

CHAPTER

**5**

**THERMODYNAMICS OF  
PROCESSES**

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# Carnot Cycle

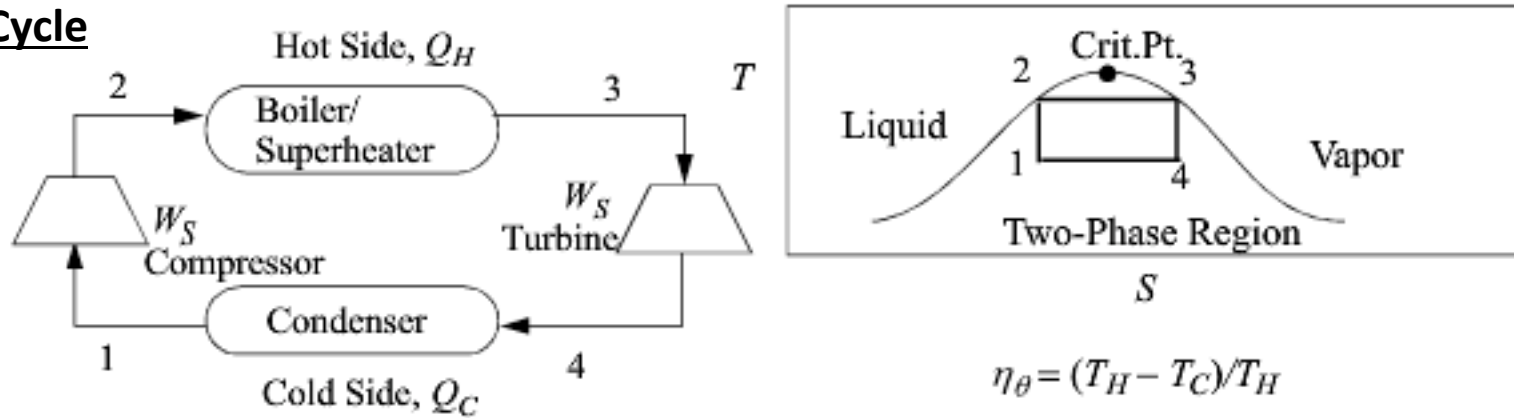
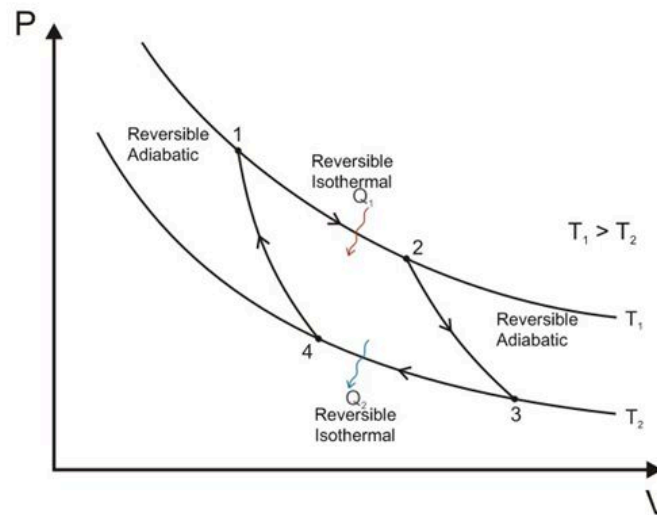


Figure 5.1 Illustration of a Carnot cycle based on steam in T-S coordinates.

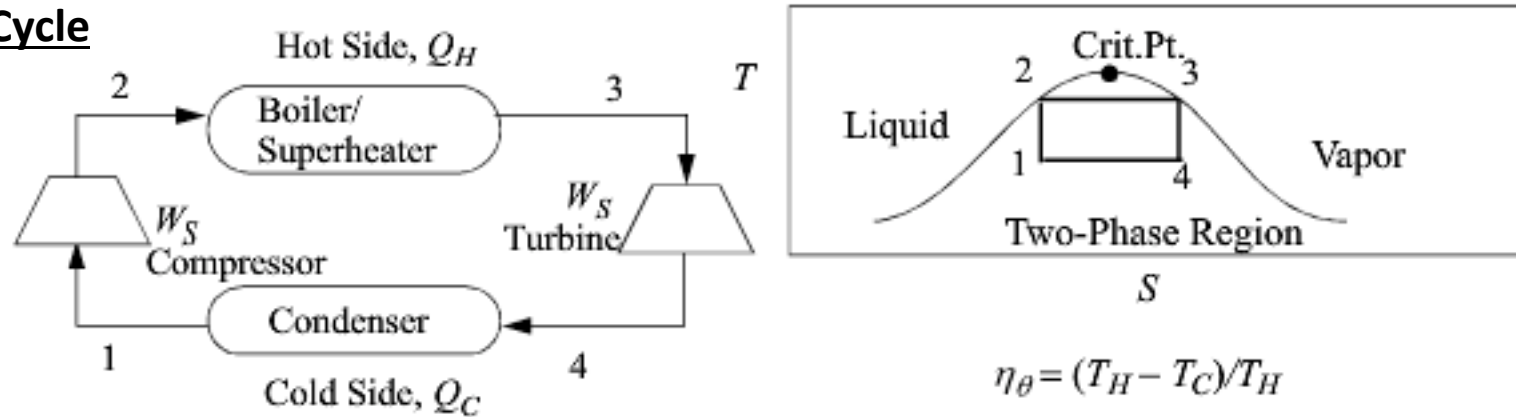
Area inside of TS curve is  $Q_H$

Area inside of PV curve is  $W_S$

Efficiency is the ratio of these two



## Carnot Cycle

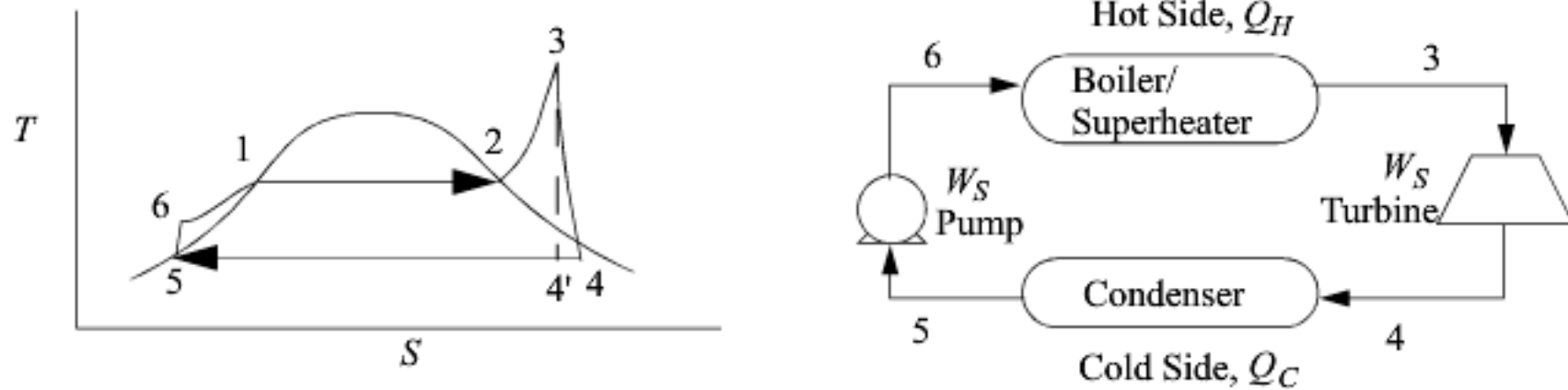


**Figure 5.1** Illustration of a Carnot cycle based on steam in T-S coordinates.

The Carnot cycle has a major advantage over other cycles. It operates at the highest temperature available for as long as possible, reducing irreversibilities at the boundary because the system approaches the reservoir temperature during the entire heat transfer. In contrast, other cycles may only approach the hot reservoir temperature for a short segment of the heat transfer. A similar argument holds regarding the low temperature reservoir. Unfortunately, it turns out that it is impossible to make full use of the advantages of the Carnot cycle in practical applications. When steam is used as the working fluid, the Carnot cycle is impractical for three reasons: 1) It is impractical to stay inside the phase envelope because higher temperatures correlate with higher pressure. Higher pressures lead to smaller heat of vaporization to absorb heat. Since the critical point of water is only  $\sim 374^{\circ}\text{C}$ , substantially below the temperatures from combustion, the temperature gradient between a fired heater and the steam would be large; 2) expanding saturated vapor to low-quality (very wet) steam damages turbine blades by rapid erosion due to water droplets; 3) compressing a partially condensed fluid is much more complex than compressing an entirely condensed liquid. Therefore, most power plants are based on modifications of the Rankine cycle, discussed below. Nevertheless, the

## 5.2 THE RANKINE CYCLE

In a Rankine cycle, the vapor is superheated before entering the turbine. The superheat is adjusted to avoid the turbine blade erosion from low-quality steam. Similarly, the condenser completely reduces the steam to a liquid that is convenient for pumping.



**Figure 5.2** Rankine cycle.  $\Delta H_{3 \rightarrow 4} = \eta_E \Delta H_{3 \rightarrow 4'}$   $H_4 = H_3 + \Delta H_{3 \rightarrow 4}$  5.1

$$\eta_\theta = \frac{-W_{S,net}}{Q_H} = \frac{-(\Delta H_{3 \rightarrow 4} + W_P)}{\Delta H_{6 \rightarrow 3}} \quad 5.2$$

### Example 5.1 Rankine cycle

A power plant uses the Rankine cycle. The turbine inlet is 500°C and 1.4 MPa. The outlet is 0.01 MPa. The turbine has an efficiency of 85% and the pump has an efficiency of 80%. Determine:

- The work done by the turbine (kJ/kg)
- The work done by the pump, the heat required, and the thermal efficiency;
- The circulation rate to provide 1 MW net power output.

**Solution:** We will refer to Fig. 5.2 for stream numbers. The recommended method for solving process problems is to establish a table to record values as they are determined. *In this text we will show values in the tables with bold borders if they have been determined by balance calculations.* The turbine outlet can be read from the temperature table without interpolation. Cells with standard borders refer to properties determined directly from the problem statement

**I** Boldfaced table cells show calculations that were determined by balances. We follow this convention in the following examples.

State	$T$ (°C)	$P$ (MPa)	$q$	$H$ (kJ/kg)	$S$ (kJ/kgK)	$V$ (m <sup>3</sup> /kg)
3	500	1.4	supV	3474.8	7.6047	
4'	45.81	0.01	0.927	2409.2	7.6047	
4	45.81	0.01	0.972	2515.8	7.9388	
5, sat L	45.81	0.01	0.0	191.8		0.00101
6			compL	193.6		

Because the turbine inlet has two state variables specified, the remainder of the state properties are found from the steam tables and tabulated in the property table. We indicate a superheated vapor with "supV" compressed liquid with "compL."

- Stepping forward across the turbine involves the same specifications as part (c) of Example 4.13 on page 168. The properties from 4 and 4' are transferred from that example to the property table. The work done is -959 kJ/kg.
- The outlet of the condenser is taken as saturated liquid at the specified pressure, and those values are entered into the table. We must calculate  $\dot{Q}_H$  and  $\dot{W}_{net}$ . So we need  $H_6$  and  $\dot{W}_{S,pump}$  which are determined by calculating the adiabatic work input by the pump to increase the pressure from state 5. Although the reversible calculation for the pump is isentropic, we may apply Eqn. 2.61 without direct use of entropy, and then correct for efficiency. For the pump,

$$\Delta H'_{pump} = W'_{S,pump} = \int V dP \approx V \Delta P .$$

$$\Delta H'_{pump} = \frac{1010 \text{ cm}^3 (1.4 - 0.01)}{\text{kg}} \left| \frac{1 \text{ J}}{\text{cm}^3 \text{ MPa}} \right| \frac{\text{kJ}}{10^3 \text{ J}} = 1.4 \text{ kJ/kg}$$

$$W_{S,pump} = W'_{S,pump} / \eta_C = 1.4 / 0.8 = 1.8 \text{ kJ/kg}$$

Thus, the work of the pump is small, resulting in  $H_6 = 191.8 + 1.8 = 193.6 \text{ kJ/kg}$ . The net work is  $W'_{S,net} = -959.0 + 1.8 = 957.2 \text{ kJ/kg}$ . The only source of heat for the cycle is the boiler/superheater. All of the heat input is at the boiler/superheater. The energy balance gives  $Q_H = (H_3 - H_6) = 3281.2 \text{ kJ/kg}$ . The thermal efficiency is

$$\eta_\theta = \frac{-W_{S,net}}{Q_H} = \left( \frac{957.2}{3281.2} \right) = 0.2917$$

If we neglected the pump work, the efficiency would be 29.23%. Note that the pump work has only a small effect on the thermal efficiency but is included for theoretical rigor.

(c) For 1 MW capacity,  $\dot{W}_S = \dot{m} W_{S,net}$ , the circulation rate is

$$\dot{m} = \frac{-1000 \text{ kJ}}{\text{s}} \left| \frac{\text{kg}}{-957.2} \right| \frac{3600 \text{ s}}{\text{h}} = 3761 \text{ kg/h}$$

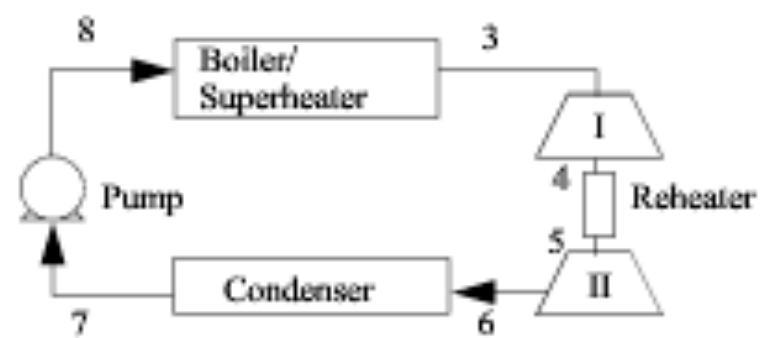
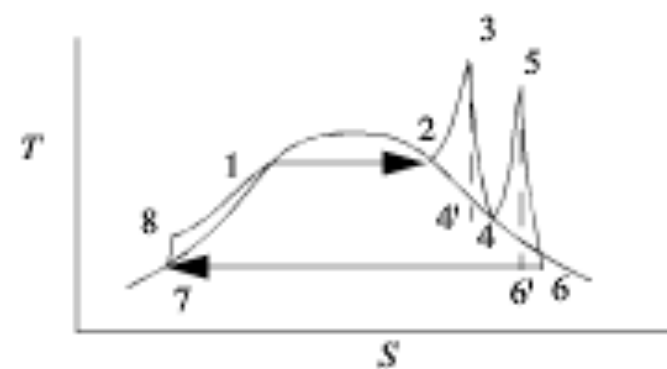


Figure 5.3 Rankine cycle with reheat.



### Example 5.2 A Rankine cycle with reheat

Consider a modification of Example 5.1. If we limit the process to a 500°C boiler/superheater with reheat, we can develop a new cycle to investigate an improvement in efficiency and circulation rate. Let us operate a cycle utilizing two reversible turbines with  $\eta_B = 0.85$  and a pump with  $\eta_C = 0.8$ . Let the feed to the first turbine be steam at 500°C and 6 MPa. Let the feed to the second stage be 1.4 MPa and 500°C (the same as Example 5.1). Determine the improvement in efficiency and circulation rate relative to Example 5.1.

**Solution:** Refer to Fig. 5.3 for stream numbers. First, let us find state 3. The inlet state values are entered in the table.  $P_4 = P_5$  because we neglect the heat exchanger pressure drop. Upon expansion through the first reversible turbine, we look at the  $S^{sat}$  at 1.4 MPa and find it lower than  $S_4$ . Therefore, the reversible state is superheated. Using  $\{S, P\}$  to find  $H$ ,

$$H_4' = 2927.9 + \frac{6.8826 - 6.7488}{6.9552 - 6.7488}(3040.9 - 2927.9) = 3001.2 \text{ kJ/kg}$$

Correcting for efficiency,

$$\Delta H_T = W_{S,T} = 0.85(3001.2 - 3423.1) = 0.85(-421.9) = -358.6 \text{ kJ/kg}$$

$$H_4 = 3423.1 - 358.6 = 3064.5 \text{ kJ/kg}$$

State	$T$ (°C)	$P$ (MPa)	$H$ (kJ/kg)	$S$ (kJ/kgK)	$V$ (m <sup>3</sup> /kg)
3	500	6	3423.1	6.8826	
4'		1.4	3001.2	6.8826	
4			3064.5		
7, sat L	45.81	0.01	191.8		0.00101

State 5 was used in Example 5.1 (as state 3). Solving the energy balance for the reheater,

$$Q_{reheat} = (H_5 - H_4) = 3474.8 - 3064.5 = 410.3 \text{ kJ/kg}$$

Turbine II was analyzed in Example 5.1. We found  $W_{S,T} = -959.0$  kJ/kg and the total work output is  $W_{S,turbines} = (-358.6 - 959.0) = -1317.6$  kJ/kg. The pump must raise the pressure to 6 MPa. Using Eqn. 2.61, and correcting for efficiency,

$$\Delta H_{pump} = W_{S,pump} = 1010 \frac{(6 - 0.01)}{1000} \frac{1}{0.8} = 7.6 \text{ kJ/kg}$$

State 7 is the same as state 5 in Example 5.1 and has been tabulated in the property table.  $H_7 = H_5 + W_{S,pump} = 191.8 + 7.6 = 199.4$  kJ/kg. The net work is thus

$$W_{S,net} = -1317.6 + 7.6 = -1310 \text{ kJ/kg}$$

The heat for the boiler/superheater is given by  $Q_{boiler} = H_3 - H_7 = 3423.1 - 199.4 = 3223.7$  kJ/kg.

### Example 5.2 A Rankine cycle with reheat (Continued)

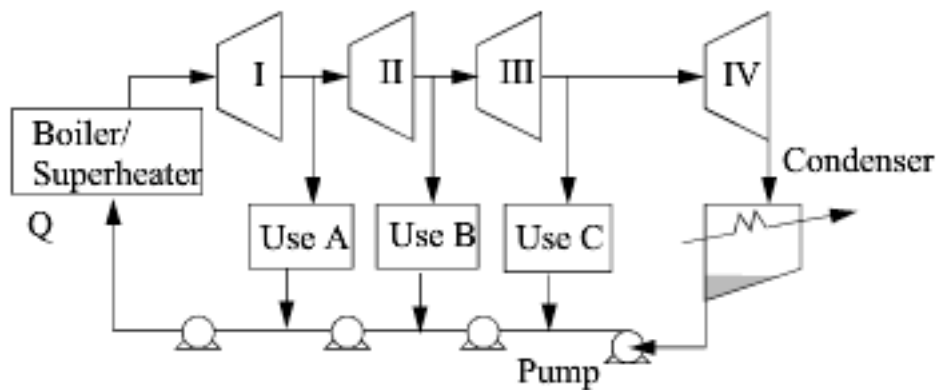
The thermal efficiency is

$$\eta = \frac{-\dot{W}_{S,net}}{\dot{Q}_H} = \frac{-\dot{W}_{S,net}}{(\dot{Q}_{reheat} + \dot{Q}_{b/s})} = \frac{1310}{410.3 + 3223.7} = 0.36$$

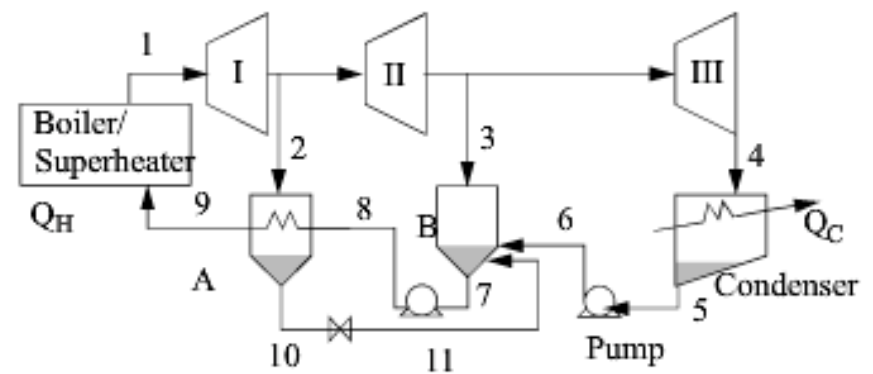
$$\dot{m} = \frac{(-1000)(3600)}{(-1310)} = 2748 \text{ kg/h}$$

The efficiency has improved by  $\frac{(0.36 - 0.29)}{0.29} \times 100 \% = 24\%$ , and the circulation rate has been decreased by 27%.

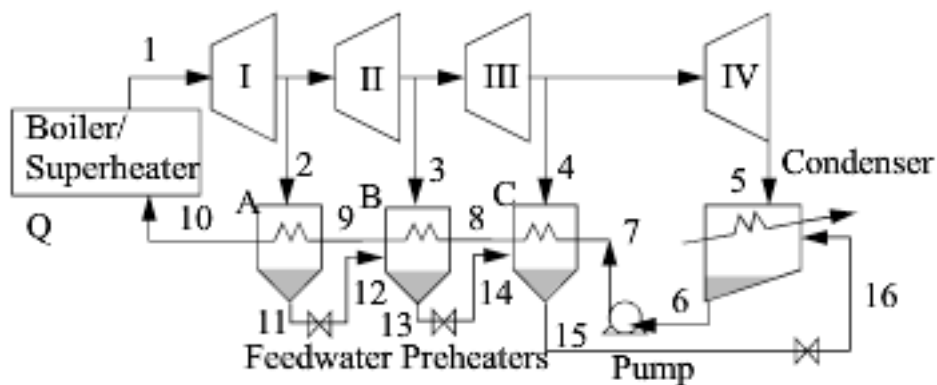
 Reheat improves thermal efficiency



**Figure 5.4** Rankine cycle with side draws for process steam. Pumps and/or throttles may be used in returning process steam to the boiler.



**Figure 5.6** Schematic for a system with a closed feedwater preheater, A, and an open feedwater preheater, B.



**Figure 5.5** Regenerative Rankine cycle using closed feedwater preheaters.

### Example 5.3 Regenerative Rankine cycle

Steam (1) exits a boiler/superheater at 500°C and 5 MPa. A process schematic is shown in Fig. 5.7. The first stage of the turbine exits (2, 3) at 1 MPa and the second stage of the turbine exits (4) at 0.1 MPa. A feed preheater is used to exchange heat with a 5°C approach temperature between streams 7 and 8. Find the net power output per kg of flow in stream 1.

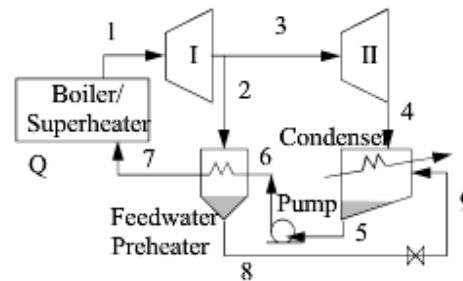


Figure 5.7 Regenerative Rankine cycle for Example 5.3.

**Solution:** First, note that streams 2 and 8 are on the same side of the feedwater preheater and are thus at the same pressure. Streams 7 and 6 must be at the boiler pressure by similar arguments. And stream 5 must likewise be at the condenser pressure. Stream 8 leaves as saturated liquid at the 1 MPa, thus we find  $H_8 = 762.5$  kJ/kg, and  $T_8 = 180^\circ\text{C}$ . Stream 7 is thus at  $175^\circ\text{C}$  and 5 MPa. Following Example 2.6 for a compressed liquid,  $H_7 = 741.02\text{kJ/kg} + (5 - 0.893\text{MPa})(1.12\text{cm}^3/\text{g}) = 745.6$  kJ/kg. Often, one of the key steps in working a problem involving a regenerative cycle is to solve for the fraction of each flow diverted rather than solving for the individual flow rates.

**Solving for flowrate ratios in regenerative cycles can be helpful when the total flowrate is unknown.**

Stream	$T(^{\circ}\text{C})$	$P(\text{MPa})$	$H(\text{kJ/kg})$	$S(\text{kJ/kg}\cdot\text{K})$
1	500	5	3434.7	6.9781
2	300	1	3051.6	7.1246
4		0.1	2615.7	7.2000
5		0.1	417.5	
6		5	422.7	
7	175	5	745.6	
8	180	1	762.5	

The flow rates of streams 7, 6, and 5 are equal to the flow rate of stream 1, and we may write the energy balance around the feedwater preheater using the mass flow rate of stream 1 together with the mass flow rate of stream 2,  $\dot{m}_1(H_6 - H_7) + \dot{m}_2(H_2 - H_8) = 0$ . Dividing by  $\dot{m}_1$  and substituting values gives  $(423 - 746) + (\dot{m}_2/\dot{m}_1)(3052 - 763) = 0$ , and  $\dot{m}_2/\dot{m}_1 = 0.14$ .

**Solution:** First, note that streams 2 and 8 are on the same side of the feedwater preheater and are thus at the same pressure. Streams 7 and 6 must be at the boiler pressure by similar arguments. And stream 5 must likewise be at the condenser pressure. Stream 8 leaves as saturated liquid at the 1 MPa, thus we find  $H_8 = 762.5 \text{ kJ/kg}$ , and  $T_8 = 180^\circ\text{C}$ . Stream 7 is thus at  $175^\circ\text{C}$  and 5 MPa. Following Example 2.6 for a compressed liquid,  $H_7 = 741.02 \text{ kJ/kg} + (5 - 0.893 \text{ MPa})(1.12 \text{ cm}^3/\text{g}) = 745.6 \text{ kJ/kg}$ . Often, one of the key steps in working a problem involving a regenerative cycle is to solve for the fraction of each flow diverted rather than solving for the individual flow rates.

Stream	$T(^{\circ}\text{C})$	$P(\text{MPa})$	$H(\text{kJ/kg})$	$S(\text{kJ/kg-K})$
1	500	5	3434.7	6.9781
2	300	1	3051.6	7.1246
4		0.1	2615.7	7.2000
5		0.1	417.5	
6		5	422.7	
7	175	5	745.6	
8	180	1	762.5	

The flow rates of streams 7, 6, and 5 are equal to the flow rate of stream 1, and we may write the energy balance around the feedwater preheater using the mass flow rate of stream 1 together with the mass flow rate of stream 2,  $\dot{m}_1(H_6 - H_7) + \dot{m}_2(H_2 - H_8) = 0$ . Dividing by  $\dot{m}_1$  and substituting values gives  $(423 - 746) + (\dot{m}_2/\dot{m}_1)(3052 - 763) = 0$ , and  $\dot{m}_2/\dot{m}_1 = 0.14$ .

The net work is given by

$\dot{W}_{S,net} = \dot{m}_1(W_{S,I}) + \dot{m}_2(W_{S,II}) + \dot{m}_1(W_{S,pump})$ , and on the basis of one kg from the boiler/superheater,  $\frac{\dot{W}_{S,net}}{\dot{m}_1} = (W_{S,I}) + \left(1 - \frac{\dot{m}_2}{\dot{m}_1}\right)(W_{S,II}) + (W_{S,pump})$ , and using enthalpies to calculate the work of each turbine,

$$\frac{\dot{W}_{S,net}}{\dot{m}_1} = (3052 - 3435) + (1 - 0.14)(2616 - 3052) + (423 - 418) = -753 \frac{\text{kJ}}{\text{kg stream 1}}$$

Referring to the tabulated values,

$$\frac{Q_H}{\dot{m}_1} = H_1 - H_7 = 3435 - 746 = 2689 \frac{\text{kJ}}{\text{kg stream 1}} \Rightarrow \eta_0 = \frac{753}{2689} = 0.280$$

**I** Solving for flowrate ratios in regenerative cycles can be helpful when the total flowrate is unknown.

## 5.4 REFRIGERATION

### Ordinary Vapor Compression Cycle

As with the Rankine cycle, we make some simplifications that would have to be reevaluated in a detailed engineering design. Again, we neglect pressure losses in piping. We assume that the vapor is saturated at the inlet to the compressor, and that the outlet of the condenser is saturated liquid. Thus, saturated vapor enters the compressor and exits heated above the condenser temperature, then cools in the condenser until it condenses to a saturated liquid. In the cyclic process, the saturated liquid is passed through a throttle valve at constant enthalpy and exits as a two-phase mixture. The evaporator is assumed to be isothermal, and accepts heat at the colder temperature to complete the vaporization. The OVC cycle is often characterized using a  $P$ - $H$  diagram as shown in Fig. 5.9.

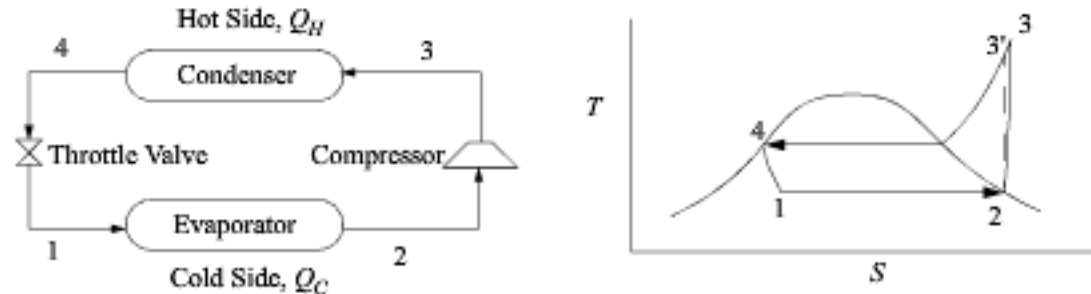


Figure 5.8 OVC refrigeration cycle process schematic and  $T$ - $S$  diagram.

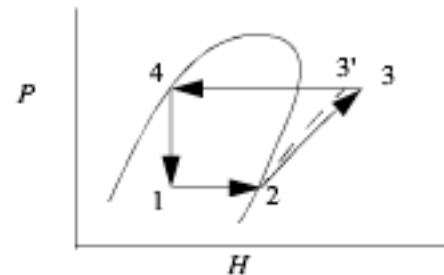


Figure 5.9 OVC refrigeration cycle plotted on the more commonly used  $P$ - $H$  diagram. State numbers correspond to Fig. 5.8.

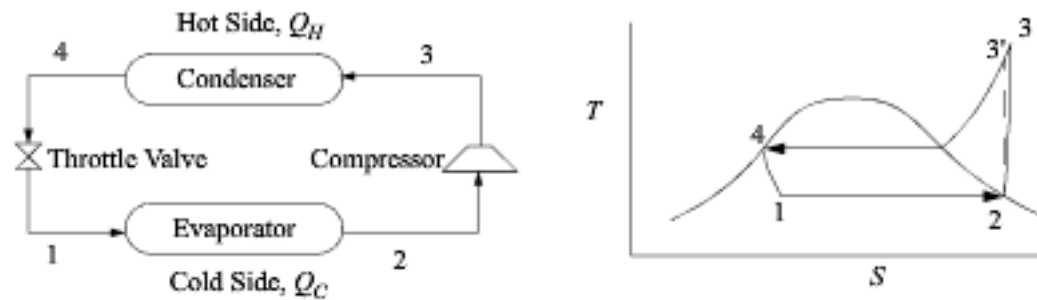
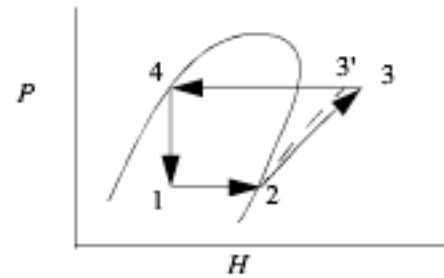


Figure 5.8 OVC refrigeration cycle process schematic and T-S diagram.

Figure 5.9 OVC refrigeration cycle plotted on the more commonly used P-H diagram. State numbers correspond to Fig. 5.8.




The COP can be related to the conditions of the process streams.

$$COP = Q_C / W_{S,net}; \quad Q_C = (H_2 - H_1)$$

$$\text{Energy balance: } W_{S,net} = \Delta H_{2 \rightarrow 3} = (H_3 - H_2)$$

$$\Rightarrow COP = (H_2 - H_1) / (H_3 - H_2) = (H_2 - H_4) / (H_3 - H_2)$$

5.3  COP for ordinary vapor compression cycle.

### Example 5.4 Refrigeration by vapor compression cycle

An industrial freezer room is to be maintained at  $-15^{\circ}\text{C}$  by a cooling unit utilizing refrigerant R134a as the working fluid. The evaporator coils should be maintained at  $-20^{\circ}\text{C}$  to ensure efficient heat transfer. Cooling water is available at  $10^{\circ}\text{C}$  from an on-site water well and can be warmed to  $25^{\circ}\text{C}$  in the condenser. The refrigerant temperature exiting the condenser is to be  $30^{\circ}\text{C}$ . The cooling capacity of the freezer unit is to be 120,000 BTU/h (126,500 kJ/h); 12,650 kJ/h is known as one *ton* of refrigeration because it is approximately the cooling rate (cooling duty) required to freeze one ton of water at  $0^{\circ}\text{C}$  to one ton of ice at  $0^{\circ}\text{C}$  in 24 h. So this refrigerator represents a 10 ton refrigerator. As a common frame of reference, typical home air conditioners are about 2–3 tons, but they typically weigh less than 100 kg. Calculate the COP and recirculation rate (except part (a)) for the industrial freezer in the following cases:

**i** 12,650 kJ/h  
is known as a ton of  
refrigeration  
capacity.

- Carnot cycle.
- Ordinary vapor compression cycle with a reversible compressor.
- Vapor compression cycle with the throttle valve replaced with an expander.
- Ordinary vapor compression cycle for which compressor is 80% efficient.

**Solution:** We will refer to Fig. 5.8 for identifying state by number. The operating temperatures of the refrigeration unit will be

$$T_H = T_4 = 303 \text{ K} \quad T_C = T_2 = 253 \text{ K}$$

#### (a) Carnot cycle

Note that  $T_3$  will be higher than  $T_4$ , but we use the condenser outlet  $T_4$  as the benchmark temperature.

$$COP = \frac{T_C}{T_H - T_C} = \frac{253}{303 - 253} = 5.06$$

#### (b) Ordinary VC cycle with reversible compressor

We will create a table to summarize results. Values determined from balances are shown in bold-faced table cells. Other values are from the R-134a chart in Appendix E. State 2 is a convenient place to start since it is a saturated vapor and the temperature is known.  $T_2 = -20^{\circ}\text{C}$ , from the chart,  $H_2^{satV} = 386.5 \text{ kJ/kg}$  and  $S_2^{satV} = 1.7414 \text{ kJ/kg-K}$ . The condenser outlet (state 4) is taken as saturated liquid at  $30^{\circ}\text{C}$ , so the pressure of the condenser will be  $P_4^{sat}(30^{\circ}\text{C}) = 0.77 \text{ MPa}$ , and  $H_4 = 241.5 \text{ kJ/kg}$ ,  $S_4 = 1.1428 \text{ kJ/kg-K}$ . Because the throttle valve is isenthalpic (Section 2.13),  $H_1 = H_4$ .



### Example 5.4 Refrigeration by vapor compression cycle (Continued)

State	$T$ (K)	$P$ (MPa)	$H$ (kJ/kg)	$S$ (kJ/kg-K)
1	253	0.13	241.5	
1' (for part (c))	253	0.13	235.0	1.1428
2, <i>satV</i>	253	0.13	386.5	1.7414
3'	311	0.77	424	1.7414
4	303	0.77	241.5	1.1428

The compressor calculation has already been performed in Example 4.17 on page 174. If the process is reversible, the entropy at state 3' will be the same as  $S_2$ . Finding  $H_3'$  from  $S_3' = 1.7414$  kJ/kg-K and  $P_3 = 0.77$  MPa, using the chart,  $H_3' = 424$  kJ/kg. Note that the pressure in the condenser, not the condenser temperature, fixes the endpoint on the isentropic line from the saturated vapor.

$$COP = \frac{Q_C}{W_{S,net}} = \frac{(H_2 - H_1)}{(H_3' - H_2)} = \frac{(H_2 - H_4)}{(H_3' - H_2)} = \frac{386.5 - 241.5}{424 - 386.5} = 3.87$$

The required circulation rate is

$$\dot{Q} = 126,500 = \dot{m}Q_C = \dot{m}(H_2 - H_1) = \dot{m}(386.5 - 241.5), \text{ which gives } \dot{m} = 872 \text{ kg/h.}$$

#### (c) VC cycle with turbine expansion

The throttle valve will be replaced by a reversible expander. Therefore,  $S_1' = S_4 = 1.1428$  kJ/kg-K. The saturation values at 253 K are  $S^{satL} = 0.8994$  kJ/kg-K and  $S^{satV} = 1.7414$  kJ/kg-K; therefore,  $S_1' = 1.1428 = q' \cdot 1.7414 + (1 - q') \cdot 0.8994$ , which gives  $q' = 0.289$ .

Then, using the saturated enthalpy values and the quality,  $H_1' = 235.0$  kJ/kg. In order to calculate the COP, we must recognize that we are able to recover some work from the expander, given by  $H_1' - H_4$ .

$$COP = \frac{Q_C}{W_{S,net}} = \frac{(H_2 - H_1')}{(H_3' - H_2) + (H_1' - H_4)} = \frac{386.5 - 235.0}{(424 - 386.5) + (235.0 - 241.5)} = 4.89$$

The increase in COP requires a significant increase in equipment complexity and cost, since a two-phase expander would probably have a short life due to erosion of turbine blades by droplets.

#### (d) Like (b) but with irreversible compressor

States 1, 2, and 4 are the same as in (b). The irreversibility simply changes state 3.

$$COP = \frac{Q_C}{W_{S,net}} = \frac{(H_2 - H_1)}{(H_3 - H_2)} = 0.8 \frac{(H_2 - H_4)}{(H_3' - H_2)} = 0.8(4.08) = 3.26$$

Refrigerant choice is dictated by several factors:

1. Environmental impact (Freon R-12 depletes ozone and has been phased out; Freon R-22 is being phased out). HFO1234yf is beginning to supersede R134a.
2. Vapor pressure  $\sim$  atmospheric at  $T_{\text{evap}}$ . Consequently, the driving force for leakage will be small, but an evaporator pressure slightly above atmospheric pressure is desirable to avoid air leaking into the cycle.
3. Vapor pressure not too high at  $T_H$  so that the operating pressure is not too high; high pressure increases compressor and equipment costs.
4. High heat of vaporization per unit mass.
5. Small  $C_p/C_v$  of vapor to minimize temperature rise and work of compressor.
6. High heat transfer coefficient in vapor and liquid.

### Flash Chamber (Economizer) Intercooling

When the temperature difference between the condenser and evaporator is increased, the compressor must span larger pressure ranges. If the compression ratio ( $P^{out}/P^{in}$ ) becomes too large, interstage cooling can be used to increase efficiency. Because the process temperatures are usually below cooling water temperatures, a portion of the condensed refrigerant stream can be flashed to provide the interstage cooling, as shown in Fig. 5.10. The interstage cooler is sometimes called an **economizer**. The economizer is considered adiabatic unless otherwise specified, and serves to disengage the liquid and vapor exiting the inlet valve. The quality out of the inlet valve is equal to  $\dot{m}_7/\dot{m}_6$ .

Flash chamber intercooling is a common method of increasing COP.

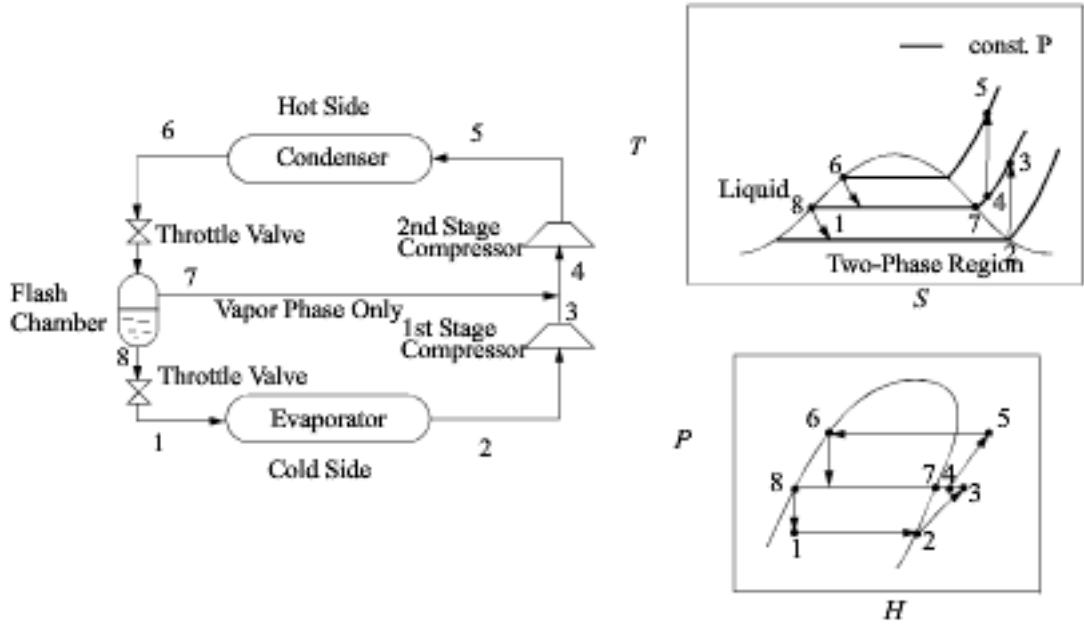
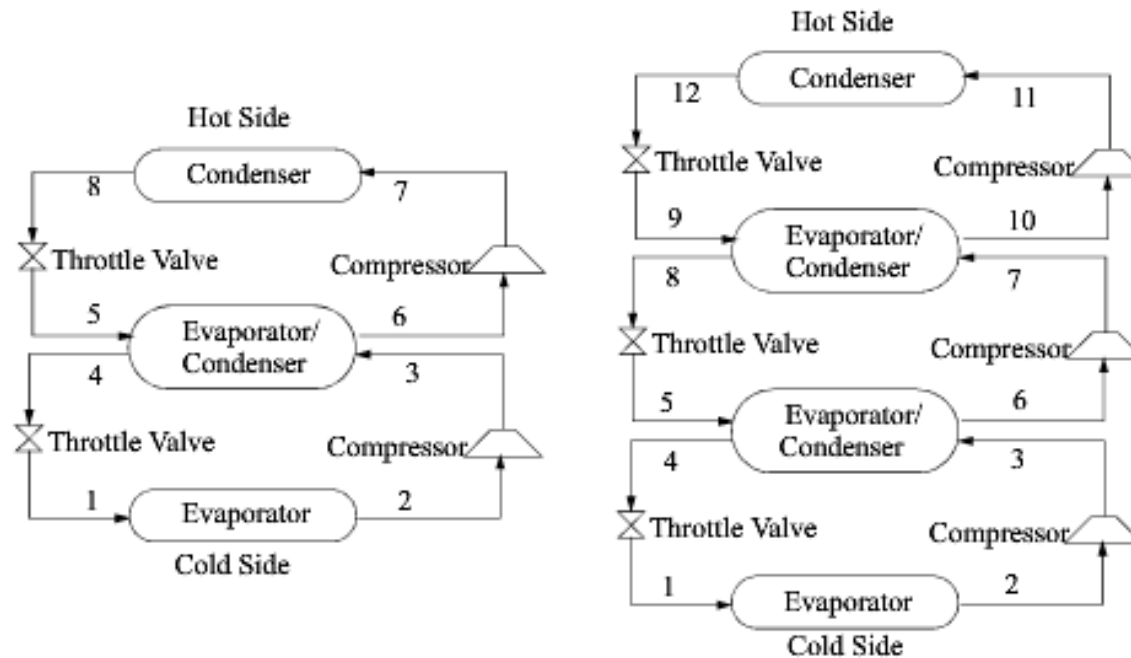


Figure 5.10 Flash chamber intercooling.

## Cascade Refrigeration

In order to span extremely large temperature ranges, a single refrigerant becomes impractical, because the compression ratio ( $P^{out}/P^{in}$ ) becomes too high and the COP decreases. A typical guideline is that the compression ratio should not be higher than about 8. Therefore, to span extremely large ranges, **binary** vapor cycles or **cascade** vapor cycles are used. In a binary cycle, a refrigerant with a normal boiling point below the coldest temperature is used on the cold cycle, and a refrigerant that condenses at a moderate pressure is used on the hot cycle. The two cycles are coupled at the condenser of the cold cycle and the evaporator of the hot cycle as shown in Fig. 5.11. Because the heat of vaporization is coupled to the saturation temperature for any refrigerant, usually the operating temperatures are selected, and the circulation rates are determined for each cycle. Certainly, there are many variables to optimize in a process design of this type. For extremely large ranges, such as for cryogenic processing of liquefied gases, cascade refrigeration can be used with multiple cycles. For example, for the liquefaction of natural gas, the three cycles might be ammonia, ethylene, and methane. Note that the evaporator in each cycle must be colder than the condenser of the cycle below to ensure heat is transferred in the correct direction.

**i** Cascade refrigeration is used to reach cryogenic temperatures.

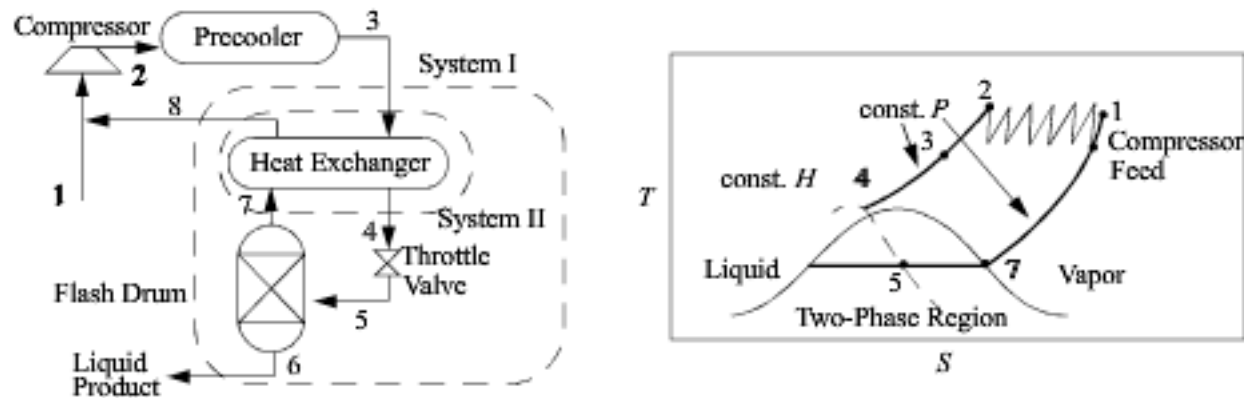


**Figure 5.11** Binary cycle (left) and three-cycle cascade (right) refrigeration cycles. The refrigerants do not mix in the evaporator/condensers.

## 5.5 LIQUEFACTION

### Linde Liquefaction

The Linde process works by throttling high-pressure vapor. The Joule-Thomson coefficient,  $\left(\frac{\partial T}{\partial P}\right)_H$ , must be such that the gas cools on expansion,<sup>2</sup> and the temperature must be low enough and the pressure high enough to ensure that the expansion will end in the two-phase region. Since less than 100% is liquefied, the vapor phase is returned to the compressor, and the liquid phase is withdrawn. Multi-stage compression is usually used in the Linde liquefaction process to achieve the required high



**Figure 5.12** Linde liquefaction process schematic. The system boundaries shown on the left are used in Example 5.5.

### Example 5.5 Liquefaction of methane by the Linde process

Methane is to be liquefied in a simple Linde process. The feed and recycle are mixed, compressed to 60 bar, and precooled to 300 K. The vapor then passes through a heat exchanger for additional cooling before being throttled to 1 bar. The unliquefied fraction leaves the separator at the saturation temperature, and passes through the heat exchanger, then exits at 295 K. (a) What fraction of the gas is liquefied in the process; and (b) what is the temperature of the high-pressure gas entering the throttle valve?

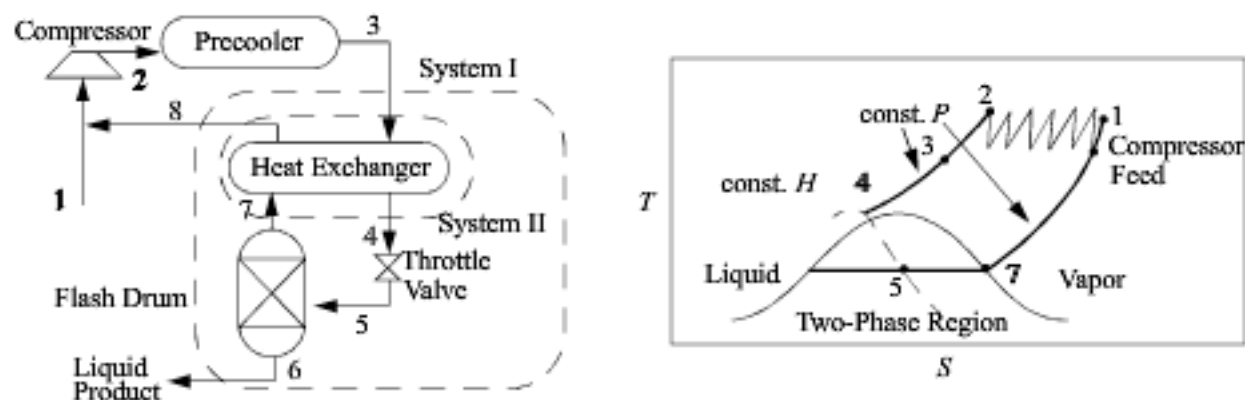
**Solution:** The schematic is shown in Fig. 5.12. To solve this problem, first recognize that states 3, 6, 7, and 8 are known. State 3 is at 300 K and 60 bar; state 6 is saturated liquid at 1 bar; state 7 is saturated vapor at 1 bar; and state 8 is at 295 K and 1 bar. Use the furnished methane chart from Appendix E.

(a) The System I energy balance is:  $H_3 - [qH_8 + (1 - q)H_6] = 0$

$$\Rightarrow q = \frac{H_3 - H_6}{H_8 - H_6} = \frac{H(60, 300) - H(1, satL)}{H(1, 295) - H(1, satL)} = \frac{1130 - 284}{1195 - 284} = 0.9286 \Rightarrow 7.14\% \text{ liquefied}$$

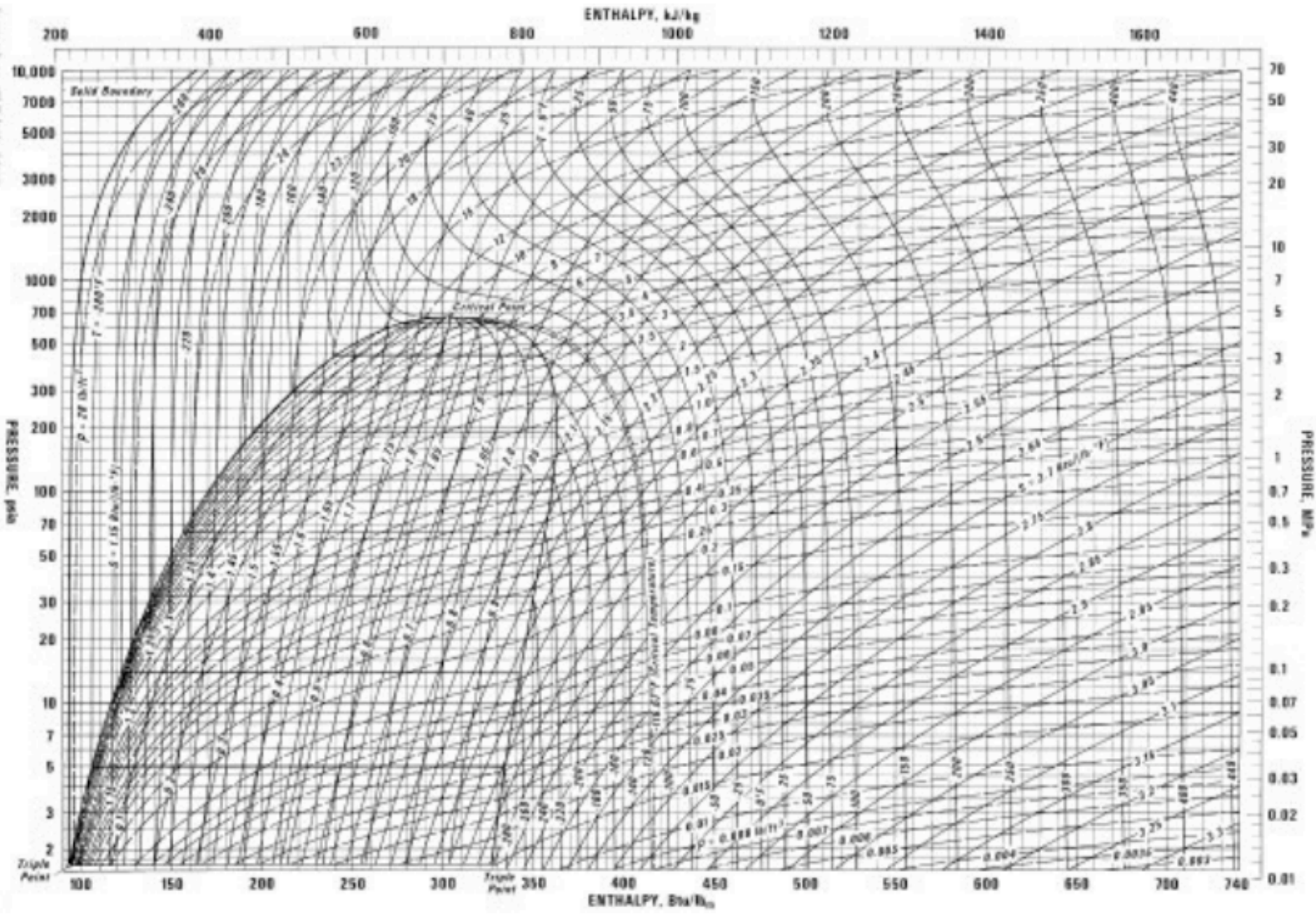
(b) The energy balance for System II is:  $H_4 - H_3 = -q(H_8 - H_7) = -0.9286(1195 - 796.1) = -370.5 \Rightarrow H_4 = 780$

$$\Rightarrow H_4 = 780 @ 60 \text{ bar} \Rightarrow \text{chart gives } -95^\circ\text{F} = 203 \text{ K}$$



**Figure 5.12** Linde liquefaction process schematic. The system boundaries shown on the left are used in Example 5.5.

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## Claude Liquefaction

The throttling process between states 4 and 5 in the Linde process is irreversible. To improve this, a reversible expansion is desirable; however, since the objective is to liquefy large fractions of the inlet stream, turbines are not practical because they cannot handle low-quality mixtures. One compromise, the Claude liquefaction, is to expand a portion of the high-pressure fluid in an expander under conditions that avoid the two-phase region, as shown in Fig. 5.13. Only a smaller fraction of the compressed gas enters the irreversible throttle valve, so the overall efficiency can be higher but more sophisticated equipment is required.

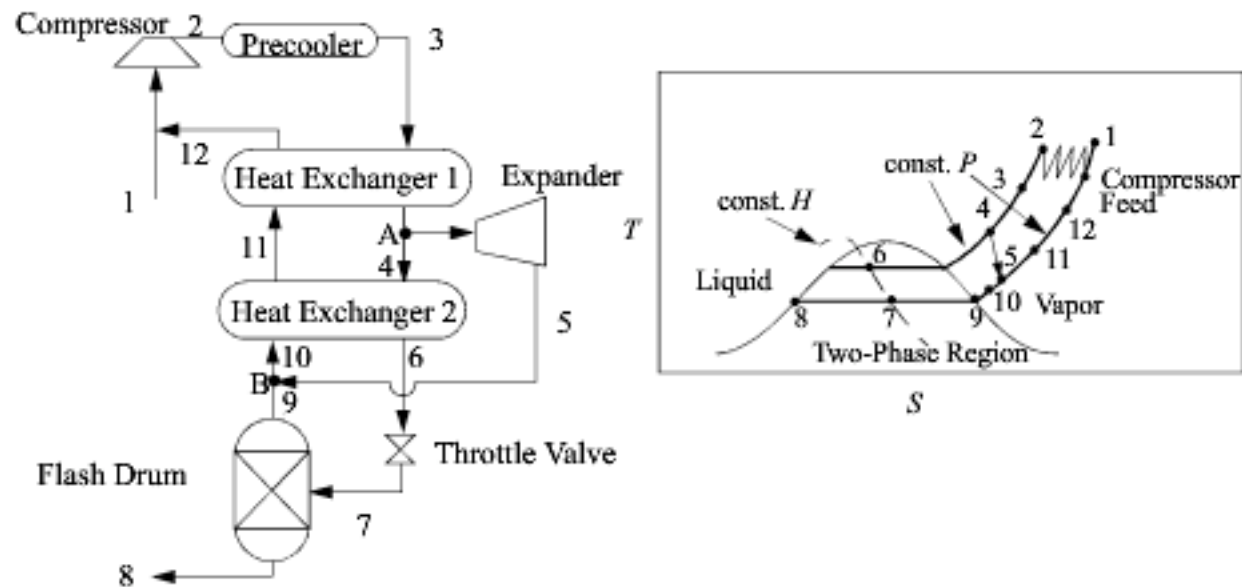


Figure 5.13 The Claude liquefaction process.