ENTROPY AND SECOND LAW OF THERMODYNAMICS

Chapter-3

DIRECTIONALITY OF PROCESSES

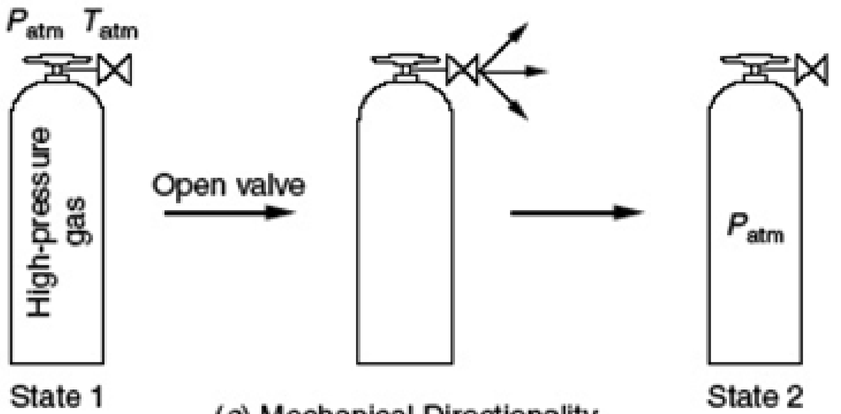
- **Reversibility** is the ability to run a process backwards and forwards infinitely without losses. This is the best case that can happen i.e. less work input maximum work output.
- A "reversible process", which is the best we can do, can go in either direction, i.e. no directionality. Irreversible processes show directionality!

SOURCES OF IRREVERSIBILITIES

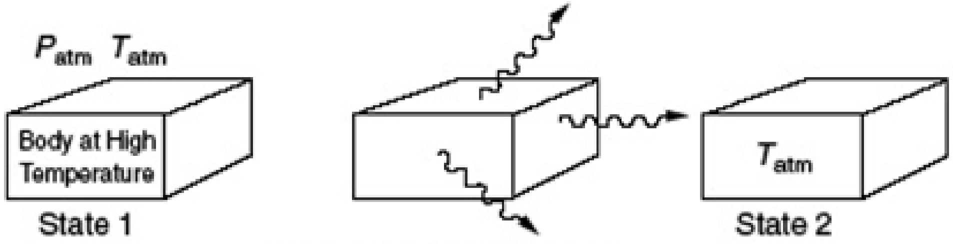
- Friction
- Voltage drops
- Pressure drops
- Temperature drops
- Concentration drops

EXAMPLES:

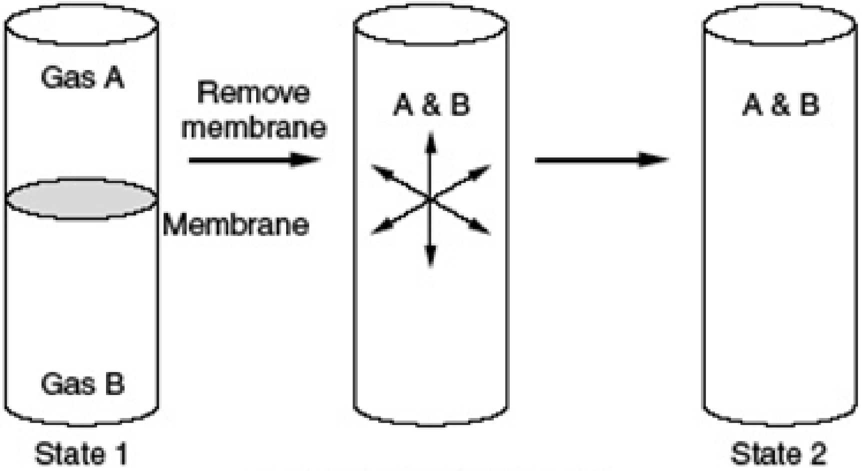
- 1st law does not tell us anything about the direction of these processes!
- In order to study and quantify the directionality of the different processes we need to define a thermodynamic property, **ENTROPY**.
- Entropy will be central in the 2nd law of thermodynamics as Internal Energy was in the 1st law.



(a) Mechanical Directionality



(b) Thermal Directionality



(c) Chemical Directionality

ENTROPY

- One of the ideas involved in the concept of entropy is that nature tends from order to disorder in isolated systems.
- It is a part of our common experience. Spend hours cleaning your desk, your basement, your attic, and it seems to spontaneously revert back to disorder and chaos before your eyes. So if you say that entropy is a measure of disorder, and that nature tends toward maximum entropy for any isolated system, then you do have some insight into the ideas of the second law of thermodynamics.

ENTROPY

- Entropy is defined in terms of heat absorbed during a reversible process. In differential form:

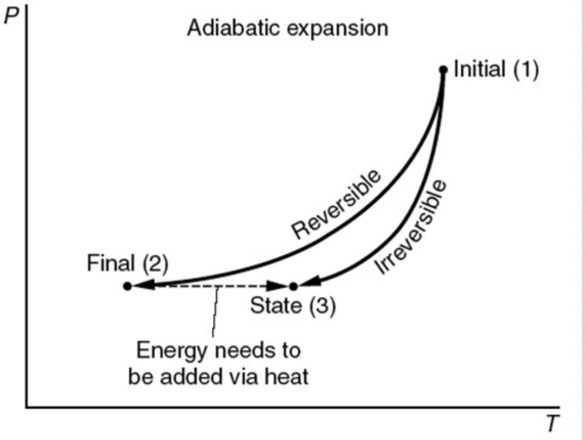
$$ds \equiv \frac{\delta q_{rev}}{T}$$

Integration:

$$\Delta s = \int_{initial}^{final} \frac{\delta q_{rev}}{T}$$

- Entropy is a state property and independent of the path. Entropy quantitatively tells us about:
  - Directionality
  - Reversibility vs. irreversibility
  - Maximum work that can be get out of a process i.e. efficiency

ADIABATIC EXPANSION-REVERSIBLE AND IRREVERSIBLE



- Reversible Adiabatic Expansion:

$$\Delta s_{univ} = \Delta s_{sys} + \Delta s_{surr}$$

$$\Delta s_{sys} = s_2 - s_1 = \int_{initial}^{final} \frac{\delta q_{rev}}{T} = 0 \quad \Delta s_{surr} = 0 \quad \boxed{\Delta s_{univ} = 0}$$

- ➢ Reversible, adiabatic process: the entropy of the system remains constant i.e. isentropic process!

- Irreversible Adiabatic Expansion:
- Definition of entropy requires a reversible process. Thus, we construct a reversible path to go from state 1 to state 3:

  1→2 (reversible adiabatic) then 2→3 (reversible isobaric)

$$\Delta s_{sys} = s_3 - s_2 = \int_{initial}^{final} \frac{\delta q_{rev}}{T} = \int_{T_2}^{T_3} \frac{c_p}{T} dT > 0 \quad \Delta s_{surr} = 0 \quad \boxed{\Delta s_{univ} > 0}$$

- ➢ Irreversible, adiabatic process: the entropy of the system increased.

$$\boxed{\Delta s_{univ} \geq 0}$$

CARNOT CYCLE

- Reversible cycle:

Cyclic process, the system returns to its initial state: $\Delta u_{cycle} = \Delta s_{cycle} = 0$

$$\text{entropy change to surroundings} = \int_{initial}^{final} \frac{\delta q_{rev}}{T} + \int_{initial}^{final} \frac{\delta q_{rev}}{T} + \int_{initial}^{final} \frac{\delta q_{rev}}{T} + \int_{initial}^{final} \frac{\delta q_{rev}}{T}$$

$\boxed{-\frac{q_H}{T_H}}$ Isothermal expansion

$\boxed{0}$ adiabatic expansion

$\boxed{-\frac{q_c}{T_C}}$ Isothermal compression

$\boxed{0}$ adiabatic compression

$$\Delta s_{surr} = -\frac{q_H}{T_H} - \frac{q_c}{T_c}$$

and

$$\frac{q_H}{q_C} = -\frac{T_H}{T_C}$$

→

$$\boxed{\Delta s_{H,surr} + \Delta s_{C,surr} = 0}$$

- Irreversible cycle:

$$\boxed{\Delta s_{H,surr} + \Delta s_{C,surr} > 0}$$

$$\boxed{\Delta s_{univ} \geq 0}$$

SECOND LAW OF THERMODYNAMICS

Second Law of Thermodynamics: In any cyclic process the entropy will either increase or remain the same.

$$\boxed{\Delta s_{univ} \geq 0}$$

- For a reversible process: This provides and additional constraint to solve a problem. Also the best we can get from a process.

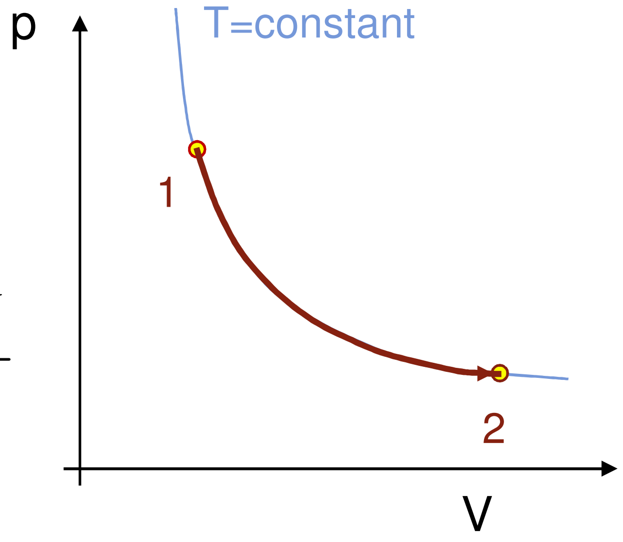
$$\boxed{\Delta s = 0}$$

- For an irreversible process: This tells us if a process is possible or not.

$$\boxed{\Delta s_{univ} > 0}$$

- <u>This tells us about the directionality. I few can determine the entropy of the universe for two states, the one with the higher entropy is the most recent one.</u>

ΔS IN ISOTHERMAL PROCESSES



Work: $dW = pdV$

First Law: $dQ = dU + dW$

So:

$$dS = \frac{dQ}{T} = \frac{dU + dW}{T} = \frac{dU + pdV}{T}$$

Special case, ideal gas:

For an ideal gas, if $dT = 0$, then $dU = 0$. Therefore:

$$dS = \frac{dQ}{T} = \frac{pdV}{T} = \frac{RTdV}{VT} = R\frac{dV}{V}$$

$$\boxed{\Delta S = R\ln\left(\frac{V_2}{V_1}\right)}$$

THE SECOND LAW IN CLOSED SYSTEMS

$$\Delta s_{surr} + \Delta s_{sys} \geq 0$$

If the surroundings are at constant temperature, T_{surr} then:

$$\Delta s_{surr} = \int_{initial}^{final} \frac{\delta Q_{surr}}{T_{surr}} = \frac{1}{T_{surr}} \int_{initial}^{final} \delta Q_{surr} = \frac{\delta Q_{surr}}{T_{surr}}$$

If heat flows into the system, it must flow out of the surroundings:

Q_{surr}=-Q

$$\Delta S_{sys} + \frac{Q_{surr}}{T_{surr}} = n(s_{final} - s_{initial}) + \frac{Q_{surr}}{T_{surr}} \geq 0$$

$$= n(s_{final} - s_{initial}) - \frac{Q}{T_{surr}} \geq 0$$

$$nds + \frac{Q_{surr}}{T_{surr}} \geq 0$$

EXAMPLE 3.2

EXAMPLE 3.3

THE SECOND LAW IN OPEN SYSTEMS

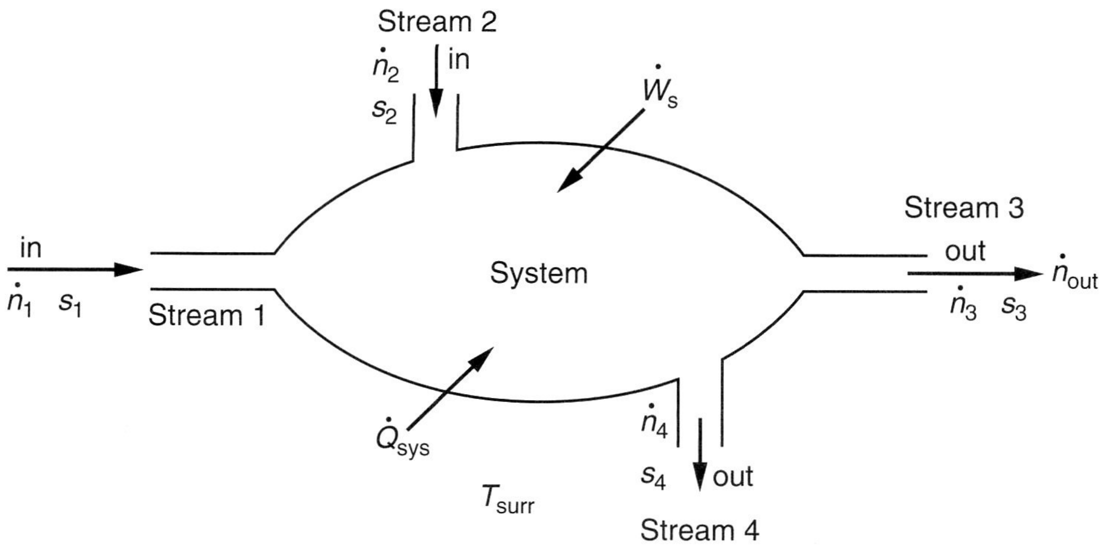
$$\left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_{\text{univ}} = \left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_{\text{sys}} + \left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_{\text{surr}} \geq 0$$

At **steady-state**, the entropy change of the system is zero:

$$\left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_{\text{sys}} = 0$$

at *constant temperature*, T_{surr}, the rate of entropy change with the surroundings can be written

$$\left(\frac{\mathrm{d}S}{\mathrm{d}t}\right)_{\text{surr}} = \sum_{\text{out}} \dot{n}_{\text{out}} s_{\text{out}} - \sum_{\text{in}} \dot{n}_{\text{in}} s_{\text{in}} + \frac{\dot{Q}_{\text{surr}}}{T_{\text{surr}}} = \sum_{\text{out}} \dot{n}_{\text{out}} s_{\text{out}} - \sum_{\text{in}} \dot{n}_{\text{in}} s_{\text{in}} - \frac{\dot{Q}}{T_{\text{surr}}}$$



THE SECOND LAW IN OPEN SYSTEMS

In the case of one stream in and one stream out,

$$\dot{n}(s_{\text{out}} - s_{\text{in}}) - \frac{\dot{Q}}{T_{\text{surr}}} \geq 0$$

where the outlet and inlet molar flow rates are identically $\dot{n}$. In *differential* form, the steady-state entropy balance becomes:

$$\dot{n}\mathrm{d}s - \frac{\delta Q}{T_{\text{surr}}} \geq 0$$

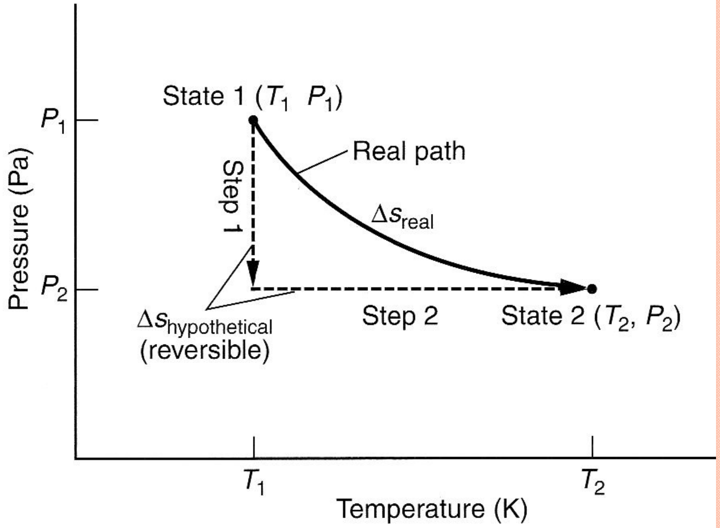
For unsteady-state problems, the entropy change of the system, $\mathrm{d}S/\mathrm{d}t)_{\text{sys}}$, must be included.

$$\boxed{\frac{\mathrm{d}S}{\mathrm{d}t} + \sum_{\text{out}} \dot{n}_{\text{out}} s_{\text{out}} - \sum_{\text{in}} \dot{n}_{\text{in}} s_{\text{in}} - \frac{\dot{Q}}{T_{\text{surr}}} > 0}$$

EXAMPLE 3.6

ΔS FOR AN IDEAL GAS

- Question: What is the entropy change of an ideal gas between two states with *P* and *T* known?



The process from state 1 to state 2 is irreversible.

Therefore, we construct two reversible processes:

- Step 1: Reversible, isothermal expansion:

$$du = \delta q_{rev} + \delta w_{rev} = 0$$

$$\delta q_{rev} = -\delta w_{rev} = P dv$$

$\Delta s_{step1} = \int \frac{\delta q_{rev}}{T} = \int \left(\frac{P}{T}\right) dv$ and $P/T = R/v$, so:

$$\boxed{\Delta s_{step1} = \int_{v_1}^{RT_1/P_2} \left(\frac{R}{v}\right) dv = R\ln\left[\frac{RT_1/P_2}{v_1}\right] = R\ln\left(\frac{P_1}{P_2}\right) = R\ln\left(\frac{P_2}{P_1}\right)}$$

ΔS FOR AN IDEAL GAS

- Step 2: Reversible, isobaric heating:

$$du = \delta q_{\text{rev}} + \delta w_{\text{rev}} = \delta q_{\text{rev}} - P dv$$

$\delta q_{\text{rev}} = du + P dv + v dP = d(u + Pv = dh$ since $dP = 0$

$$\boxed{\Delta s_{\text{step2}} = \int \frac{\delta q_{\text{rev}}}{T} = \int \frac{dh}{T} = \int_{T_1}^{T_2} \frac{c_P}{T} dT}$$

$$\boxed{\Delta s = \Delta s_{\text{step2}} + \Delta s_{\text{step1}} = \int_{T_1}^{T_2} \frac{c_P}{T} dT - R \ln\left(\frac{P_2}{P_1}\right)}$$

- NOTE:

This equation can be applied to any process, reversible or irreversible, including an ideal gas from P_1, T_1 to P_2, T_2.

EXAMPLE 3.8

VAPOR-COMPRESSION POWER AND REFRIGERATION CYCLES

We want to examine the basic elements of common industrial power and refrigeration cycles.

- ✓ These systems employ a thermodynamic cycle in which a fluid is alternatively vaporized and condensed as it flows through a set of four processes.
- ✓ After completing a cycle, the fluid returns to its initial state, so that the cycle can be repeated.
- ✓ We use 1st and 2nd laws to analyze the performance of these cycles.
- ✓ We study:
  - a) Rankine cycle: to convert a fuel source to electrical power.
  - b) Vapor-compression cycle: to produce refrigeration.

THE RANKINE CYCLE

- ✓ To convert a fossil fuel into net Electrical power.
- ✓ Is used in practical steam plants.
- ✓ Is composed of a turbine, condenser, compressor and a boiler.
- ✓ Each of the processes are open steady state systems.
- ✓ Assume reversible processes, hence, the efficiency is the maximum for a given design scenario.

- **Turbine**
  - ➢ Generates electrical power
- **Boiler**
  - ➢ Energy via combustion of fuel is input via heat transfer
- **Condenser**
  - ➢ Energy transfer to bring the system to its initial state
- **Compressor**
  - ➢ Work input to bring the system to its initial state

THE RANKINE CYCLE-ANALYSIS

- *Superheated vapor enters the Turbine*

$$\dot{W}_s = \dot{m}(\hat{h}_2 - \hat{h}_1)$$

Reversible process with negligible heat transfer:

$$\hat{s}_1 = \hat{s}_2$$

- Steam enters as *superheated* vapor and does not condense significantly in the turbine. If it enters as saturated vapor (black line), condensation occurs significantly which causes *erosion* and wear of the turbine blades.

- *Steam to the condenser exists as saturated liquid*

$$\dot{Q}_C = \dot{m}(\hat{h}_3 - \hat{h}_2)$$

- *The compressor increases the pressure of the liquid*

$$\dot{W}_C = \dot{m}(\hat{h}_4 - \hat{h}_3) = \dot{m}\hat{v}_l(P_4 - P_3)$$

- The liquid that enters the compressor should be saturated since most compressors could not handle a two phase fluid!

THE RANKINE CYCLE-ANALYSIS

- *The boiler isobarically produces superheated vapor*

$$\dot{Q}_H = \dot{m}(\hat{h}_1 - \hat{h}_4)$$

The cycle is repeated…

- Outcome from this cycle:
- A small fraction of the power produced by the turbine is used to compress the liquid in the compressor. The rest is the net power obtained by the cycle.
- *Efficiency:*

$$\eta_{Rankine} = \frac{\left|\dot{W}_S\right| - \dot{W}_C}{\dot{Q}_H} = \frac{\left|(\hat{h}_2 - \hat{h}_1\right| - (\hat{h}_4 - \hat{h}_3)}{(\hat{h}_1 - \hat{h}_4)}$$

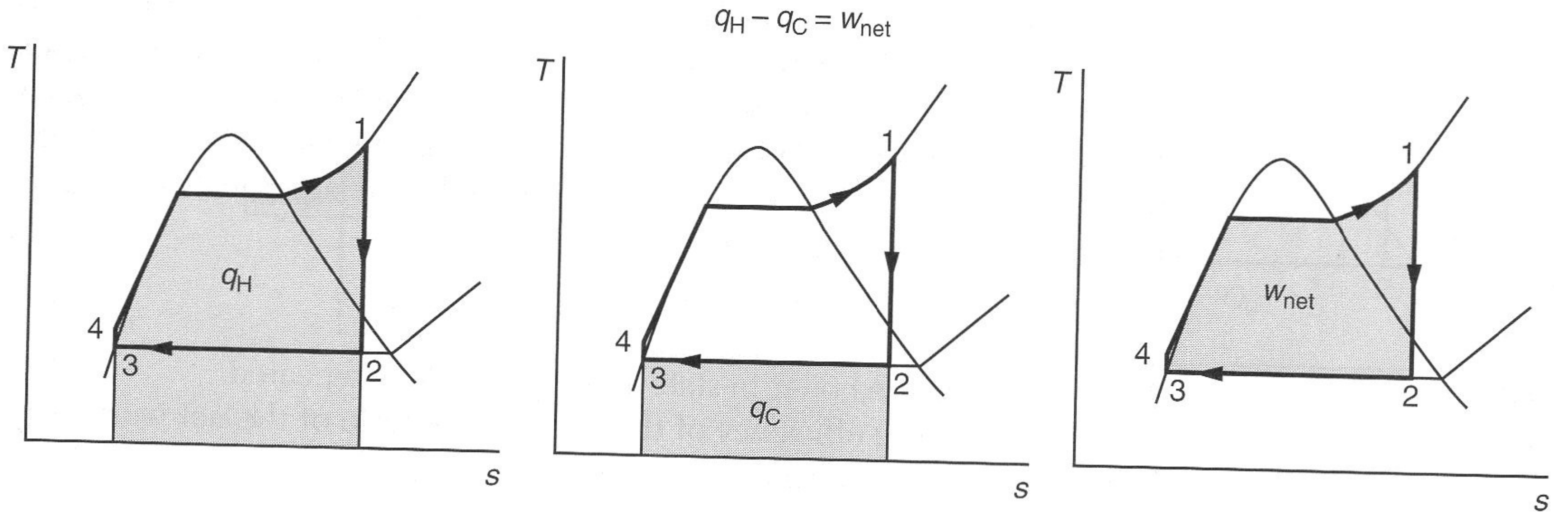
GRAPHICAL REPRESENTATION OF THE RANKINE CYCLE EFFICIENCY

- From the definition of entropy:

$$q_{rev} = \int T ds$$

- All cycles are assumed to be reversible, thus, q_H and q_C are equal to respective area under the *Ts* curve.
- The net work produced by the cycle is:

$$q_H - |q_C| = |w_s| - w_C = w_{net}$$



EXAMPLE 3.14

THE VAPOR-COMPRESSION REFRIGERATION CYCLE

- Implemented where refrigeration is required. The working fluid is a refrigerant.
- Is a Rankine cycle operated in reverse: heat is absorbed from a cold source!
- **Evaporator**: Heat is transferred from the refrigerant unit to the working fluid.

$$\dot{Q}_{\mathrm{C}} = \dot{n}(h_2 - h_1)$$

- **Compressor**: The refrigerant is compressed high enough to condense at T_H.

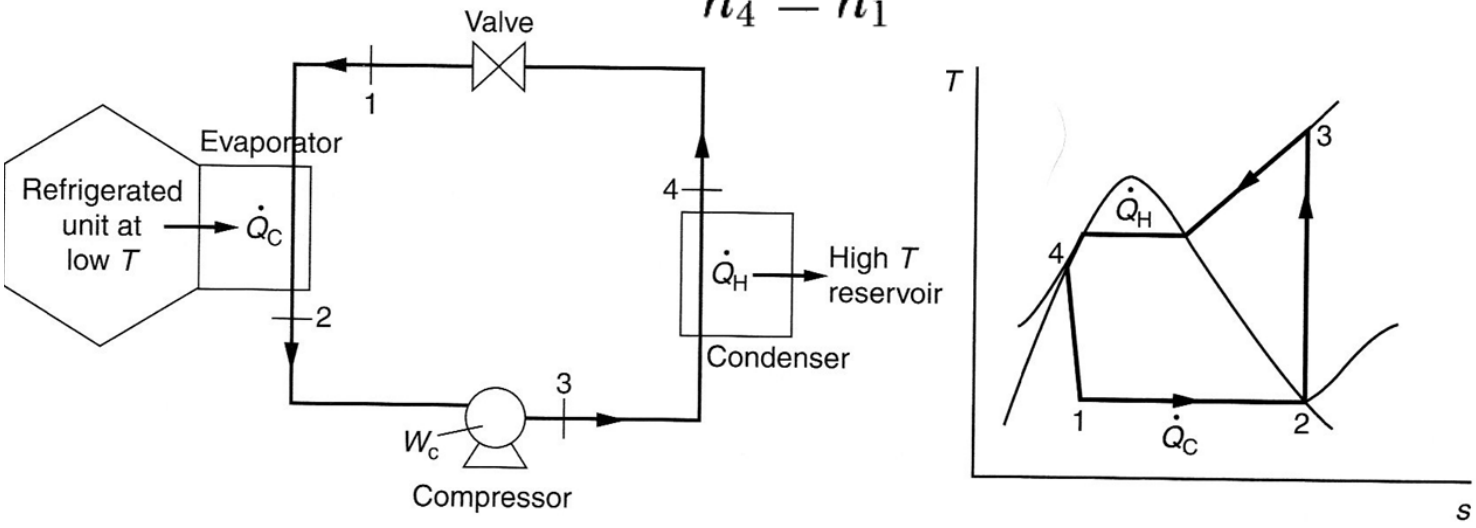
$$\dot{W}_c = \dot{n}(h_3 - h_2) \text{ and } s_3 = s_2$$

- **Condenser**: The high pressure vapor is then condensed expelling heat

$$\dot{Q}_{\mathrm{H}} = \dot{n}(h_4 - h_3)$$

- **Throttling Valve**: A valve is used since the work produced by a turbine is small.

$$h_4 = h_1$$



THE VAPOR-COMPRESSION REFRIGERATION CYCLE

- The coefficient of performance:

$$\boxed{\mathrm{COP} = \frac{\dot{Q}_{\mathrm{C}}}{\dot{W}_c} = \frac{h_2 \quad h_1}{h_3 - h_2}}$$

- Example 3.16