

# Thermodynamics

## Chapter 1- Introduction

System - whatever we are studying

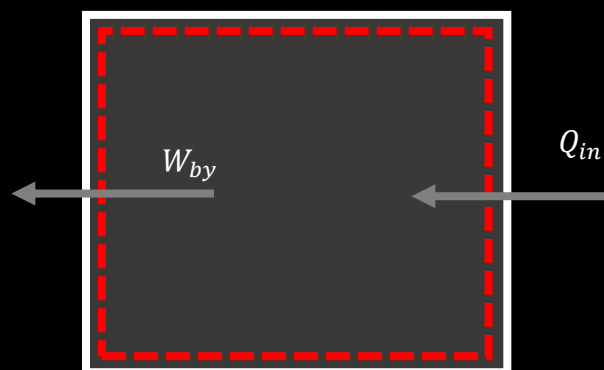
- Quantity of matter
- rigid walled tank
- pipeline
- Composition inside can be fixed or can be changing through chemical/nuclear relations
- The shape/volume is not necessarily constant (like a piston or a balloon)

Surroundings- everything external to the system

Boundary- what separates the system from the surroundings. When interactions occur between the surroundings and the system they must occur over the boundary (also called the control surface)

Closed systems- constant quantity of matter (also called control mass)

- Defined when a particular quantity of mass is under study
- Always contains the same matter
- No transfer of mass across the boundary
- Isolated system- a closed system that does not interact in any way with its surroundings



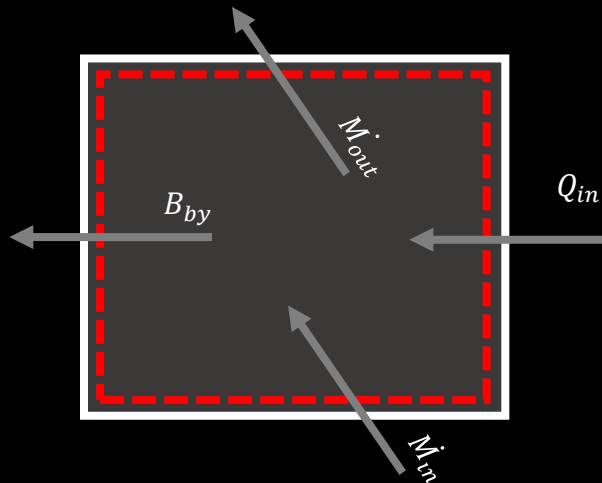
*Work and heat can be added but mass cannot change*

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Control volume- refers to a region of space through which mass may flow (also called open system)

- Mass can move across the boundary freely

- A region with a prescribed boundary
- The volume can change



*Work and heat can be added and mass can move across the boundary*

The system boundary would be delineated carefully based on:

1. What is known about a possible system (particularly its boundaries)
2. The objectives of the analysis

Macroscopic approach (classical thermodynamics)

- A model or structure that is no molecular, atomic or on the subatomic levels
- Behaviors of this system can be affected by molecular structures

Microscopic approach (statistical thermodynamics)

- To characterize by statistical means the average behavior of particles making up a system or interest
  - Involve lasers, plasmas, high speed gas flows, chemical kinetics, and very low temperatures (cryogenics)
- Used to interpret internal energy and entropy
- Used to develop data (like ideal gas specific heats)

Property- macroscopic characteristic of a system (like mass, volume, energy, pressure, and temperature)

State- refers to the condition of a system as described by its properties

- Sometimes relationships between the different properties in the system
- All other properties are in terms of the few

Process- transformation from one state to another

- If a process exhibits the same values at two different times it is in the same state
- There are several quantities that are not properties (mass, flow rates, energy transfers by work and heat)
- A quantity is a property if and only if its change in value between two states is independent of the process

Steady state- if none of the properties change with time

Cycle- process with the same start and end points

Extensive Property- value for an overall system that is the sum of values of part of the system

- Mass, volume, energy
- Depend on the size or extent of the system
- Can change with time

Intensive properties- values that are independent of the size or extent of the system and can vary from place to. Place in the system

- Function of both time and position
- Temperature, pressure

Equilibrium- a condition of balance maintained by an equality of opposing forces

- To be incomplete equilibrium there must be a balance in mechanical thermal phase and chemical forces
- Equilibrium state- isolate the system from its surroundings and watch for changes in its observable properties. If there are no changes, we conclude that the system was in equilibrium and the moment it was isolated
- When a system is isolated, it does not interact with its surroundings, but its state can change because of spontaneous events that occur internally. When all changes cease the system is in equilibrium

Quantity	Units	
	SI	English
Mass	Kilogram (kg)	pound mass (lb)
Length	Meter (m)	foot (ft)
Time	Second (s)	Second (s)
Force	Newton ( $1N = 1kg \cdot m/s^2$ )	Pound force ( $1lbf = 32.1740 lb \cdot ft/s^2$ )

Factor	Prefix	Symbol
$10^{12}$	tera	T
$10^9$	giga	G
$10^6$	mega	M
$10^3$	kilo	k
$10^2$	hecto	h
$10^{-2}$	centi	c
$10^{-3}$	milli	m
$10^{-6}$	micro	$\mu$
$10^{-9}$	nano	n
$10^{-12}$	pico	p

## Unit Conversions

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$$1 \text{ ft} = 0.3048 \text{ m}$$

$$12 \text{ in} = 1 \text{ ft}$$

$$1 \text{ lb} = 0.45359237 \text{ kg}$$


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**Specific Volume**- property of materials that defines the number of cubic meters occupied by one kilogram of a substance

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$$v = \lim_{V \rightarrow 0} \left( \frac{V}{m} \right)$$


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- Specific volume is the inverse of density
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$$\rho = \frac{1}{v} = \lim_{V \rightarrow 0} \left( \frac{m}{V} \right)$$


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- The density is an intensive property that may vary from point to point within a system
  - Specific volume is the volume per unit mass ( $\text{lb/ft}^3$ ,  $\text{g/cm}^3$ ,  $\text{kg/m}^3$ )
  - Molar volume- attained by multiplying the molar mass by the specific volume
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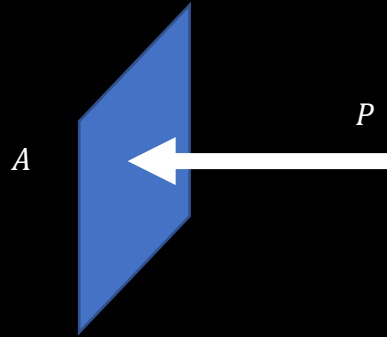
$$\bar{v} = Mv$$


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- Mole-the amount of a given substance numerically equal to its molecular weight
- Molar mass- conversion used to go between mass and moles

**Pressure**- the amount of force applied normal to a surface at a specific point

$$p = \lim_{A \rightarrow 0} \left( \frac{F_{normal}}{A} \right)$$



- The pressure in all directions is the same in all directions as long as the fluid is at rest
- Pressure can vary from point to point within a fluid at rest
  - Variation in atmospheric pressure as elevation increases
  - Variation in pressure with depth in ocean, lake, and other bodies of water
- Normal stress- component normal to the area
- Shear stress- the two components in the plane of the area
- The magnitudes of the stresses vary with the orientation of the area
- Fluid mechanics- state of stress in a fluid in motion
- Absolute pressure- pressure with respect to the zero pressure of a complete vacuum
- The lowest possible value of absolute pressure is zero
- Pressure measuring devices
  - Manometers and barometers measure pressure in terms of the length of a column of liquid (mercury, water, or oil)
    - Frequently expressed in terms of the length in millimeters, inches of mercury or inches of water
  - Piezoelectric effect- a charge is generated within certain solid materials when they are deformed. This mechanical input/electrical output provides the basis for pressure measurement as well as displacement and force measurements
- Buoyancy- force that occurs when body is completely or partially submerged in a liquid
  - Since pressure increases with depth from the liquid surface, pressure forces acting from below are greater than pressure forces acting from above; thus, the buoyant force acts vertically upward
  - The buoyant force has a magnitude equal to the weight of the displaced liquid

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$$1 \text{ pascal} = 1 \text{ N/m}^2$$

$$1 \text{ kPa} = 10^3 \text{ N/m}^2$$

$$1 \text{ bar} = 10^5 \text{ N/m}^2$$

$$1 \text{ MPa} = 10^6 \text{ N/m}^2$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ N/m}^2 = 14.696 \text{ lbf/in}^2 = 760 \text{ mmHg} = 29.92 \text{ inHg}$$

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- Gage pressure- pressure with respect to atmospheric pressure
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$$P_{\text{gage}} = p_{\text{abs}} - P_{\text{atm(abs)}}$$

$$P_{\text{abs}} = p_{\text{gage}} + P_{\text{atm(abs)}}$$

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Temperature- a measure of the warmth or coldness of an object or substance with reference to some standard value

- Thermal (heat) interaction- an interaction between two blocks with two different temperatures causes the warmer block to decrease with time and the colder block increases with time. Eventually there is no observable change
  - Thermal equilibrium- when all visible changes cease and the two blocks have equal temperature
  - Zeroth Law of Thermodynamics- If we know that two objects are in equilibrium with a third then we know that the two objects are in equilibrium
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$$T(^{\circ}\text{R}) = 1.8T(\text{K})$$

$$T(^{\circ}\text{C}) = T(\text{K}) - 273.15$$

$$T(^{\circ}\text{F}) = T(^{\circ}\text{R}) - 459.67$$

$$T(^{\circ}\text{F}) = 1.8T(^{\circ}\text{C}) + 32$$

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### Solving Thermodynamic Problems

- State what is known
- State what needs to be found
- Draw a sketch and label the diagram with relevant information and record all the properties and values that are given
- List all assumptions and show how problem can be simplified
- Solve the simplified problem
- Consider if the answer is reasonable

## Chapter 2- Energy and the First Law of Thermodynamics

Energy- the capacity of an object to do work

- Kinetic energy- a scalar quantity that is related to the movement of an object

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$$\Delta KE = KE_f - KE_i = \frac{1}{2}m(V_2^2 - V_1^2) = \int_{s_i}^{s_f} F \cdot ds$$

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- Extensive property
- The work done on the body can be considered a transfer of energy to the body where it is stored as kinetic energy
- Potential Energy- stored energy that depends upon the relative position of various parts of a system

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$$\Delta PE = PE_f - PE_i = m(z_2 - z_1) = \int_{z_i}^{z_f} mg \cdot dz$$

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- Energy conversion- the total work of the forces acting on the body from the surroundings
- If energy is conserved:

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$$\frac{1}{2}m(V_2^2 - V_1^2) = m(z_2 - z_1)$$

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- conservation of energy is extended to include a wide variety of ways in which systems interact with their surroundings

Work- equal to the amount of force multiplied by the distance over which it is applied

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$$W = \int_{s_1}^{s_2} F \cdot ds$$

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- work is done by a system on its surroundings if the sole effect on everything external to the system could have been the raising of a weight
- work is a means for energy transferring
  - does not refer to what is being transferred between systems or to what is stored within systems
- energy is transferred and stored when work is done
  - if  $W$  is positive then the work is done by the system
  - if  $W$  is negative then work is being done on the system
- work is not a property because it depends on the path taken

- Power is the differential of work and is inexact (because it depends on the on the process linking the two)

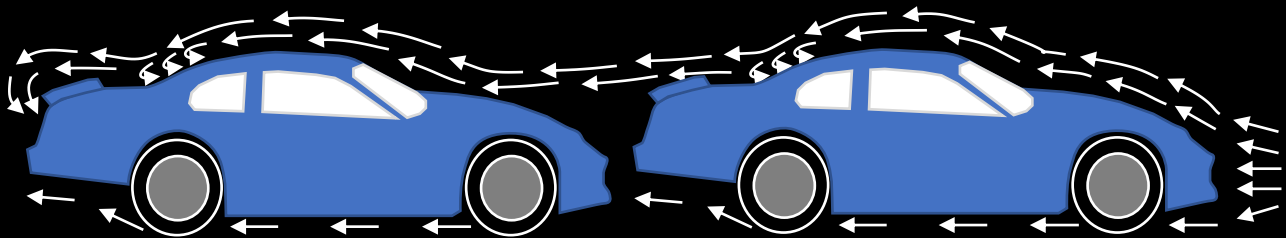
$$\text{power} = \dot{W} = \frac{dW}{dt} = F \cdot V$$

$$W = \int_{t_1}^{t_2} \dot{W} dt = \int_{t_1}^{t_2} F \cdot V dt$$

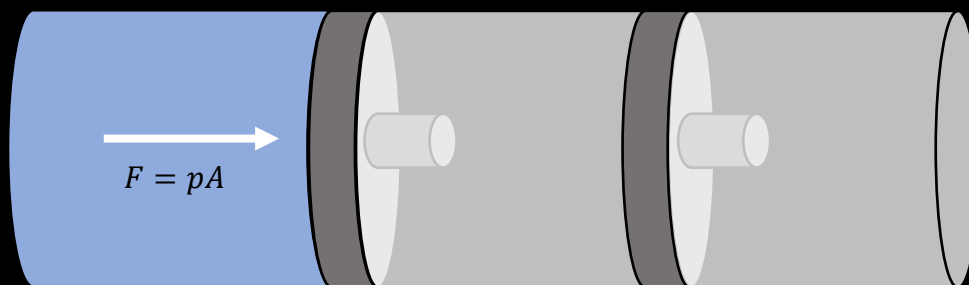
- Drag Force

$$F_{\text{Drag}} = \frac{1}{2} C_d A \rho V^2$$

- Drafting- occurs when two or more bodies are aligned closely this the first reduces the overall effect of drag on the second



- Expansion or Compression Work
  - gas pressure exerts a normal force on the piston



$$W = (pA)\Delta x = \int p dV$$

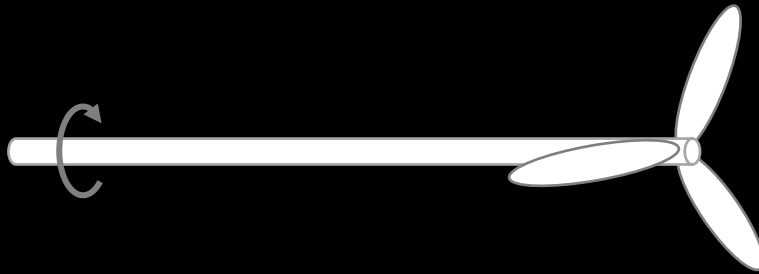
$$\text{If pressure is constant, then } W = \int p dV \Rightarrow W = p \int dV$$

- Quasiequilibrium-process where the departure from thermodynamic equilibrium is at most infinitesimal. All states through which the system passes in a quasiequilibrium process may be considered equilibrium states.



- This is akin to the use of idealizations such as the point mass or the frictionless pulley in mechanics for the purpose of simplifying an analysis.
- instrumental in deducing relationships that exist among the properties of systems at equilibrium
  - polytropic process- quasiequilibrium process described by  $pV^n = \text{constant}$  where  $n$  is constant
- Shaft Work/Power
  - work associated with a rotating object (shaft, axel motor)

$$W = F_t V = (\tau/R)(R\omega) = \tau\omega$$



- Electric Power
  - The current or flow of electric charge and voltage of the potential of charge to deliver energy

$$\dot{W} = -\varepsilon i$$

$i = \text{electric current}$

$\varepsilon = \text{electric potential crossing boundary}$

## Internal Energy

- In each of these examples the change in system energy cannot be attributed to changes in the system's overall kinetic or gravitational potential energy the change in energy can be accounted for in terms of internal energy, as considered next
- internal energy ( $U$ ) is an extensive property of the system
- The specific internal energy is symbolized by  $u$  or  $\bar{u}$  respectively, depending on whether it is expressed on a unit mass or per mole basis.

$$E_2 - E_1 = (U_2 - U_1) + (PE_2 - PE_1) + KE_2 - KE_1$$

$$\Delta E = \Delta U + \Delta PE + \Delta KE$$

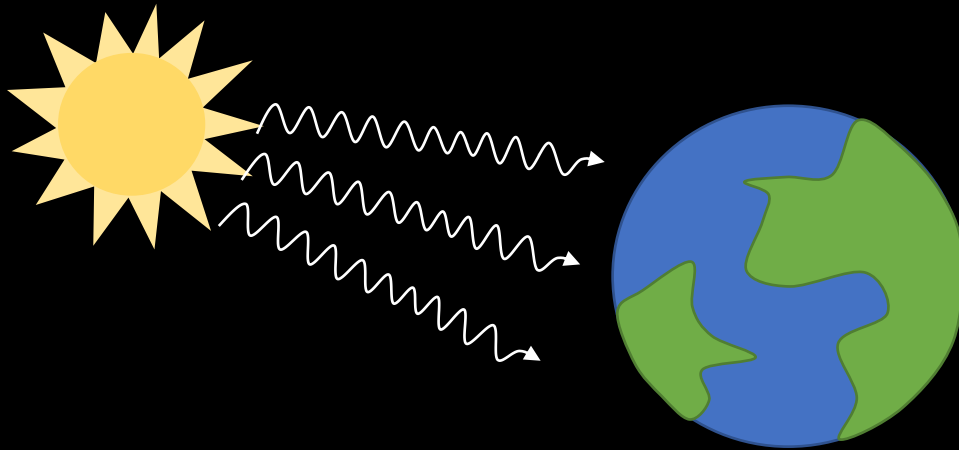
- microscopic interpretation of internal energy- think of the energy attributed to the motions and configurations of the individual molecules, atoms, and subatomic particles making up the matter in the system. Gas molecules move about, encountering other molecules or the walls of the container.
- Part of the internal energy of the gas is the translational kinetic energy of the molecules.
  - Other contributions to the internal energy include the kinetic energy due to rotation of the molecules relative to their centers of mass
  - kinetic energy associated with vibrational motions within the molecules

## Heat Transfer

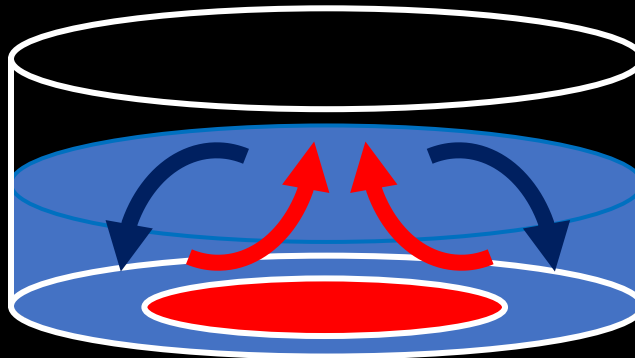
- we know that energy transfers by heat are induced only because of a temperature difference between the system and its surroundings and occur only in the direction of decreasing temperature.
- $Q$  is the symbol that is associated with energy transfer through heat
- Heat transfer into a system is taken to be positive, and heat transfer from a system is taken as negative.
  - $Q > 0$ : heat transfer to the system
  - $Q < 0$ : heat transfer from the system
- Heat is not a property because it changes based on the process
- $\dot{Q}$  is the rate of net heat transfer
- Adiabatic- system that undergoes a process involving no heat transfer with its surroundings
- Conduction
  - Can take places in solids liquids and gases
  - Transfer of energy from one or more energetic particles of a substance to adjacent particles that are less energetic due to interactions between particles



- Radiation
    - Changes in the electron configurations of the atoms or molecules within it
    - Energy is transferred by electromagnetic waves
    - Requires no medium to transfer heat
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- Convection
    - Energy transfer between solid surface and an adjacent fluid (liquid or gas)
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## First Law of Thermodynamics

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$$\Delta E = Q_{in} - W_{by}$$
$$\Delta U + \Delta PE + \Delta KE = Q_{in} - W_{by}$$
$$\frac{dE}{dt} = \dot{Q}_{in} - \dot{W}_{by}$$

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- Energy accounting system

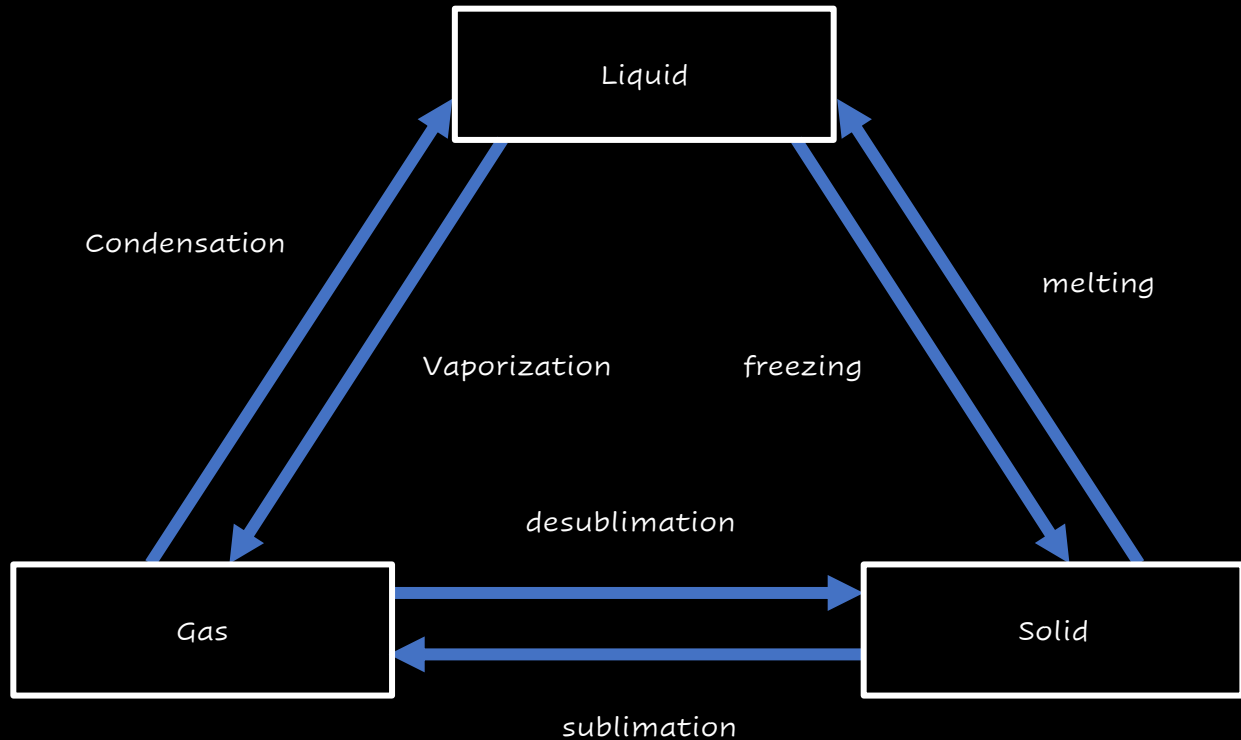
## Cycle

- Same start and end point
- Therefore, the net energy is 0 and  $Q_{in} = W_{by}$

## Chapter 3- Evaluating properties

Phase- quantity of matter that is homogeneous throughout in both chemical composition and physical structure

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- Homogeneity in physical structure- means matter is all solid liquid or vapor
  - Systems can contain multiple phases
    - Two phases can coexist during changes in phase (vaporization, melting and sublimation)

Pure substance- substance that is uniform and invariable in chemical composition

- Can exist in more than one phase
- Chemical composition must be the same in each phase

Not all properties are independent of each other, and states can be determined by giving the values the independent properties

State principle- guide for determining the number of independent properties required to fix the state of a system

Simple compressible systems- intensive states of systems of commonly encountered pure substances (water or uniform mixture of nonreacting gases)

- The state principle indicates that two independent intensive thermodynamic properties will fix the values of all other intensive thermodynamic properties

### p-V-T Relation

- P-v-T surface - The relationship between pressure and the independent variables (specific volume and temperature)
- The critical temperature- the maximum temperature at which liquid and vapor phases can coexist in equilibrium
  - Critical pressure - the pressure at the critical point
  - Critical specific volume - the special volume at the critical point
  - Used for bringing out the general relationships among the three phases of matter normally under consideration

### Phase Diagram

- The projection of p-v-t surface onto the pressure-temperature plane that creates a property diagram
- When projected this way the two-phase regions reduce to lines
- Saturation Temperature- designates the temperature at which a phase change takes place at a given pressure
- Saturation pressure- the designated pressure at which a phase change takes place
- Triple point- the point where the three phases exist at equilibrium

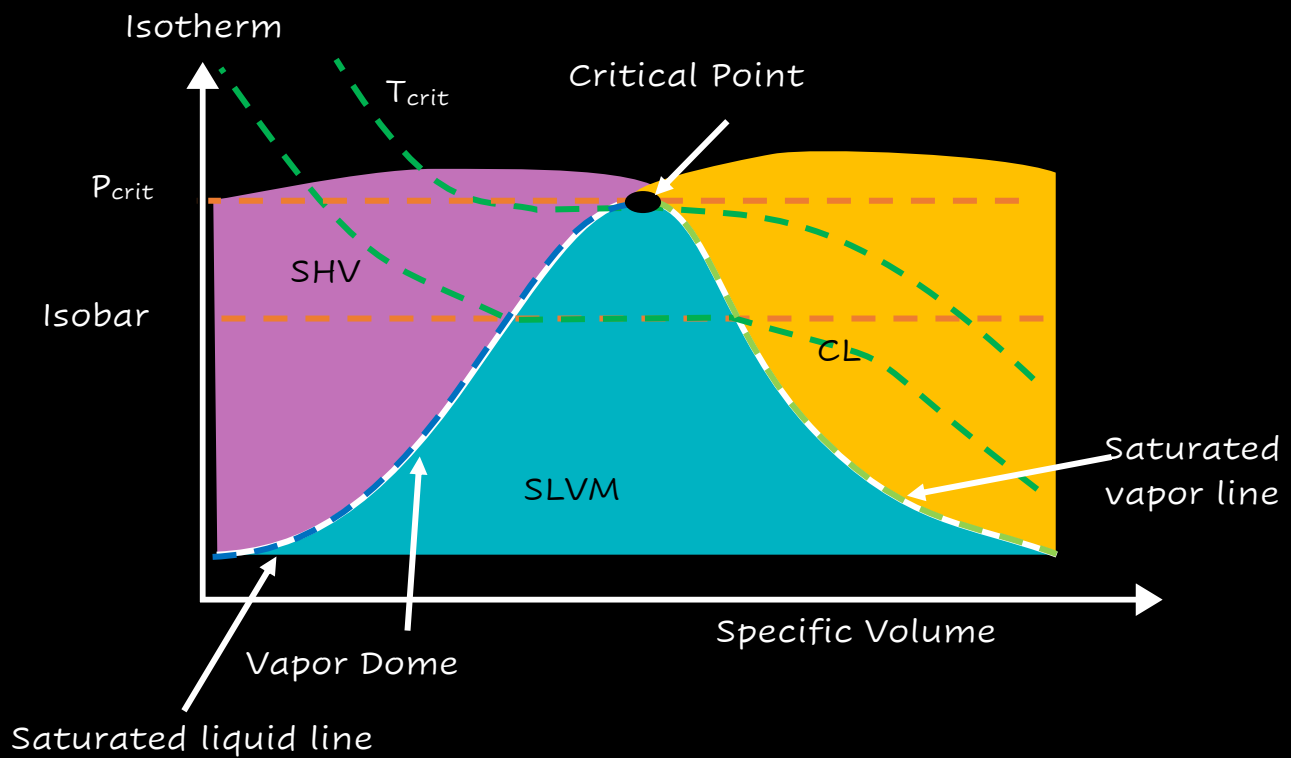
Isobar- line of constant pressure

Isotherm- line of constant temperature

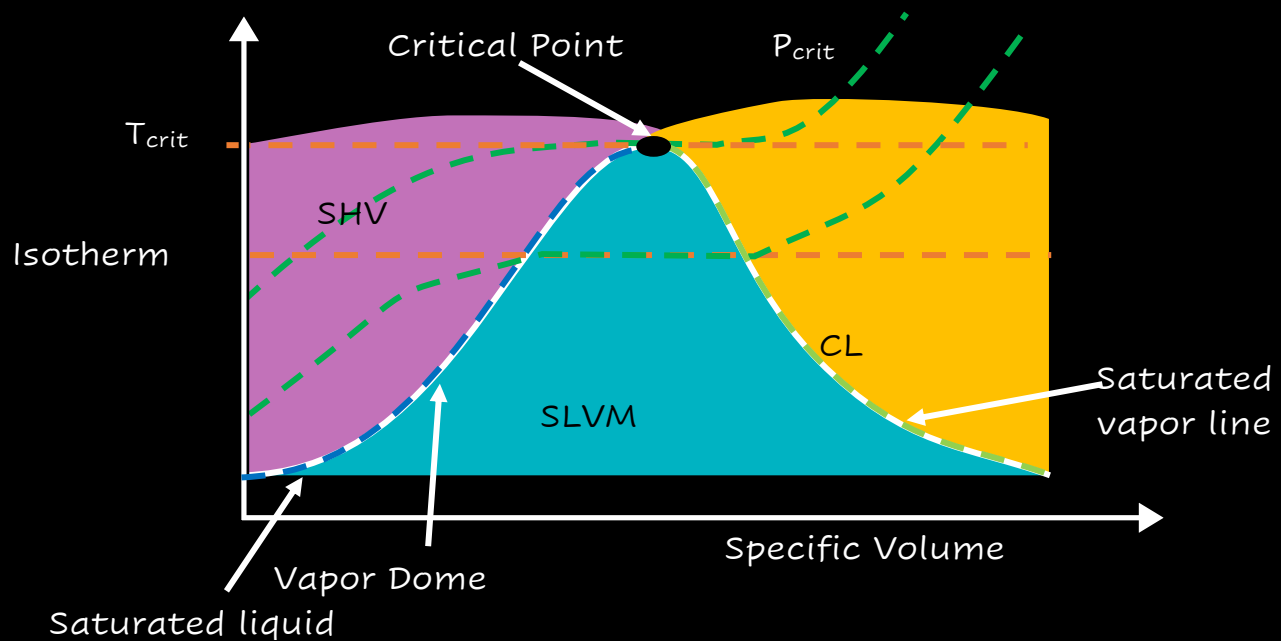
Critical point- peak of the vapor dome

p-v diagram - projection of the p-v-T surface onto the pressure-specific volume plane

- Saturation temperature- the specific temperature at which a phase change takes place at a given pressure (saturation pressure)
- The triple point of water is used as a reference in defining temperature scales



T-v diagram- projection of the  $p$ - $v$ - $T$  surface onto the Temperature-specific volume plane



### Phase Change

- As a system is heated at constant pressure the temperature increases while the specific volume increases slightly

- then the system is brought to a state where the pressure and temperature remains constant, but the specific volume increases because the energy from heat goes to turning the liquid to gas
- Once all of the molecules have changes phases the pressure and temperature increase while the specific volume increases slightly
- Quality- the ratio of the mass of vapor present to the total mass of the mixture

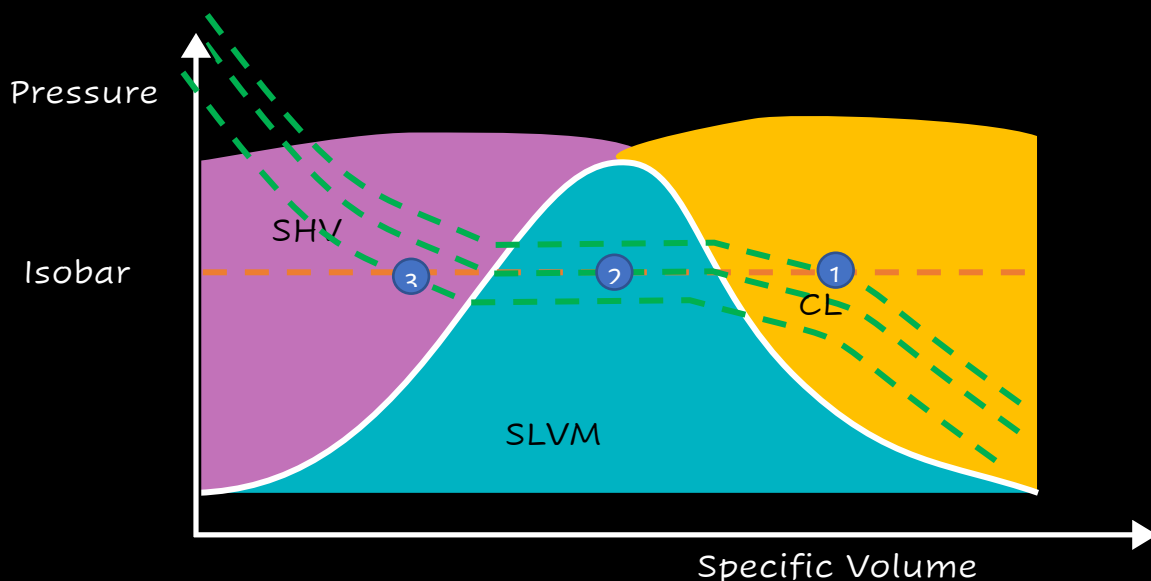
$$x = \frac{m_{\text{vapor}}}{m_{\text{liquid}} + m_{\text{vapor}}}$$

Using the quality to find the saturation liquid vapor mixture properties

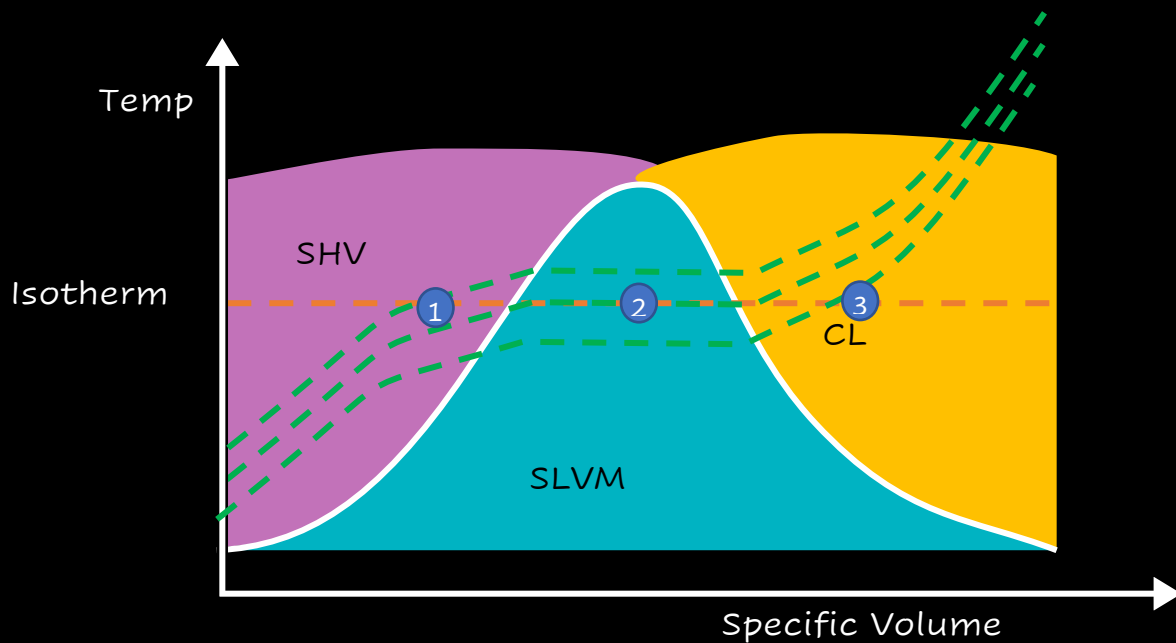
$$z = z_f(1 - x) + z_g x$$

### Determining the Phase

- If  $T = T_{\text{sat}}$ 
  - If  $P < P_{\text{sat}}$  - condensed liquid
  - If  $P = P_{\text{sat}}$  - saturated liquid vapor mixture
  - If  $P > P_{\text{sat}}$  - superheated vapo



- If  $P = P_{\text{sat}}$ 
  - If  $T < T_{\text{sat}}$  - superheated vapor (1)
  - If  $T = T_{\text{sat}}$  - saturated liquid vapor mixture (2)
  - If  $T > T_{\text{sat}}$  - condensed liquid (3)



## Enthalpy

- Property that is equal to the total heat in the system
- Created because  $U + pV$  constantly appears in thermodynamics

$$H = U + pV$$

- We can also find the specific enthalpy of a system

$$h = \frac{H}{m} = u + pv$$

$$\bar{h} = \bar{u} + p\bar{v}$$

## Specific Heats $c_v$ and $c_p$

- the amount of heat that must be added to one unit of mass to raise it by one degree

$$c_v = \left( \frac{\partial u}{\partial T} \right)_v \text{ constant volume}$$

$$c_p = \left( \frac{\partial u}{\partial T} \right)_p \text{ constant pressure}$$



- relate the temperature change of a system to the amount energy added by heat transfer

$$k(\text{specific heat ratio}) = \frac{c_p}{c_v}$$

- The specific heat ratio is usually greater than 1 (because  $c_p > c_v$ )

Approximations for Liquids using saturated liquid data

$$v(T, p) \approx v_f(T)$$

$$u(T, p) \approx u_f(T)$$

- Using this volume approximations, we can approximate the enthalpy

$$h(T, p) \approx u_f(T) + pv_f(T) \rightarrow h(T, p) \approx h_f(T) + v_f(T)[p - p_{\text{sat}}(T)]$$

*When there is only a small deviation from the pressure and the saturation pressure*

$$h(T, p) \approx h_f(T)$$

Incompressible substance model

- Used to simplify evaluations involving liquids or solid
- The specific volume (and density) are assumed to be constant and the specific internal energy are assumed to vary only with temperature

$$c_v(T) = \frac{du}{dT}$$

$$h(T, p) = u(T) + pv$$

$$c_v = c_p$$

$$\Delta h = \Delta u + v(\Delta p)$$

Ideal Gas Model

- Used to simplify evaluations involving gases
- Assumes that the molecules have no interaction with each other
- Pressure must be small (compared to critical pressure) and/or temperature is relatively large compared to the critical temperature

$$pv = RT$$

$$p\bar{v} = \bar{R}T \quad \bar{R} = R \text{ universal}$$

$$pV = \bar{n}RT$$

$$u = u(T)$$

$$h = h(T) = u(T) + RT$$

$$c_v(T) = \frac{du}{dT}$$

$$\Delta u = \int_{T_1}^{T_2} c_v(T) dT$$

$$c_p(T) = \frac{dh}{dT}$$

$$\Delta h = \int_{T_1}^{T_2} c_p(T) dT$$

$$\frac{dh}{dT} = \frac{du}{dT} + R$$

$$c_p(T) = c_v(T) + R$$

$$k = \frac{c_p(T)}{c_v(T)}$$

$$c_p(T) \approx \text{constant} \rightarrow \Delta h = c_p(T_2 - T_1)$$

$$c_v(T) \approx \text{constant} \rightarrow \Delta u = c_v(T_2 - T_1)$$

Polytropic Process Relationships- quasiequilibrium process described by  $pV^n = \text{constant}$

- Therefore  $p_1 V_1^n = p_2 V_2^n$

## Chapter 4- Control Volume Analysis

Conservation of mass- the idea that mass is not created or destroyed in chemical reactions but can move in and out of the system

$$\frac{dm_{cv}}{dt} = \sum \dot{m}_{in} - \sum \dot{m}_{out}$$

Mass flow rate- movement of mass per unit time (kg/s)

$$\dot{m} = \frac{VA}{\Delta t} = \rho VA$$

$$m = \frac{\dot{m}}{t}$$

One dimensional flow- flow is normal to the boundary where mass enters the control volume and all intensive properties (like velocity and density) are uniform with position over each inlet or exit area through which matter flows

When a process is at **steady flow**

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$$\frac{dm_{cv}}{dt} = 0$$
$$\sum \dot{m}_{in} = \sum \dot{m}_{out}$$

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Conservation of energy

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$$\frac{dE_{cv}}{dt} = \dot{Q}_{in\ cv} - \dot{W}_{by\ cv} + \sum \dot{m}_{in} (h + ke + pe) - \sum \dot{m}_{out} (h + ke + pe)$$

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And the work is equal to

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$$\dot{W} = \dot{W}_{cv} + (p_{out}A_{out})V_{out} - (p_{in}A_{in})V_{in}$$
$$\dot{W} = \dot{W}_{cv} + \dot{m}_{out}(p_{out}v_{out}) - \dot{m}_{in}(p_{in}v_{in})$$

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When at a steady state  $\frac{d..._{cv}}{dt} = 0$

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$$0 = \dot{Q}_{in\ cv} - \dot{W}_{by\ cv} + \sum \dot{m}_{in} (h + ke + pe) - \sum \dot{m}_{out} (h + ke + pe)$$

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transient Application- process which states change with time so  $\frac{d..._{cv}}{dt} \neq 0$

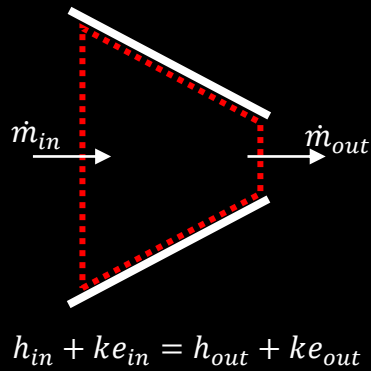
Nozzle- flow passage of varying cross-sectional area in which the velocity of a gas or liquid increases in the direction of flow

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$$A_{in} > A_{out} \text{ and } V_{in} < V_{out}$$

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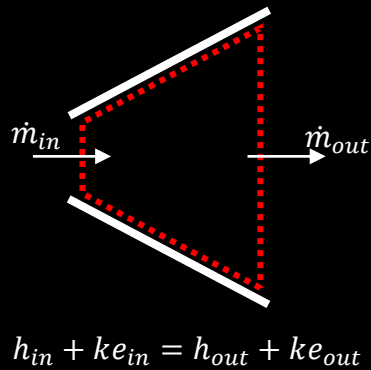
- Steady state and steady flow
- Adiabatic
- No "other" work
- Potential energy is negligible



Diffuser- the fluid decelerates in the direction of flow (opposite of nozzle)

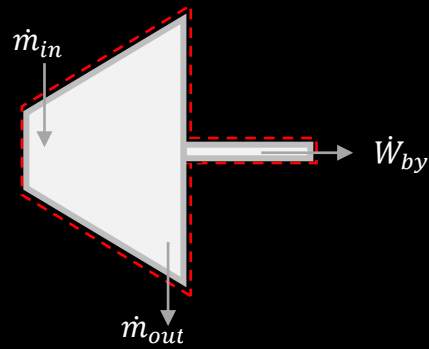
$$A_{in} < A_{out} \text{ and } V_{in} > V_{out}$$

- Steady state and steady flow
- Adiabatic
- No “other” work
- Potential energy is negligible



Turbines- device where powers is developed as a results of gas or liquid passings through a set of blades attached to a shaft free to rotates

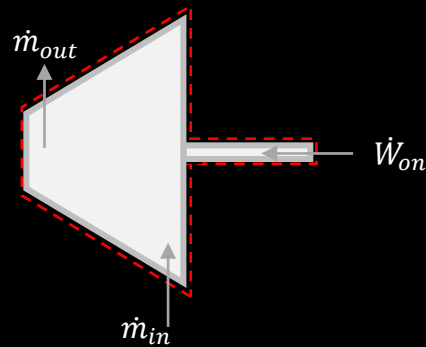
- Steady state and steady flow
- Adiabatic
- Potential energy and kinetic energy are negligible



$$\dot{w} = \dot{m}(h_{in} - h_{out})$$

Compressors and pumps- devices which work is done on the substance flowing through them in order to change the state of the substance

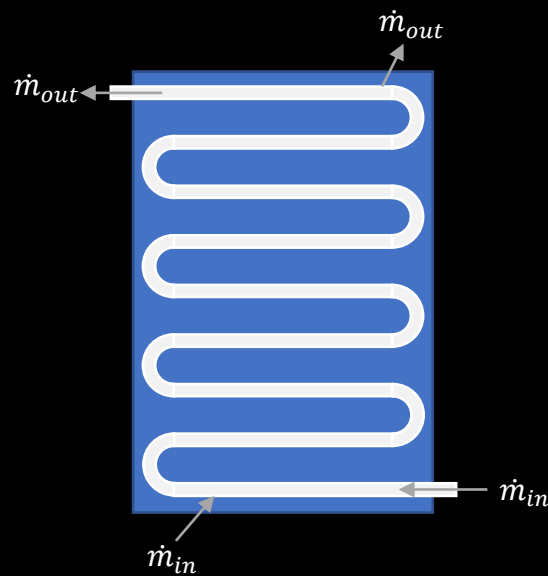
- Steady state and steady flow
- Adiabatic
- Kinetic energy and potential energy



$$\dot{w} = \dot{m}(h_{out} - h_{in})$$

Heat Exchangers- used to transfer heat from a higher energy substance to a lower energy substance

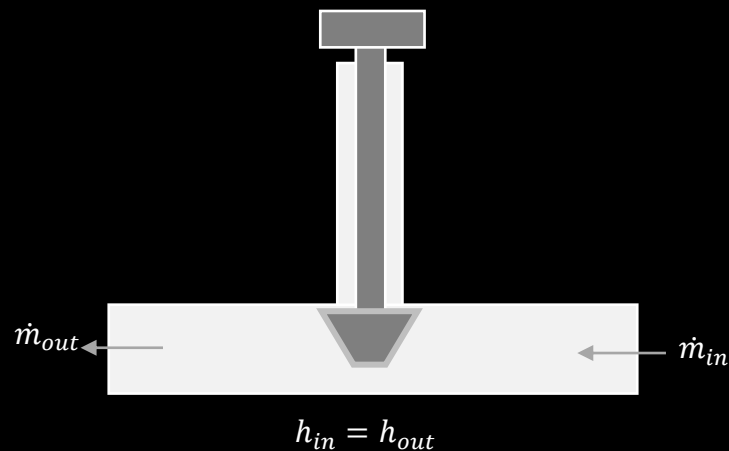
- Steady state
- Adiabatic
- Change in potential and kinetic energy is negligible



$$\dot{m}_f(h_{in} - h_{out}) = -\dot{m}_a(h_{in} - h_{out})$$

### Throttling Device

- Steady state and steady flow
- Adiabatic
- No other work
- change in potential and kinetic energy is negligible



system integration- combining components to achieve the objective

transient Application- process which states change with time so  $\frac{d..._{cv}}{dt} \neq 0$

$$\Delta E = \dot{Q}_{in\ CV} - \dot{W}_{by\ CV} + \sum \dot{m}_{in}(h + ke + pe) - \sum \dot{m}_{out}(h + ke + pe)$$

## Chapter 5- Second Law of Thermodynamics

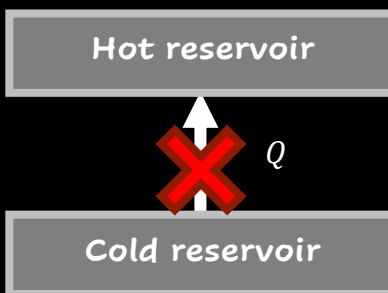
These considerations can be summarized by noting that when an imbalance exists between two systems, there is an opportunity for developing work that would be irrevocably lost if the systems were allowed to come into equilibrium in an uncontrolled way. Recognizing this possibility for work, we can pose two questions:

1. What is the theoretical maximum value for the work that could be obtained?
2. What are the factors that would preclude the realization of the maximum value?

#### Aspects of second law

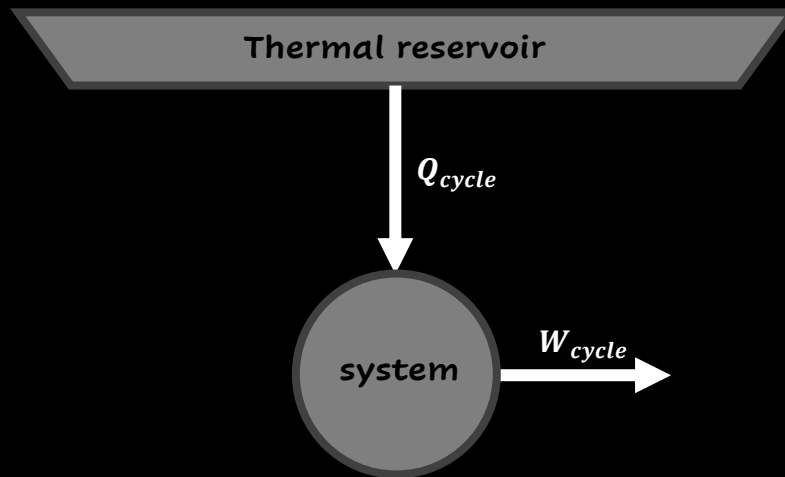
1. predicting the direction of processes.
2. establishing conditions for equilibrium.
3. determining the best theoretical performance of cycles, engines, and other devices.
4. evaluating quantitatively the factors that preclude the attainment of the best theoretical performance level.
5. defining a temperature scale independent of the properties of any thermometric substance.
6. developing means for evaluating properties such as  $u$  and  $h$  in terms of properties that are more readily obtained experimentally.

Clausius Statement- it is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body



Thermal reservoir- a special kind of system that always remains at constant temperature even through energy is added or removed by heat transfer

Kelvin-Planck Statement- it is impossible for any system to operate in a thermodynamic cycle and deliver net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir



$$W_{cycle} \leq 0$$

$W_{cycle} = 0$  if the cycle is irreversible

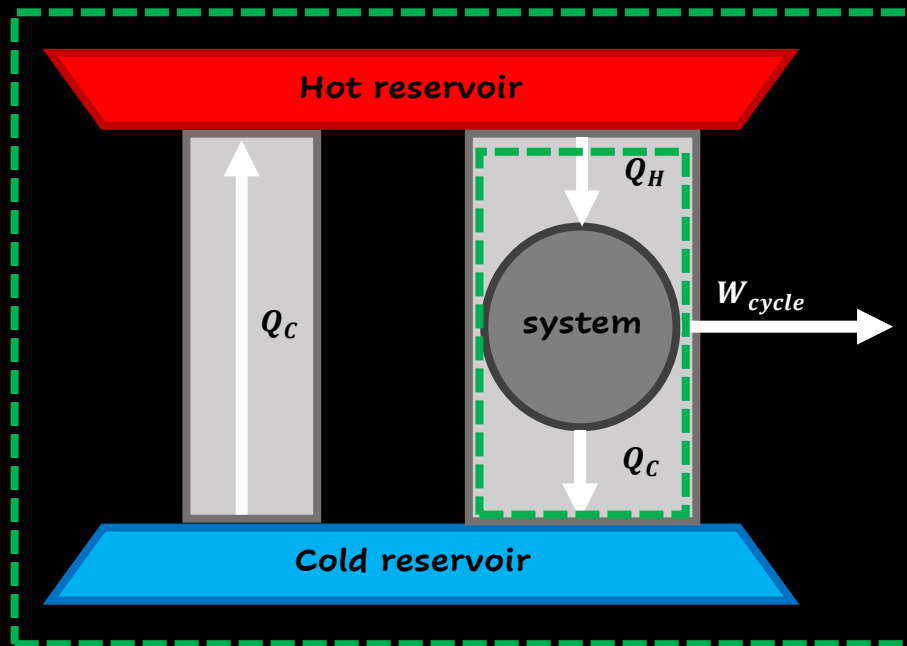
$W_{cycle} < 0$  if the cycle is not irreversible

---

### The equivalence of the Clausius and Kelvin–Planck statements

- The combined system can be regarded as executing a cycle because one part undergoes a cycle, and the other two parts experience no net change in their conditions.
- Moreover, the combined system receives energy by heat transfer from a single reservoir, the hot reservoir, and produces an equivalent amount of work.
- the combined system violates the Kelvin–Planck statement. Thus, a violation of the Clausius statement implies a violation of the Kelvin–Planck statement.





Entropy- extensive property that is affected by the second law

- like mass and energy entropy can be transferred across the system boundary (through heat/mass transfer)
- *entropy is produced (or generated) within systems whenever nonidealities (called irreversibility's) such as friction are present*
- entropy statement of the second law states- It is impossible for any system to operate in a way that entropy is destroyed.

reversible if both the system and surroundings can be returned to their initial states. Irreversible processes are the subject of the present discussion.

irreversible if the system and all parts of its surroundings cannot be exactly restored to their respective initial states after the process has occurred

1. Heat transfer through a finite temperature difference
2. Unrestrained expansion of a gas or liquid to a lower pressure
3. Spontaneous chemical reaction
4. Spontaneous mixing of matter at different compositions or state
5. Friction—sliding friction as well as friction in the flow of fluids
6. Electric current flow through a resistance
7. Magnetization or polarization with hysteresis
8. Inelastic deformation

internal irreversibilities- are irreversibility's that occur within the system

External irreversibilities- are irreversibility's that occur within the surroundings

## Thermal efficiency

---

$$\eta = \frac{W_{cycle}}{Q_H}$$

---

- The thermal efficiency of an irreversible power cycle is always less than the thermal efficiency of a reversible power cycle when each operates between the same two thermal reservoirs.
  - All reversible power cycles operating between the same two thermal reservoirs have the same thermal efficiency.
- 

$$\beta = COP_{ref} = \frac{Q_C}{W_{cycle}} = \frac{Q_C}{Q_H - Q_C}$$

$$\gamma = COP_{HP} = \frac{Q_H}{W_{cycle}} = \frac{Q_H}{Q_H - Q_C}$$

---

1. The coefficient of performance of an irreversible refrigeration cycle is always less than the coefficient of performance of a reversible refrigeration cycle when each operates between the same two thermal reservoirs.
2. All reversible refrigeration cycles operating between the same two thermal reservoirs have the same coefficient of performance.

For a reversible power cycle, the ratio of the heat transfers  $\left(\frac{Q_C}{Q_H}\right)$  depends only on the temperatures of the two reservoirs  $\left(\frac{Q_C}{Q_H}\right)_{rev} = f(T_C, T_H)$

- The developed the creation of the kelvin scale where  $\left(\frac{Q_C}{Q_H}\right)_{rev} = \frac{T_C}{T_H}$

Maximum Performance Measures for Cycles operating between two reservoirs

$$\eta_{max} = 1 - \frac{T_C}{T_H}$$

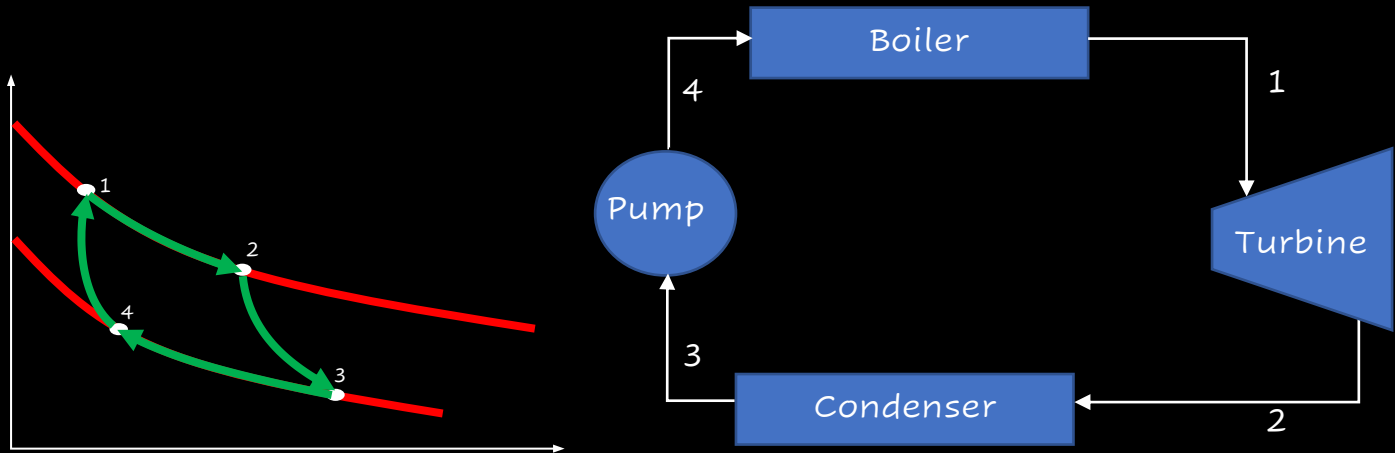
- This is known as the Carnot efficiency
- Thermal efficiency increases as  $T_H$  increases
- Conventional power cycles have a thermal efficiencies ranging up to 40%

$$\beta_{max} = COP_{ref, re} = \frac{T_C}{T_H - T_C}$$

$$\gamma_{max} = COP_{HP,rev} = \frac{T_H}{T_H - T_C}$$

Carnot Cycle- system executing the cycle undergoes a series of four internally reversible processes (2 adiabatic alternated with two isothermal processes)

- 1-2 isothermal expansion at  $T_H$
- 2-3 adiabatic expansion to  $T_C$
- 3-4 isothermal compression at  $T_C$
- 4-1 adiabatic compression to  $T_H$



- The devices involved in the system don't matter
- What does matter is
  - the Carnot cycle *always* has the same four internally reversible processes: two adiabatic processes alternated with two isothermal processes.
  - the thermal efficiency of the Carnot power cycle is *always* given by Eq. 5.9 in terms of the temperatures evaluated on the Kelvin or Rankine scale.

## Clausius Inequality

$$\left( \int_b \frac{\delta Q_{in}}{T} \right)_{cycle} \leq 0$$

$$\left( \int_b \frac{\delta Q_{in}}{T} \right)_{cycle} = -\sigma_{cycle}$$

$$\left( \int_b \frac{\delta \dot{Q}_{in}}{T} \right)_{cycle} = -\dot{\sigma}_{cycle}$$

$\sigma$  is the entropy production/generation

- $\sigma > 0$  process is irreversible (natural process)
- $\sigma = 0$  process is reversible
- $\sigma < 0$  process is impossible

## Chapter 6- Entropy

$$\Delta S = \left( \int_1^2 \frac{\delta Q}{T} \right)_{int rev}$$

Super-heated vapor  $s = s(T, p)$

Saturated liquid vapor mixture  $s = (1 - x)s_f + xs_g$

Condensed liquid  $s = s(T, p) \approx s_f(T)$

TdS equations

- $Tds = dh - vdp$
- $Tds = du + pdv$

Incompressible substance

- $ds = \frac{c(T)dT}{T}$
- When specific heat is constant  $\Delta s = c \ln\left(\frac{T_2}{T_1}\right)$

Ideal Gas

- $pv = RT \rightarrow pdv + vdp = RT$
- $du = c_v(T)dT$
- $dh = c_p(T)dT$

---

$$\begin{aligned} ds &= \frac{c_v(T)dT}{T} + R \left( \frac{dv}{v} \right) \\ \Delta s &= \int_{T_1}^{T_2} \frac{c_v(T)dT}{T} + R \ln\left(\frac{v_2}{v_1}\right) \\ \Delta s &= s^\circ(T_2) - s^\circ(T_1) + R \ln\left(\frac{v_2}{v_1}\right) \end{aligned}$$

$$\begin{aligned} ds &= \frac{c_p(T)dT}{T} - R \left( \frac{dp}{p} \right) \\ \Delta s &= \int_{T_1}^{T_2} \frac{c_p(T)dT}{T} - R \ln\left(\frac{p_2}{p_1}\right) \\ \Delta s &= s^\circ(T_2) - s^\circ(T_1) - R \ln\left(\frac{p_2}{p_1}\right) \end{aligned}$$

---

Isentropic Ideal Gas ( $ds = 0$ )

- $0 = s^\circ(T_2) - s^\circ(T_1) - R \ln\left(\frac{p_2}{p_1}\right)$

$$\frac{p_2}{p_1} = \frac{p_r(T_2)}{p_r(T_1)}$$

$$\frac{v_2}{v_1} = \frac{v_r(T_2)}{v_r(T_1)}$$

Perfect gas

$$\Delta s = c_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)$$

$$\Delta s = c_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{p_2}{p_1}\right)$$

- Isentropic Ideal Gas ( $ds = 0$ ) and  $k = \frac{c_p}{c_v}$

$$\frac{p_2}{p_1} = \left(\frac{T_2}{T_1}\right)^{\frac{k}{k-1}}$$

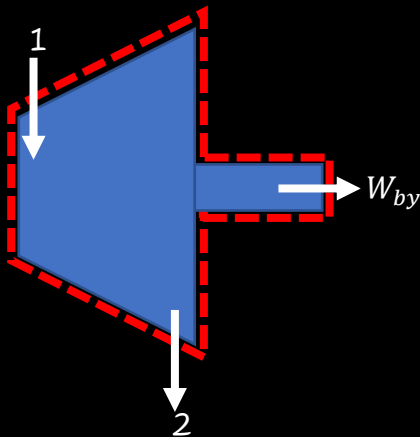
$$\frac{v_2}{v_1} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{1-k}}$$

$$\frac{p_2}{p_1} = \left(\frac{v_2}{v_1}\right)^{-k}$$

Device Isentropic Efficiencies

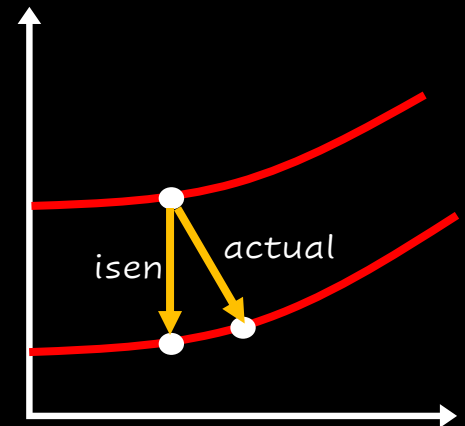
- Turbine

- $\eta_{\text{turbine}} = \frac{\dot{W}_{\text{actual}}}{\dot{W}_{\text{isen}}} = \frac{h_1 - h_2}{h_1 - h_{2s}}$
- $\eta \approx 0.7 - 0.9$  (always less than 1)



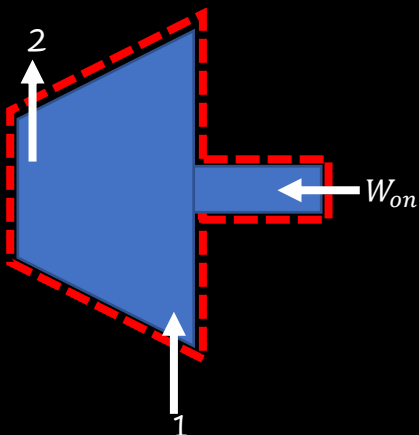
Assumptions

- adiabatic
- internally reversible
- isentropic



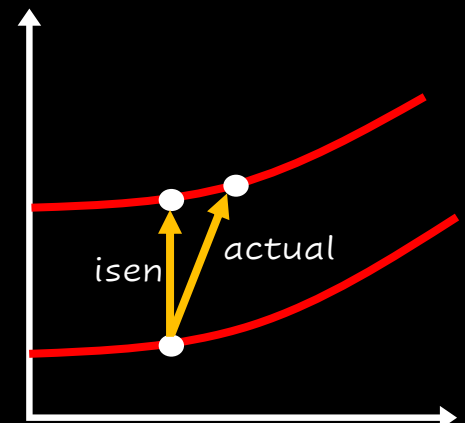
- Compressor

- $\eta_{\text{compressor}} = \frac{\dot{W}_{\text{actual}}}{\dot{W}_{\text{isen}}} = \frac{h_1 - h_{2s}}{h_1 - h_2}$
- $\eta \approx 0.75 - 0.85$  (always less than 1)



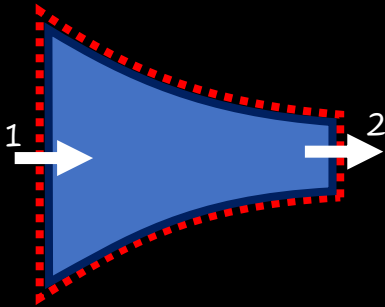
Assumptions

- adiabatic
- internally reversible
- isentropic



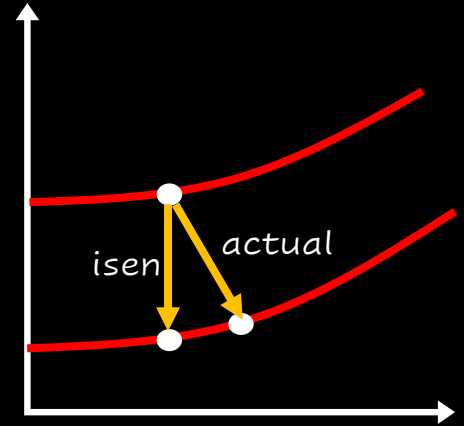
- Nozzle

- $\eta_{nozzle} = \frac{\frac{1}{2}V_2^2}{\frac{1}{2}V_{2s}^2} = \frac{\frac{1}{2}V_2^2 + h_1 - h_2}{\frac{1}{2}V_2^2 + h_1 - h_{2s}}$
- $\eta \approx 0.95$  (always less than 1)



#### Assumptions

- adiabatic
- internally reversible
- isentropic

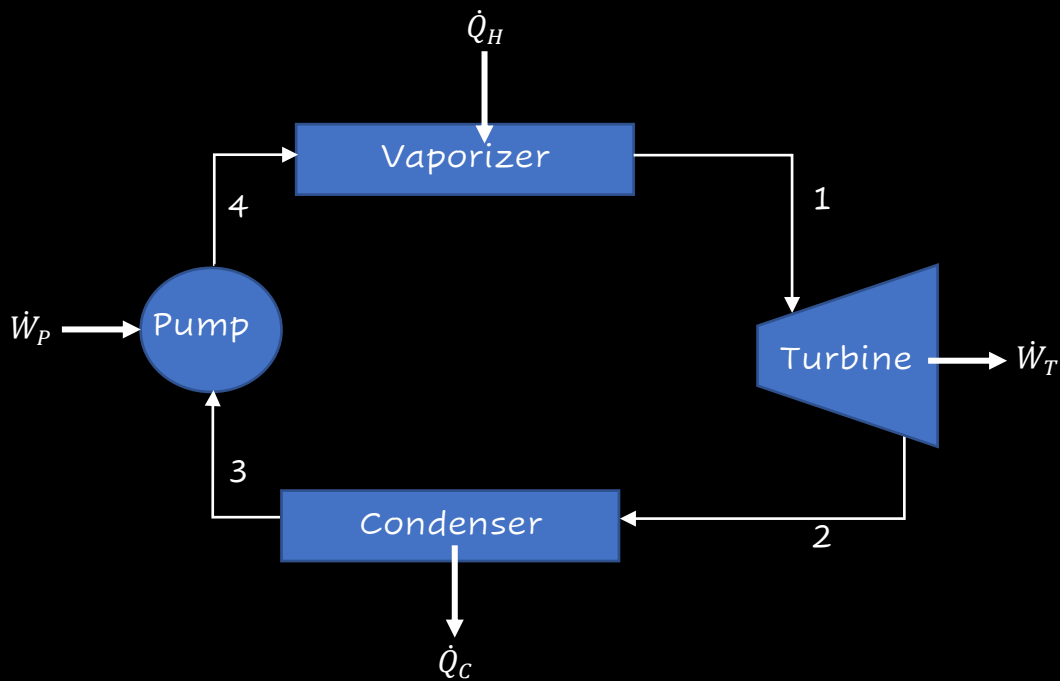


#### Bernoulli's Equation

- Assume: Internally reversible  $\dot{\sigma} = 0$ , Steady state  $\frac{ds}{dt} = 0$ , One inlet one outlet, Difference element
  - $0 = \frac{\delta \dot{Q}_{into}}{T} - \dot{m}ds$
- $Q_{in} = \dot{m} \int_1^2 T ds$ 
  - $\frac{W_{on}}{m} = \int_1^2 v dp + \Delta ke + \Delta pe$
- Incompressible substance
- $\frac{W_{on}}{m} = v\Delta p + \Delta ke + \Delta pe$
- Passive System
  - $0 = \int_1^2 v dp + \Delta ke + \Delta pe$
- Negligible change in kinetic and potential energy
  - $\frac{W_{on}}{m} = \int_1^2 v dp$

## Chapter 7- Cycles

### Rankine Cycle



$$\text{Turbine: } \dot{W}_{out} = \dot{m}(h_1 - h_2)$$

$$\text{Pump: } \dot{W}_{in} = \dot{m}(h_4 - h_3)$$

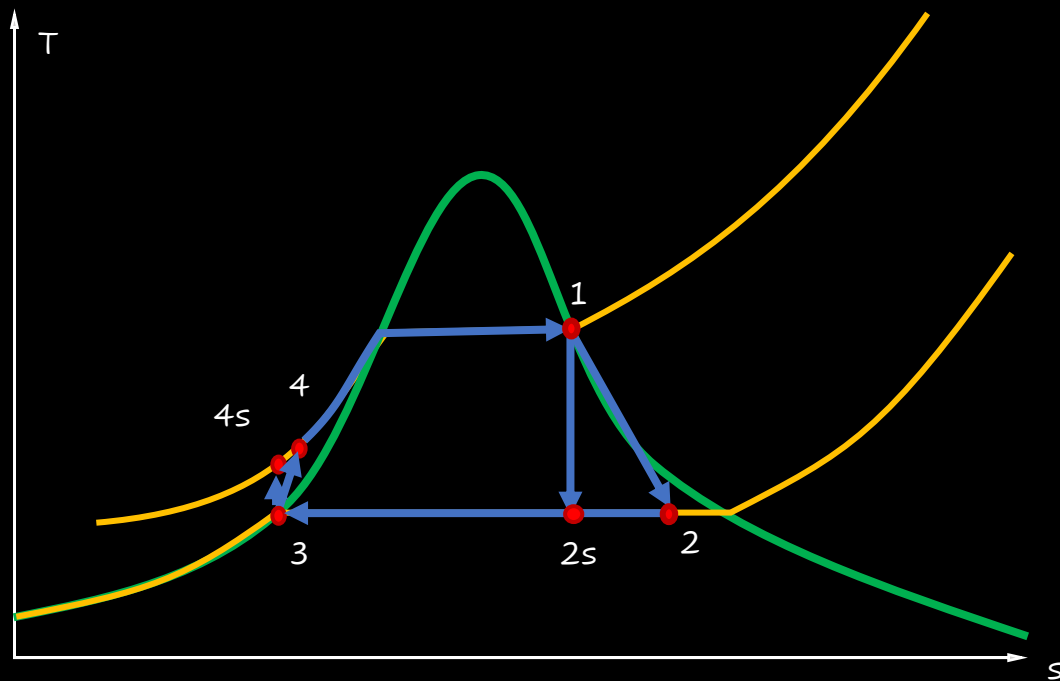
$$\text{Vaporizer: } \dot{Q}_{in} = \dot{m}(h_1 - h_4)$$

$$\text{Condenser: } \dot{Q}_{out} = \dot{m}(h_2 - h_3)$$

$$\text{Thermal efficiency of power cycle: } \eta = \frac{\dot{W}_{out,net}}{\dot{Q}_{in}}$$

## Ideal Rankine Cycle

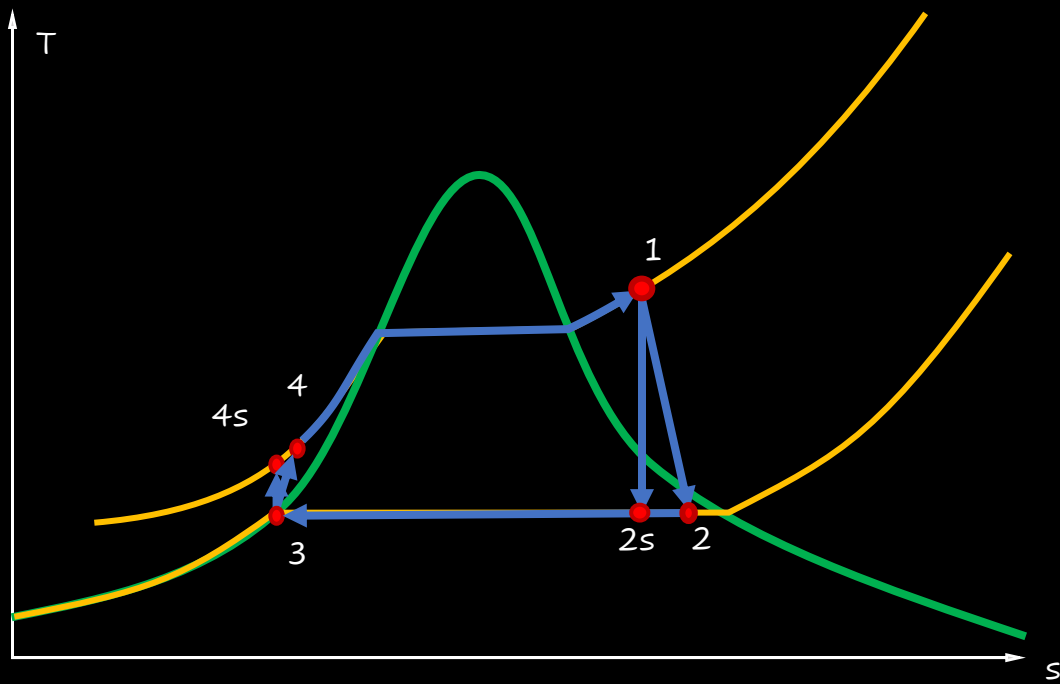
- Process 1-2s: isentropic expansion of the working fluid from saturated vapor through the turbine
- Process 2s-3: heat transfer from the working fluid as it flows at constant pressure through the condenser to a saturated liquid state
- Process 3-4s: isentropic compression of the working fluid in the pump in the compressed liquid region
- Process 4s-1: heat transfer to the working fluid as it flows at constant pressure through the boiler
- The thermal efficiency of the power cycle increases as the average temperature at which the heat is added in the boiler increases and the average temperature (or pressure) at which the heat is rejected in the condenser decreases



- The Carnot cycle has a larger thermal efficiency than an ideal Rankine cycle since the average temperature at which heat is added in the boiler is smaller for the Rankine cycle due to the path from 4s-1
- Increasing the average temperature at which heat is added may be achieved by increasing the boiler pressure or by moving state 1 into a super-heated vapor phase. Increasing the boiler pressure can be costly due to the increased stress on the pipe system however moving state 1 into a super-heated vapor phase is relatively easy. Moving into the superheated vapor cycle is known as Rankine cycle with superheat
- The lowest possible condenser temperature/pressure corresponds to just larger than the conditions of the surrounding since this is where the heat is being rejected

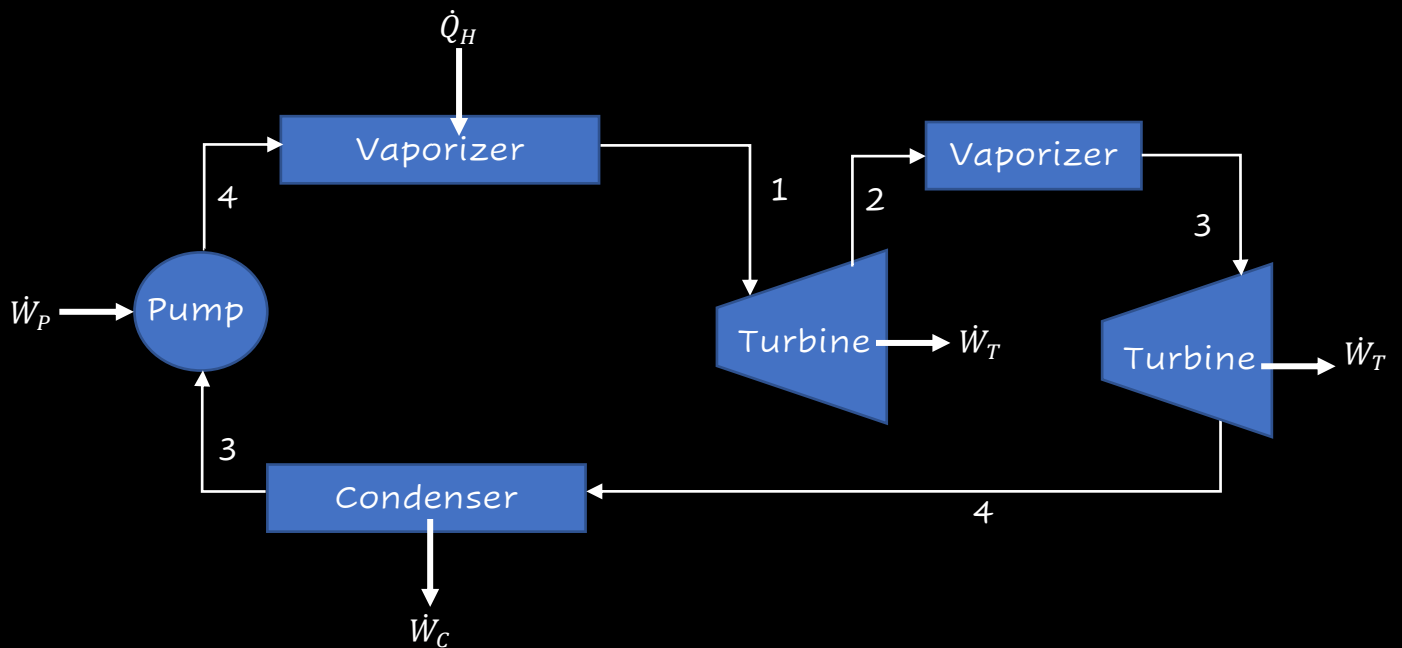
### Rankine Cycle with Superheat

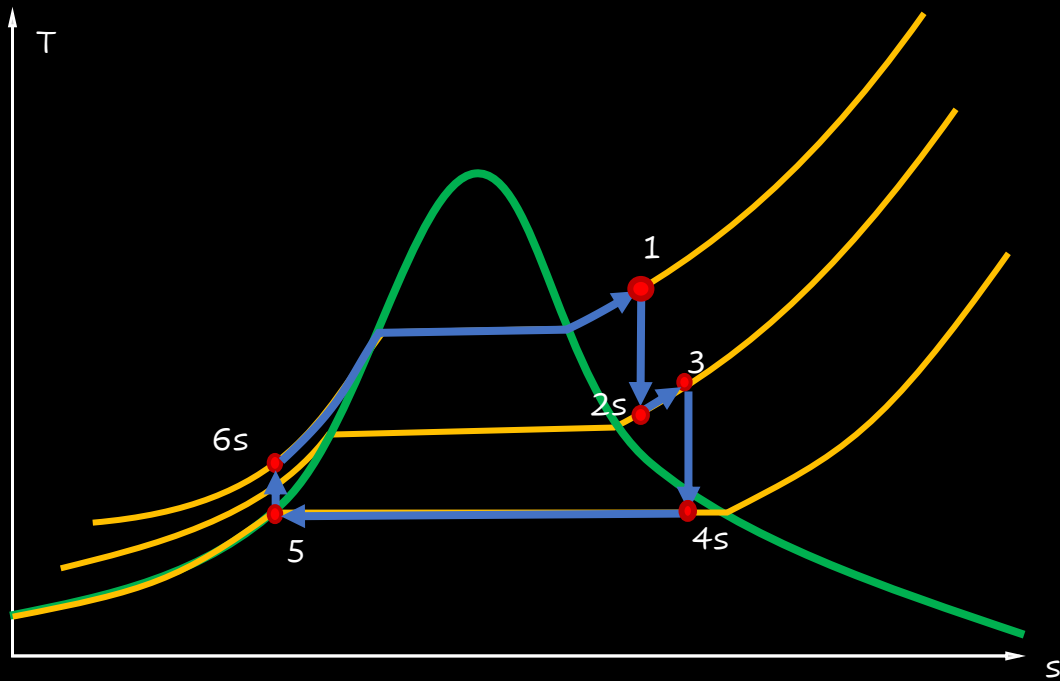




- Larger average temperature at which heat is added results in larger efficiency

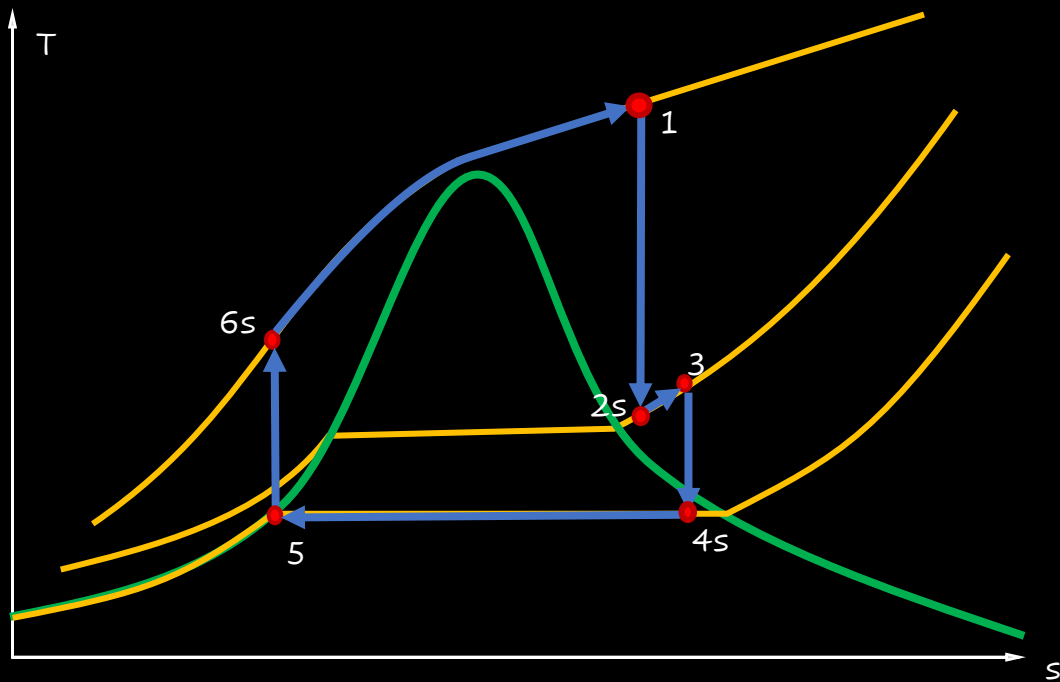
Rankine cycle with reheat





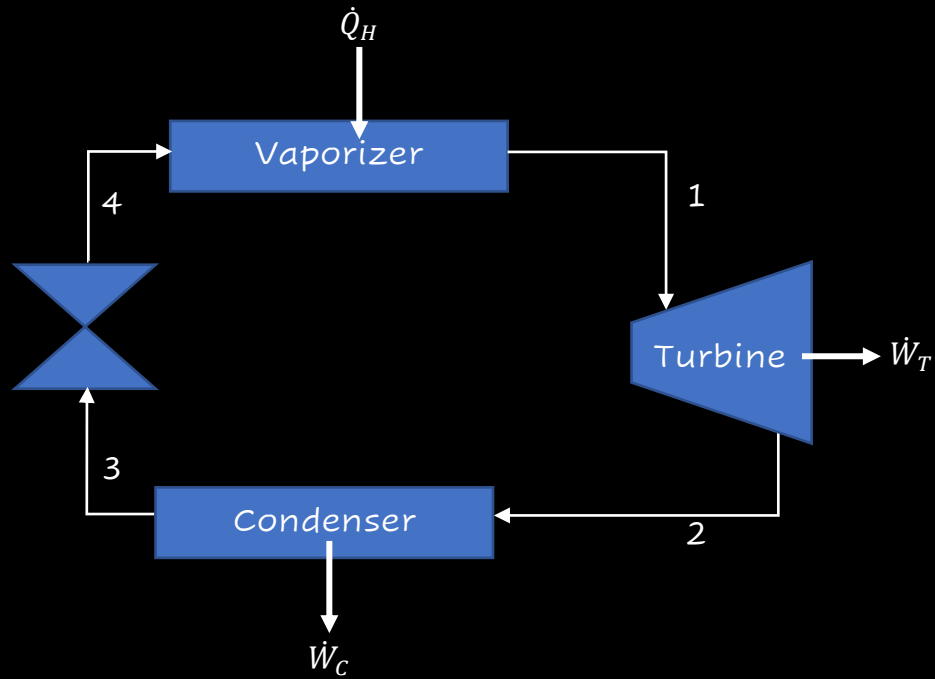
- Larger average temperature at which heat is added in a Reheat Rankine cycle results in a larger efficiency as compared to an ordinary Rankine cycle

#### Rankine Cycle with Supercritical Reheat



- The larger average temperature at which heat is added in a Supercritical Rankine cycle results in a larger efficiency than an ordinary Rankine Cycle
- Efficiencies up to 47% can be achieved in supercritical Rankine cycle power plant

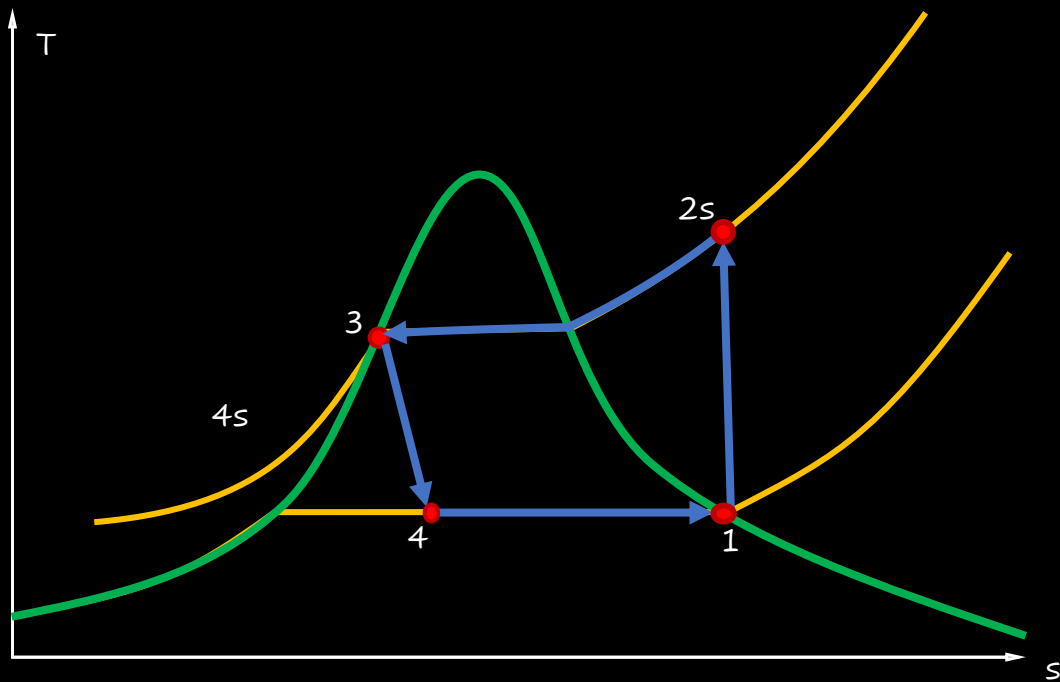
## Vapor Compression Refrigeration Cycle



$$\frac{\dot{W}_{on\ comp}}{\dot{m}} = h_2 - h_1$$

$$\frac{\dot{Q}_{added}}{\dot{m}} = h_1 - h_4 \text{ where } \dot{Q}_{added} \text{ is known as the refrigeration capacity}$$

$$\frac{\dot{Q}_{removed}}{\dot{m}} = h_2 - h_3$$

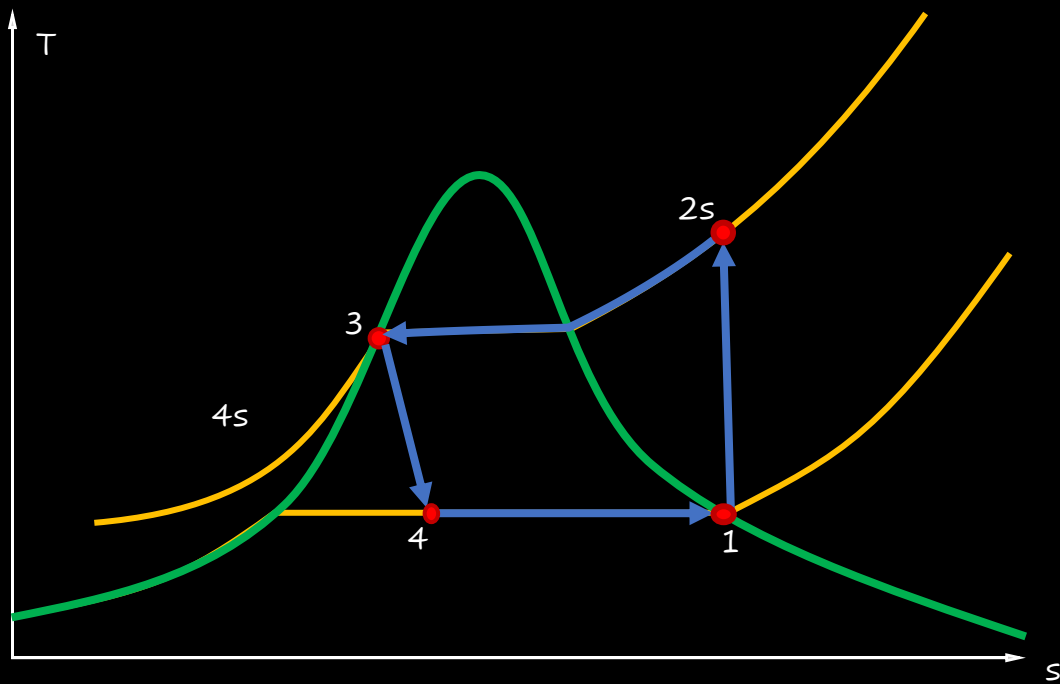
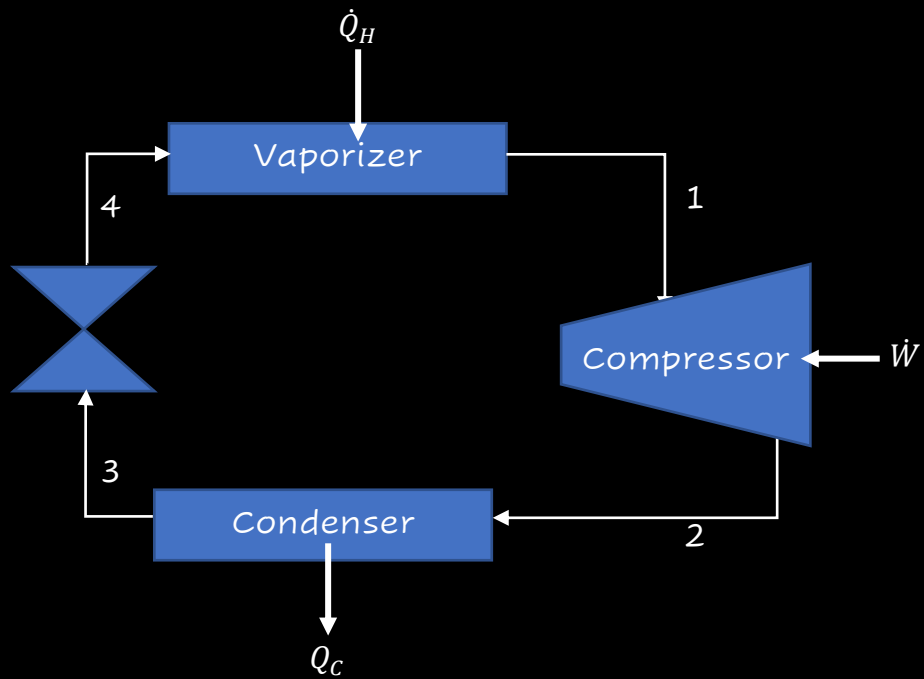


$$h_4 = h_3 \text{ throttling process}$$

$$COP_{ref} = \frac{h_1 - h_4}{h_2 - h_1}$$

*Operate best in dry vapor conditions rather than two phase region*

## Heat Pumps



$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{in}}$$

$$COP_{HP,rev} = COP_{HP,max} = \frac{\dot{T}_H}{\dot{T}_H - \dot{T}_C}$$

As  $T_C$  increases COP increases

---

A/C

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$$COP_R = \frac{\dot{Q}_C}{\dot{W}_{in}}$$

$$\text{Energy Efficiency Ratio (EER)} = \frac{\dot{Q}_C}{\dot{W}_{in}} = \left[ \frac{\text{Btu}}{\text{W} \cdot \text{h}} \right] \quad (17.1 - 21.1)$$

$$\text{Seasonal Energy Efficiency Ratio (SEER)} = \frac{\dot{Q}_C}{\dot{W}_{in}} \Big|_{\text{season}} = \left[ \frac{\text{Btu}}{\text{W} \cdot \text{h}} \right] \quad (18 - 27.5)$$

( $T_H$  changes over the season)

---

HP

---

$$COP_{HP} = \frac{\dot{Q}_H}{\dot{W}_{in}} \quad (3.1 - 4.1)$$

$$\text{Heating Seasonal Performance Factor (HSPF)} = \frac{\dot{Q}_H}{\dot{W}_{in}} \Big|_{\text{season}} = \left[ \frac{\text{Btu}}{\text{W} \cdot \text{h}} \right] \quad (8.5 - 12.5)$$

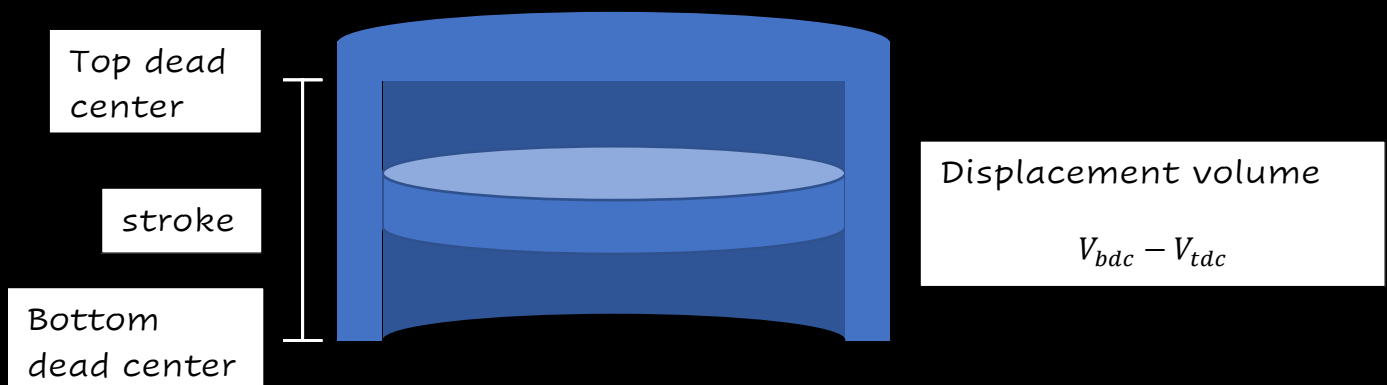
( $T_C$  changes over the season)

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Otto Cycle- spark ignition engine

Diesel Cycle- compression-ignition engine

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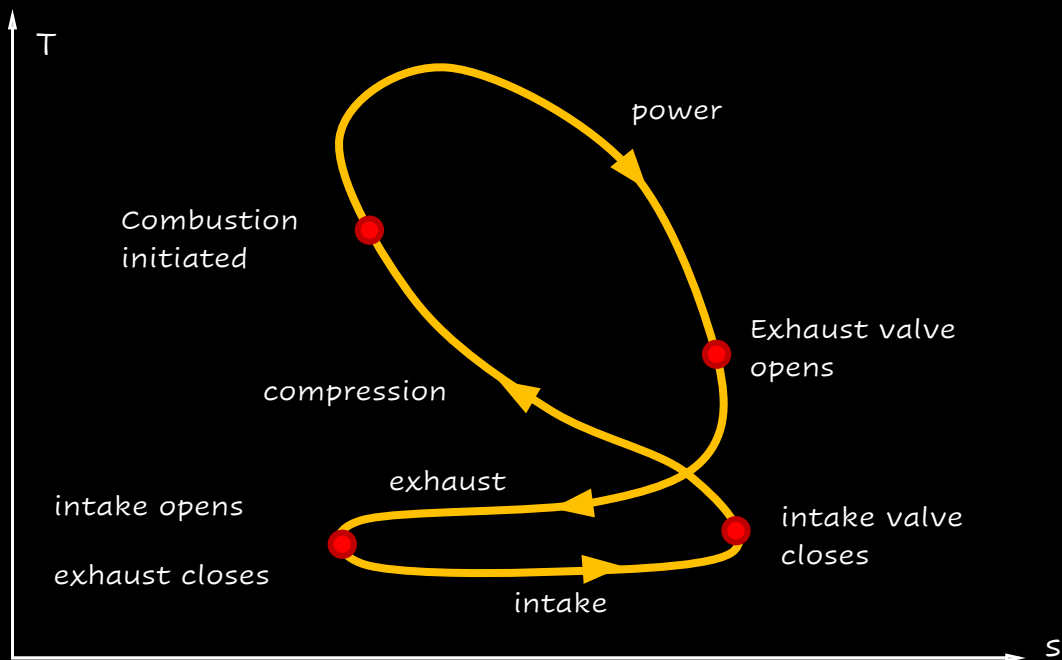


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Air Standard Analysis

- Highly simplified to provide qualitative understanding
- Fixed mass of air modeled as an ideal gas
- Combustion modeled as a heat addition process
- No intake or exhaust process

- Exhaust modeled as a constant volume heat removal process
- All processes are internally reversible

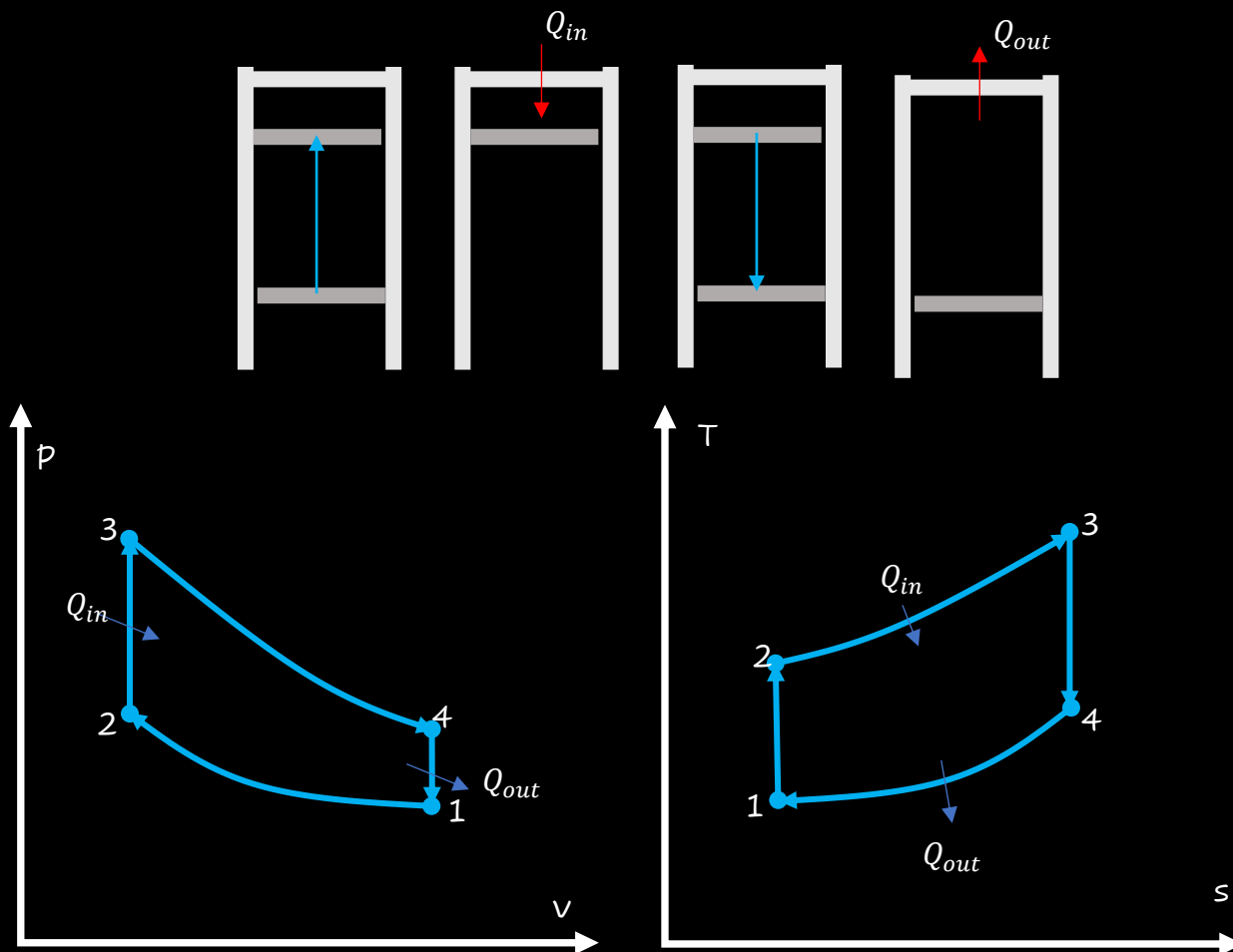


$$\text{Mean Effective Pressure (MEP)} = \frac{W_{out,net}}{V_{bdc} - V_{tdc}}$$

$$\text{compression ratio } r = \frac{V_{bdc}}{V_{tdc}}$$

## Otto Cycle

- Process 1-2: isentropic compression of the working fluid as the piston moves from bottom dead center to top dead center ( $-w_{out} = u_2 - u_1$ )
- Process 2-3: constant volume heat transfer to the working fluid while the piston is at top dead center (ignition of the fuel-air mixture) ( $q_{in} = u_3 - u_2$ )
- Process 3-4: isentropic expansion (power stroke) ( $-w = u_4 - u_3$ )
- Process 4-1: constant volume heat transfer from the working fluid while the piston is at bottom dead center (mimicking the removal and replenishing of the air in the cylinder) ( $-q_{out} = u_1 - u_4$ )



$$\eta = \frac{W_{out,net}}{Q_{in}} = 1 - \frac{Q_{out\ 4-1}}{Q_{in\ 2-3}}$$

$$MEP = \frac{W_{out,net}}{V_{bdc} - V_{tdc}}$$

$$r = \frac{v_{bdc}}{v_{tdc}}$$

$$\text{For isentropic compression (and expansion)} \ r = \frac{v_1}{v_2} = \frac{v_4}{v_3} = \frac{v_r(T_1)}{v_r(T_2)} = \frac{v_r(T_4)}{v_r(T_3)}$$

$$\text{For Perfect Gas } \frac{T_2}{T_1} = r^{k-1} \text{ and } \frac{T_4}{T_3} = r^{1-k} \text{ so } \eta_{otto} = 1 - \frac{T_1}{T_2} = 1 - \frac{1}{r^{k-1}}$$

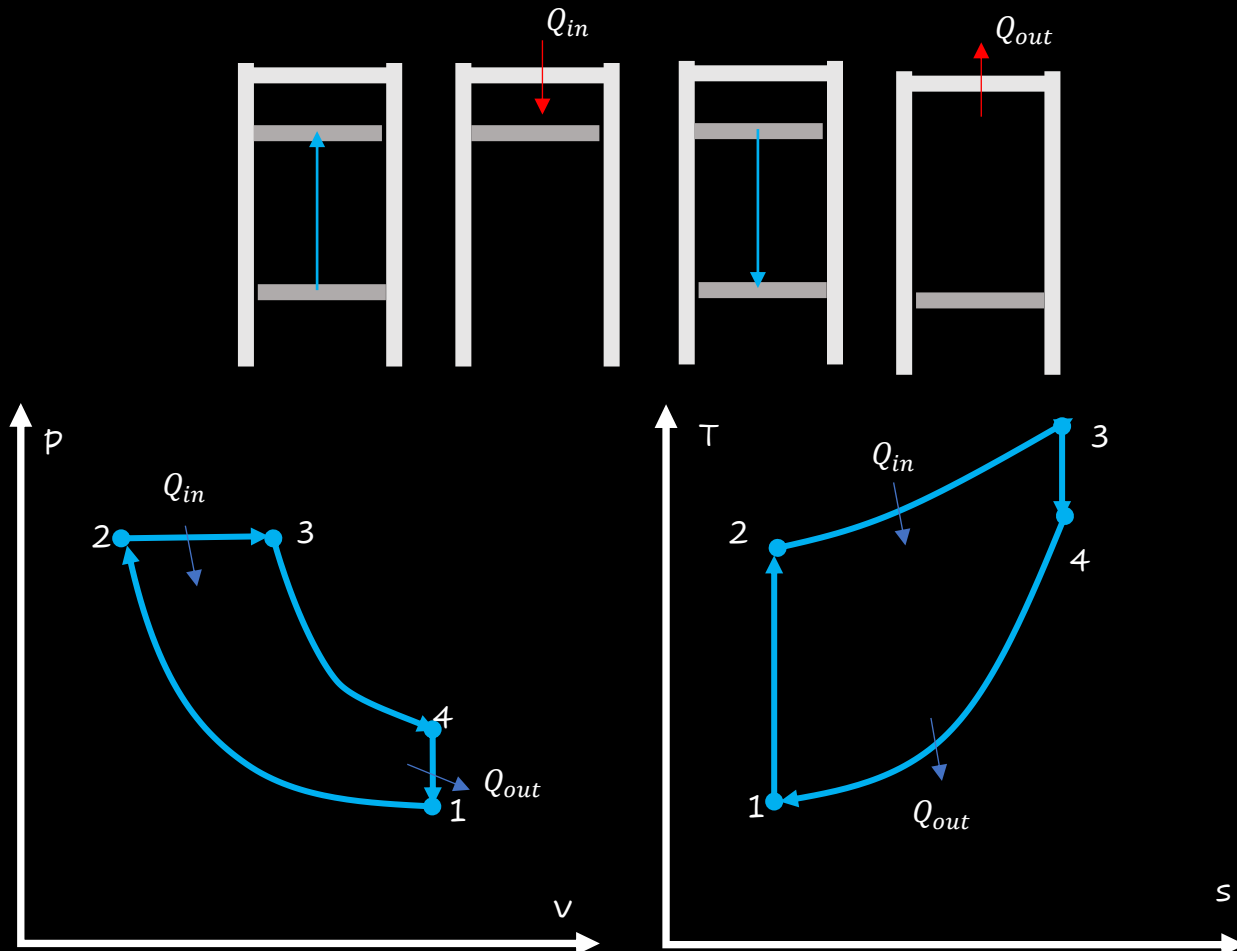
$r$  is typically between 8-10

$\eta$  is typically between 30%-35%

## Diesel Cycle

- Process 1-2: isentropic compression of the working fluid as the piston moves from bottom dead center to top dead center ( $-w_{out} = u_2 - u_1$ )

- Process 2-3: constant pressure heat transfer to the working fluid while the piston is at top dead center (ignition of the fuel-air mixture) ( $q_{in} = h_3 - h_2$ )
- Process 3-4: isentropic expansion (power stroke) ( $-w = u_4 - u_3$ )
- Process 4-1: constant volume heat transfer from the working fluid while the piston is at bottom dead center (mimicking the removal and replenishing of the air in the cylinder) ( $q_{in} = u_1 - u_4$ )



$$\eta = \frac{W_{out,net}}{Q_{in}} = 1 - \frac{u_4 - u_1}{h_3 - h_2}$$

$$r_c = \frac{v_3}{v_2} = \frac{T_3}{T_2}$$

$r$  is typically between 12-25

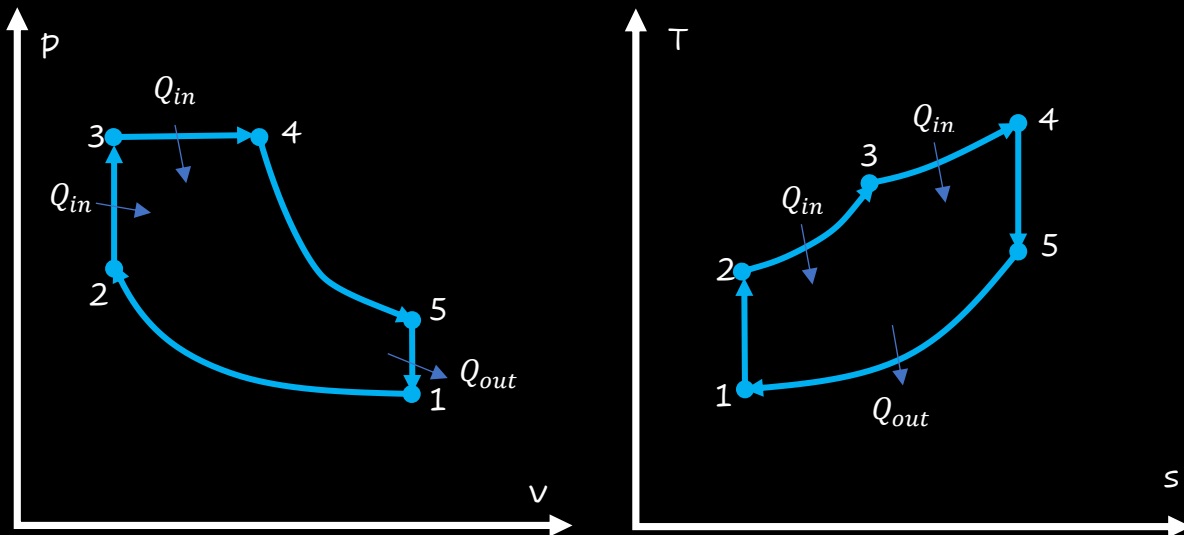
$\eta$  is typically between 40%-45%

## Dual Cycle

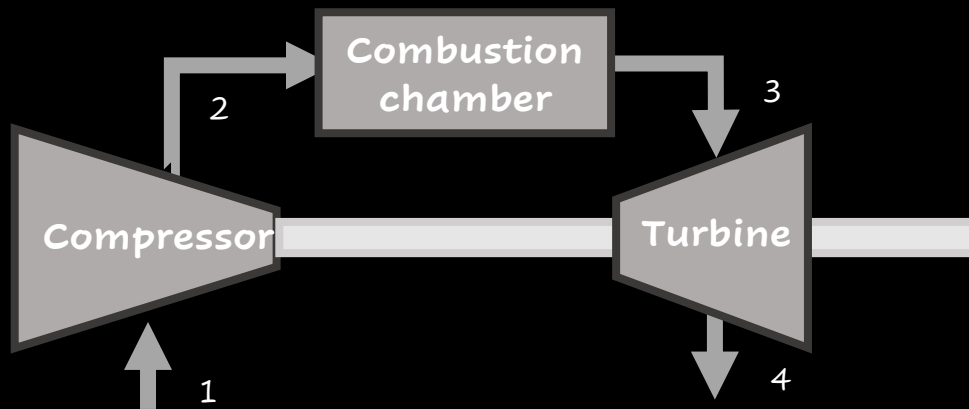
- Process 1-2: isentropic compression of the working fluid as the piston moves from bottom dead center to top dead center ( $-w_{out} = u_2 - u_1$ )
- Process 2-3: constant volume heat transfer to the working fluid while the piston is at top dead center (ignition of the fuel-air mixture) ( $q_{in} = u_3 - u_2$ )

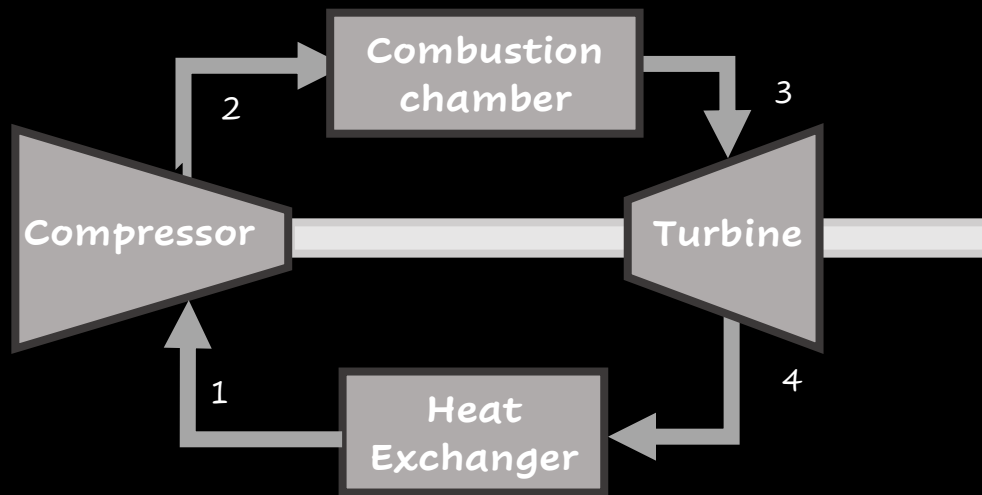


- Process 3-4: constant pressure heat transfer to the working fluid while the piston is at top dead center (ignition of the fuel-air mixture) ( $q_{in} = h_4 - h_3$ )
- Process 4-5: isentropic expansion (power stroke) ( $-w = u_5 - u_4$ )
- Process 5-1: constant volume heat transfer from the working fluid while the piston is at bottom dead center (mimicking the removal and replenishing of the air in the cylinder) ( $q_{in} = u_1 - u_5$ )



## Brayton Cycle





$$\frac{\dot{W}_{by\ turbine}}{\dot{m}} = h_3 - h_4 \text{ and } \frac{\dot{W}_{on\ compressor}}{\dot{m}} = h_2 - h_1$$

$$\frac{\dot{Q}_{added}}{\dot{m}} = h_3 - h_2 \text{ and } \frac{\dot{Q}_{removed}}{\dot{m}} = h_4 - h_1$$

$$\eta = \frac{\dot{W}_{net,out}}{\dot{Q}_{added}} = 1 - \frac{\dot{Q}_{removed}}{\dot{Q}_{added}}$$

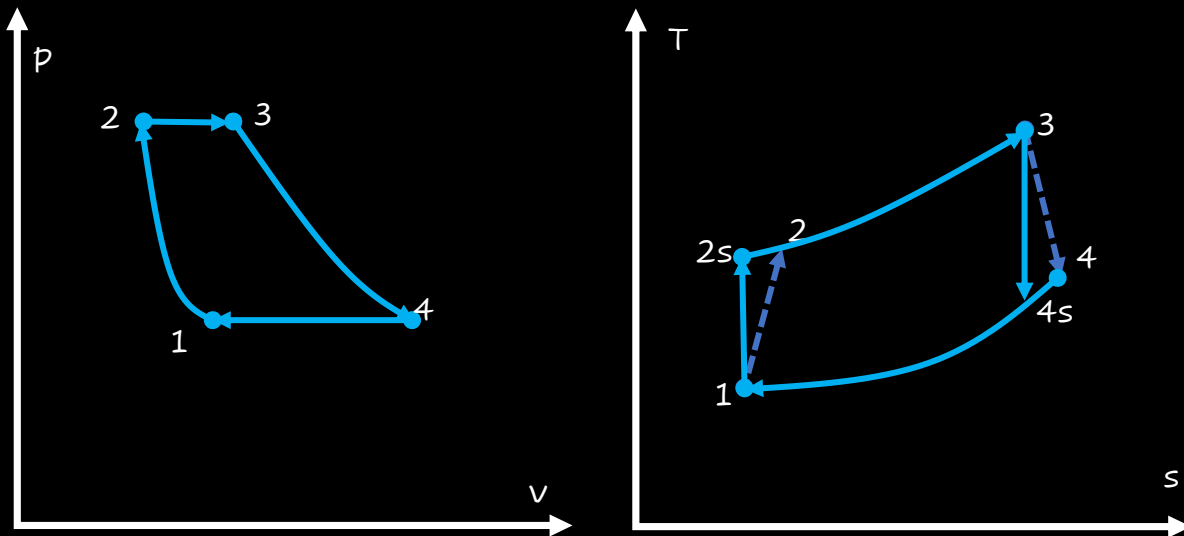
$$\text{Back work ratio } bwr = \frac{\dot{W}_{on\ comp}}{\dot{W}_{by\ turb}} = \frac{h_2 - h_1}{h_3 - h_4}$$

*Typical gas turbine bwr 40%-80%*

*Typical vapor power plant (rankine cycle) bwr 1%-2%*

### Ideal Air-Standard Brayton Cycle

- Process 1-2s: isentropic compression of the working fluid through the compressor
- Process 2s-3: constant pressure heat transfer to the working fluid as it flows through the heat exchanger
- Process 3-4s: isentropic expansion of the working fluid through the turbine
- Process 4s-1: constant pressure heat transfer from the working fluid as it flows through the heat exchanger



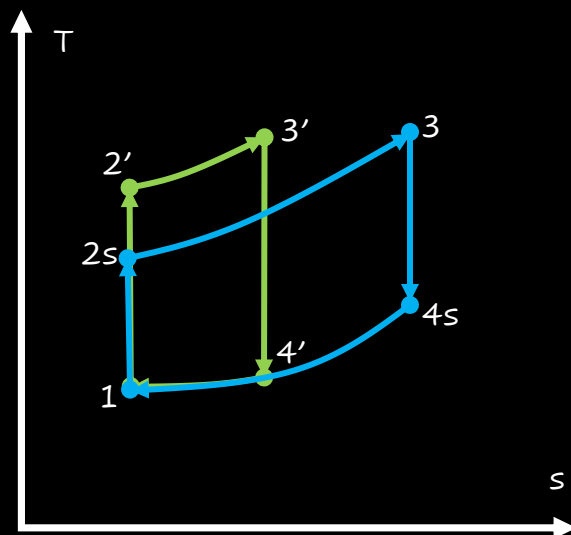
$$\frac{p_2}{p_1} = \frac{p_r(T_{2s})}{p_r(T_1)} \rightarrow p_r(T_{2s}) = p_r(T_1) \left( \frac{p_2}{p_1} \right)$$

$$\frac{p_4}{p_3} = \frac{p_r(T_{4s})}{p_r(T_3)} \rightarrow p_r(T_{4s}) = p_r(T_3) \left( \frac{p_2}{p_1} \right) = p_r(T_3) \left( \frac{p_4}{p_3} \right)$$

$$\eta = \frac{\dot{W}_{out,net}}{\dot{Q}_{in}} = 1 - \frac{h_4 - h_1}{h_3 - h_2}$$

$$\text{Typical } \eta = 35\% - 60\%$$

- A larger pressure ratio across the compressor gives a larger efficiency
- Increasing the temperature leading into the turbine also leads to a larger efficiency

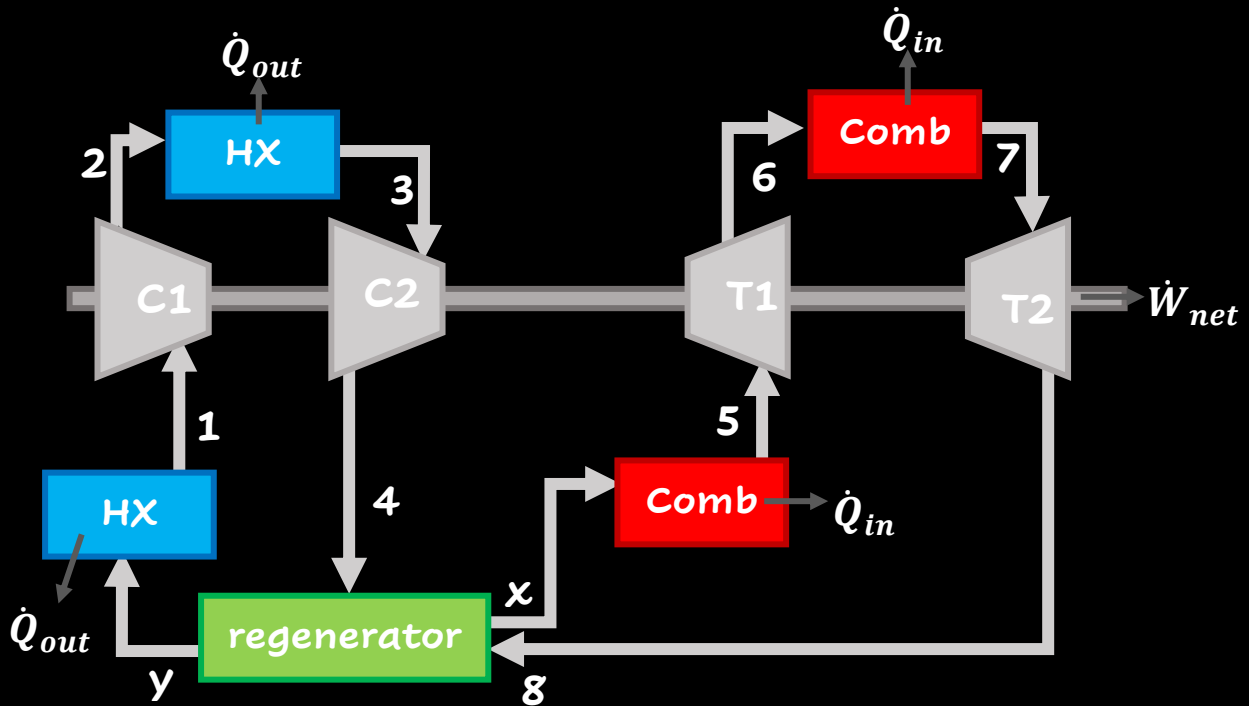


Cycle A: 1-2'-3-4'

Cycle B: 1-2s-3-4s

The area enclosed by cycle B is larger than that of cycle A. Cycle B has a larger work power per unit mass flow rate. For cycle A to produce the same amount of work a larger mass flow rate would be required

## Brayton Cycle Improvements



- Intercooling- between successive compressor stages is used to decrease the specific volume of the working fluid
  - Temperature decreases volume decreases (and the work required decreases)
- Reheating between successive turbine stages is used to increase the specific volume of the working fluid
  - Temperature increases volume increases (and the work produced increases)
- Regenerator
  - Working fluid is preheated in a heat exchanger using combustion gas to reduce the amount of heat (and fuel) needed in the combustor
  - Regenerator effectiveness  $\eta_{reg} = \frac{h_x - h_4}{h_8 - h_4}$

