid propane as a domestic foil
  - Liquid oxygen in rocket
  - Liquid natural gas for ocean transport
  - Liquid nitrogen for low temperature refrigeration
  - Gas mixture are liquefied for separation
- Cooled to a temperature in the two-phase region:
  - By heat exchanger at constant pressure
  - By an expansion process from which work is obtained
  - By a throttling process



- By heat exchanger at constant pressure path 1
- By an (isentropic) expansion process path 2
- By a throttling process the initial state must be at a high enough pressure and low enough temperature prior to throttling path 3':
  - The change of state from A to A': compression of the gas to B, followed by constant-pressure cooling
  - Then, isentropic expansion 3' results in the formation of liquid

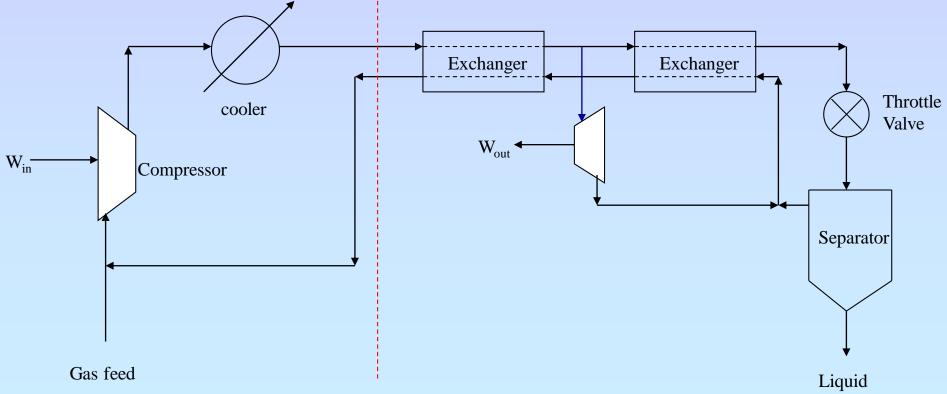
#### The Linde liquefaction process

- Depends solely on throttling expansion:
  - Compression cooling to ambient temperature (even further by refrigeration) – throttling and liquefaction.



#### The Claude liquefaction process

- Replace the throttle valve by an expander:
  - Gas expander saturated or slightly superheated vapor cooled and throttled to produce liquefaction (as in the Linde process) unliquefied portion mixes with the expander exhaust and returns for recycle.



Natural gas, assumed here to be pure methane, is liquefied in a Claude process. Compression is to 60 bar and precooling is to 300 K. The expander and throttle exhaust to a pressure of 1 bar. Recycle methane at this pressure leaves the exchanger system at 295 K. Assume no heat leaks into the system from the surroundings, an expander efficiency of 75%, and an expander exhaust of saturated vapor. For a draw-off to the expander of 25% of the methane entering the exchanger system, what fraction of the methane is liquefied, and what is the temperature of the high-pressure steam entering the throttle valve?

For superheated methane:  $\begin{aligned} H_4 &= 1140.0 \frac{kJ}{kg} \quad (at \ 300 \ K \ and \ 60 \ bar) \\ H_{15} &= 1188.9 \frac{kJ}{kg} \quad (at \ 295 \ K \ and \ 1 \ bar) \end{aligned}$ For saturated liquid:  $\begin{aligned} H_9 &= 285.4 \frac{kJ}{kg} \quad (T^{sat} = 111.5 \ K \ and \ 1 \ bar) \\ For saturated vapor: \end{aligned}$   $\begin{aligned} H_{12} &= 796.9 \frac{kJ}{kg}, \quad S_{12} &= 9.521 \frac{kJ}{kg \cdot K} (T^{sat} = 111.5 \ K \ and \ 1 \ bar) \end{aligned}$ 

An energy balance on the right of the dashed vertical line:  $\dot{m}_9 H_9 + \dot{m}_{15} H_{15} - \dot{m}_4 H_4 = \dot{W}_{out}$ The expander operates adiabatically: A mass balance:  $\dot{W}_{out} = \dot{m}_{12}(H_{12} - H_5)$   $\dot{m}_{15} = \dot{m}_4 - \dot{m}_9$   $z = \dot{m}_{12}/\dot{m}_4$   $z = \dot{m}_{12}/\dot{m}_4$  $z = \dot{m}_{12}/\dot{m}_4$ 

The equation defining expander efficiency:  $\Delta H = H_{12} - H_5 = \eta (\Delta H)_S = \eta (H'_{12} - H_5)$ 

Guess 
$$T_5 \rightarrow H_5$$
,  $S_5 \rightarrow isentropic expansion \rightarrow H'_{12} \rightarrow H_{12} \rightarrow check if satisfied?
$$T_5 = 253.6 \ K, \ H_5 = 1009.8 \frac{kJ}{kg} \ (at \ 60 \ bar)$$

$$z = \frac{x(H_{12} - H_5) + H_4 - H_{15}}{H_9 - H_{15}} = \frac{0.25(796.9 - 1009.8) + 1140.0 - 1188.9}{285.4 - 1188.9} = 0.113$$$ 

11.3 % of the methane entering the exchanger system is liquefied!

An energy balance on the exchanger I: 
$$\dot{m}_4(H_5 - H_4) + \dot{m}_{15}(H_{15} - H_{14}) = 0$$
  
A mass balance:  $\dot{m}_{15} = \dot{m}_4 - \dot{m}_9$   $z = \dot{m}_9 / \dot{m}_4$   
 $H_{14} = \frac{H_5 - H_4}{1 - z} + H_{15} = \frac{1009.8 - 1140.0}{1 - 0.113} + 1188.9 = 1042.1 \frac{kJ}{kg}$   $T_{14} = 227.2 \text{ K}$  (at 60 bar)  
An energy balance on the exchanger II:  $\dot{m}_7(H_7 - H_5) + \dot{m}_{14}(H_{14} - H_{12}) = 0$   
A mass balance:  $\dot{m}_7 = \dot{m}_4 - \dot{m}_{12}$   $\dot{m}_{14} = \dot{m}_4 - \dot{m}_9$   
 $H_7 = H_5 - \frac{1 - z}{1 - x} (H_{14} - H_{12}) = 719.8 \frac{kJ}{kg}$   $T_7 = 197.6 \text{ K}$  (at 60 bar)

 $x \uparrow \quad T_7 \downarrow$ 

Eventually approaching the saturation temperature in the separator and requiring an exchanger of infinite area! (i.e., cost increases)

For the Linde system, 
$$x = 0$$
:  $z = \frac{x(H_{12} - H_5) + H_4 - H_{15}}{H_9 - H_{15}} \longrightarrow z = 0.0541$ 

5.41 % of the methane entering the throttle valve emerges as liquid!

$$\left| H_{7} = H_{4} - (1 - z) \left( H_{15} - H_{10} \right) = 769.2 \frac{kJ}{kg} \right| T_{7} = 206.6 \ K \quad (at \ 60 \ bar)$$