THERMODYNAMICS AND STATISTICAL MECHANICS

CHAPTER 3 –THERMODYNAMICS MACHINES

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Thermodynamics Machines

There are 3 main types of thermodynamics machines:

- **Heat Engine** : A device that absorbs heat from a high-temperature reservoir, converts part of this energy into useful mechanical work, and rejects the remaining heat to a lower-temperature reservoir. (*Heat engines do not "burn fuel" in general; they convert heat into work*.)
- **Refrigerator**: A device that removes heat from a low-temperature region and transfers it to a higher-temperature region. This process requires external work to operate.
- **Heat Pump**: Operates on the same physical principle as a refrigerator, but the desired output is the heat delivered to the high-temperature region. Commonly used for heating buildings by extracting heat from colder surroundings (air, ground, or water).

Cyclic Operation and Energy Balance

Since the system returns to its initial state, reversal process, after one cycle:

$$\Delta U_{\text{cycle}} = 0$$

From the First Law of Thermodynamics:

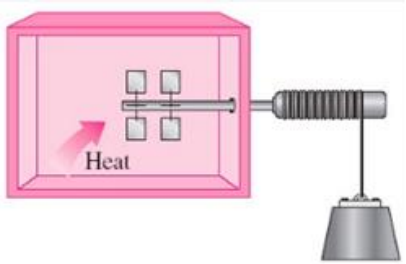
$$Q_{net} = W_{\text{net}}$$

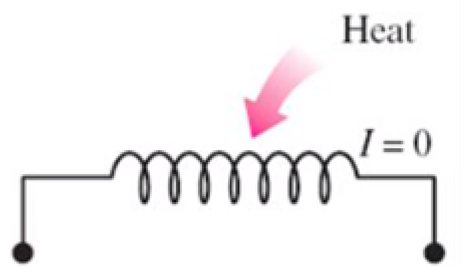
The net heat absorbed by the machine during a cycle equals the net work done by the machine.

Irreversible Process

A process that cannot be undone without leaving a permanent change in the system or surroundings. Such processes either involve non-quasistatic changes, dissipative effects

.Example of Irreversible Process:.





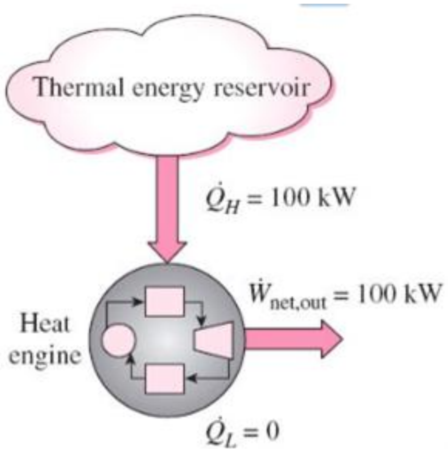
Action	**Spontaneous Result**	**Impossible Reverse**
Coffee in a Room	Coffee cools down.	Coffee absorbs room heat to get hotter.
Paddle Wheel	Rotation generates heat (friction).	Adding heat makes the wheel spin.
Electric Wire	Current generates heat (I^2R).	Heating a wire generates a current.

These examples reflect 2nd law of thermodynamics: Every real-world process increases the disorder of the universe, $\Delta S \geq 0$.

Thermodynamics Machines

- **Kelvin-Planck Statement (Heat Engine Statement)**

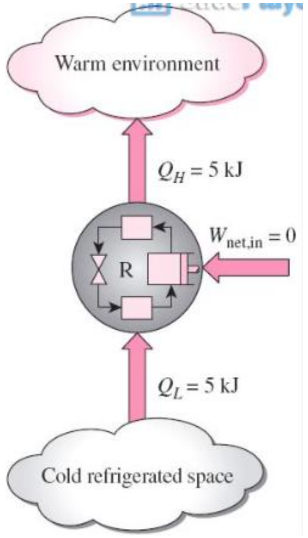
The Kelvin-Planck statement of Second Law of Thermodynamics states: It is impossible for any process to have as its sole effect the absorption of heat from a single thermal reservoir and the complete conversion of that heat into work.



No perfect heat engine (100% efficiency is impossible)

- **Clausius Statement**

The Clausius statement of the second law of thermodynamics states: It is impossible for any process to have as its sole effect the transfer of heat from a colder body to a hotter body.



No perfect Refrigerators or heat pump (external work is always required)

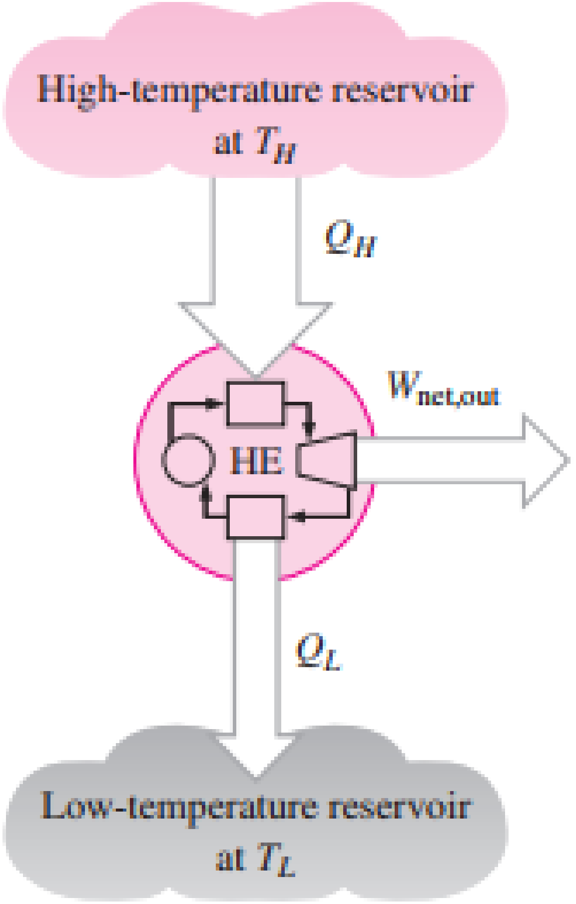
Heat Engines

For a reversible process:

$$dQ = T\,dS \text{ (we will look later)}$$

The amount of entropy:

$$S_H = \frac{|Q_H|}{T_H}$$



It is IMPOSSIBLE to convert all heat into work. To return the system to its initial state and complete a thermodynamic cycle, a portion of the absorbed heat must be rejected to a lower-temperature reservoir.

The entropy that enters the system with the heat Q_H must leave the system with the heat Q_L; otherwise, entropy would accumulate within the system, preventing cyclic operation

Heat Engines

Net flow of heat into the system:

$$\Delta Q = |Q_H| - |Q_L|$$

Since for one cycle, $\Delta U = 0$ and $\Delta U = \Delta Q - \Delta W_{by}$

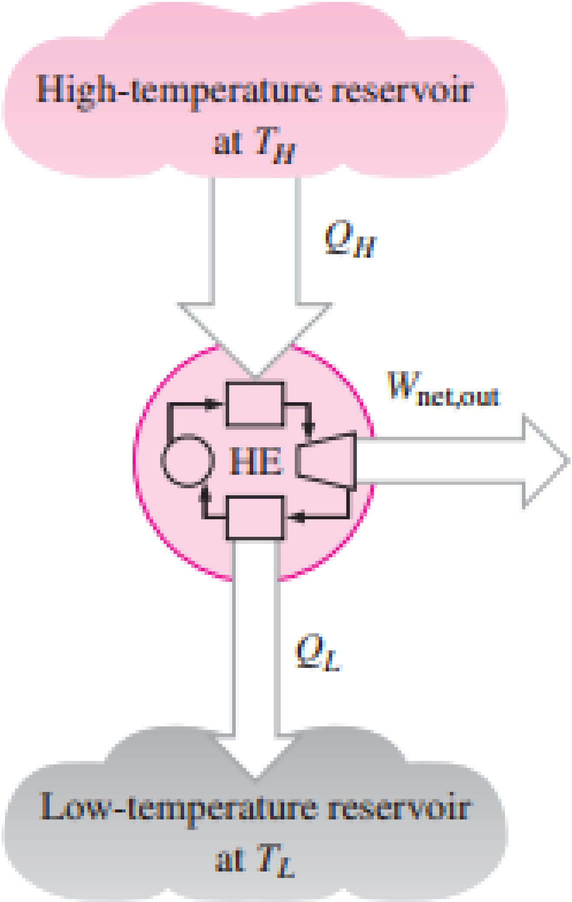
$$|W| = |Q_H| - |Q_L|$$

The system return to its original state at the completion of one cycle, when

$$S_H = S_L \leftrightarrow \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

$$\frac{|Q_H|}{T_H} = \frac{|Q_H| - |W|}{T_L} \rightarrow \frac{|Q_H|(T_H - T_L)}{T_L T_H} = \frac{|W|}{T_L}$$

$$\frac{|W|}{|Q_H|} = \frac{(T_H - T_L)}{T_H}$$



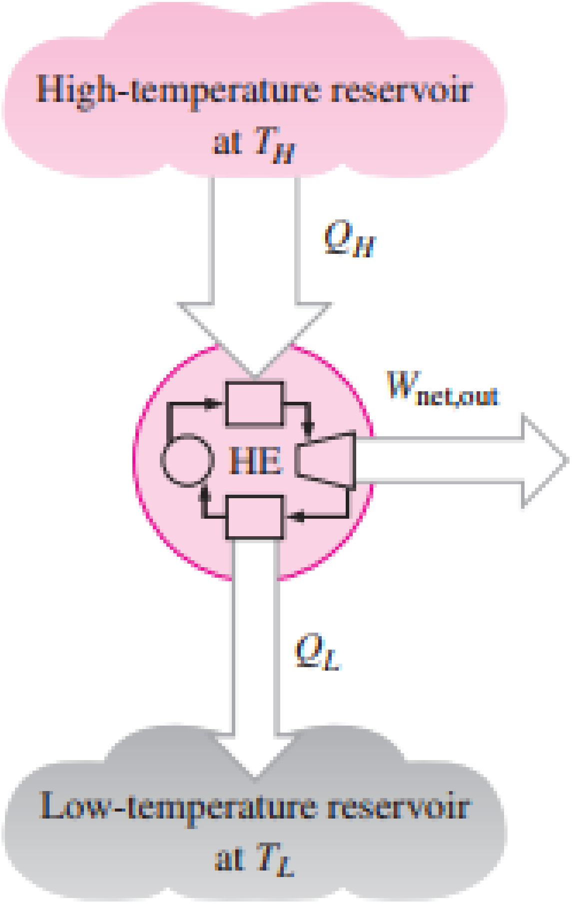
Heat Engines

The efficiency η is given by

$$\eta_C = \frac{W}{Q_H} = 1 - \frac{T_L}{T_H}$$

Where η_C is efficiency of a reversible engine, which is caller Carnot efficiency.

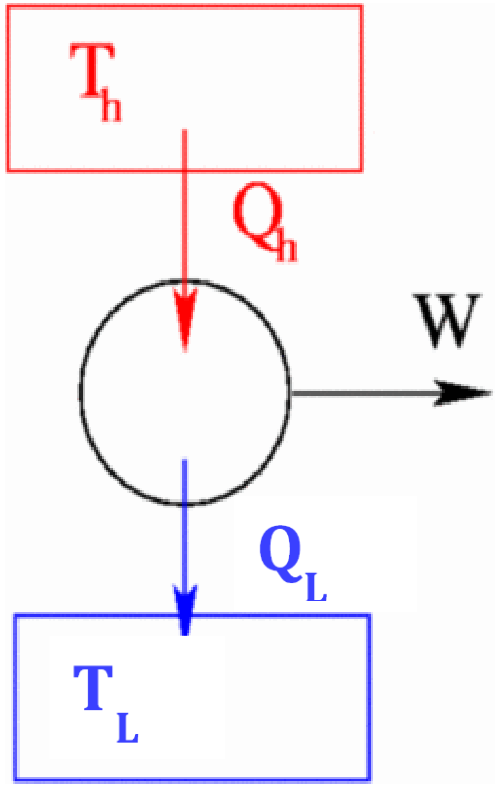
Since the engine considered operates reversibly between two temperatures, it is the maximum efficiency possible for any engine operating between these same two temperatures.



Heat Engines (Irreversible steps)

If an engine contains **irreversible steps**, part of the work produced from the heat input is lost as **dissipative work** (due to friction, viscosity, electrical resistance, etc.). Dissipative work is ultimately converted into heat and is therefore associated with **entropy generation**.

The entropy produced by irreversible processes **must be expelled from the system during each cycle**; otherwise, the engine cannot return to its initial state.



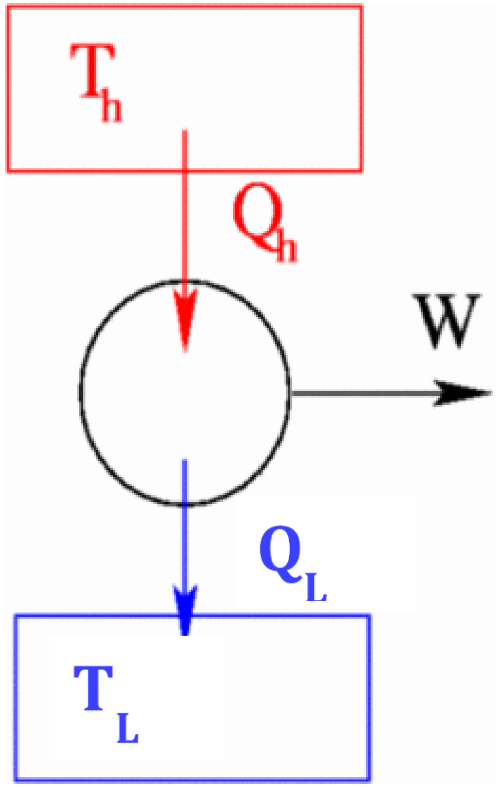
Heat Engines (Irreversible steps)

For a heat engine operating between a hot reservoir at temperature T_H and a cold reservoir at temperature T_L. For irreversible process:

$$S_L \geq S_H \Rightarrow Q_L \geq \frac{|Q_H|}{T_H} T_L$$

$$W = |Q_H| - |Q_L| \leq Q_H \left(1 - \frac{T_L}{T_H}\right) = Q_H \eta_C$$

$$\frac{W}{Q_H} \leq \eta_C$$



Where η_C is the **Carnot efficiency,** which represents the maximum possible efficiency of any heat engine operating between the same two reservoirs

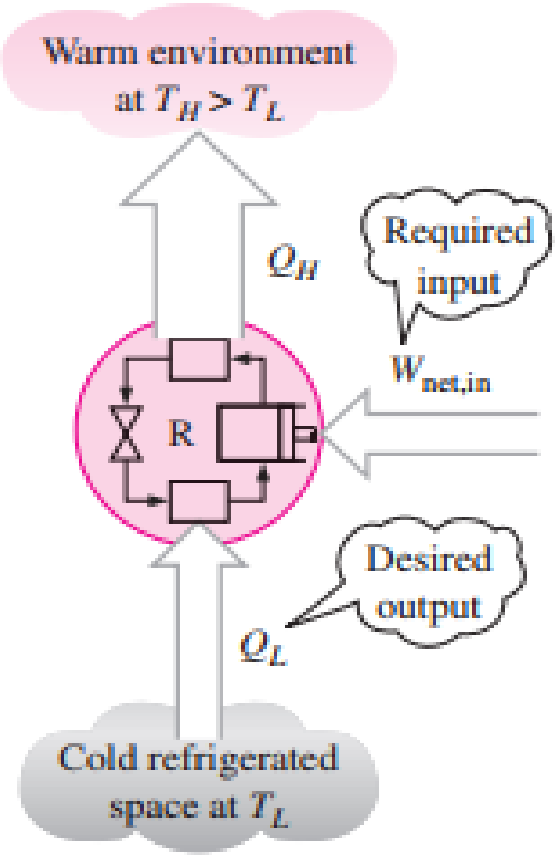
A reversible engine achieves this limit, which is called Carnot inequality.

Example 3.1

A Carnot engine extracts 240 J from its high-temperature reservoir during each cycle and rejects 100 J to the environment at $15^{o}\ C$. What's the temperature of the hot reservoir?

Refrigerator

A Carnot engine that is operated in reverse: do work W on the system, remove Q_C from the low temperature reservoir, and an amount of heat Q_H is exhausted into the high temperature reservoir



Refrigerator

of course,

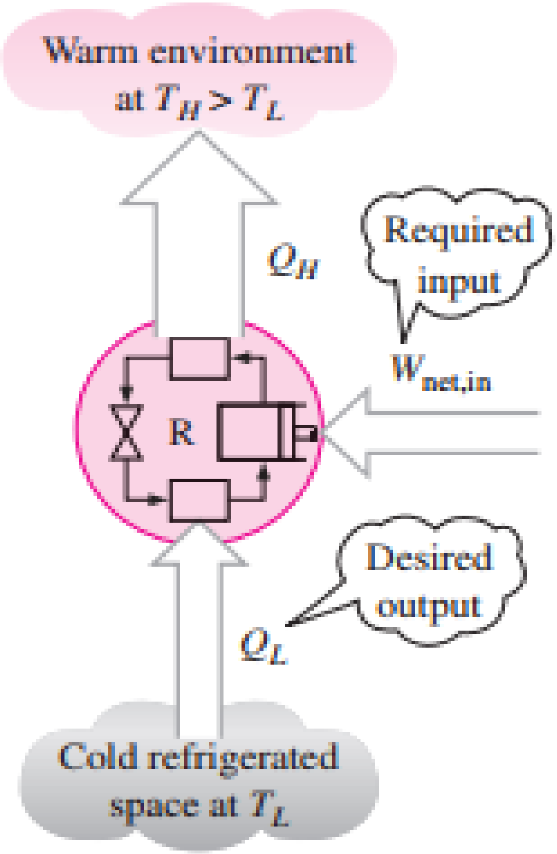
$$S_{in} = S_{out} \rightarrow \frac{Q_L}{T_L} = \frac{Q_H}{T_H}$$

$$Q_H = Q_L \frac{T_H}{T_L}$$

For the Carnot refrigerator we have $Q_L + W = - Q_H$

Here we are taking the work done on the system as positive, heat flowing into the system as positive, and heat flowing out of the system as negative.

$$|Q_H| = |W| + |Q_L|$$



Refrigerator

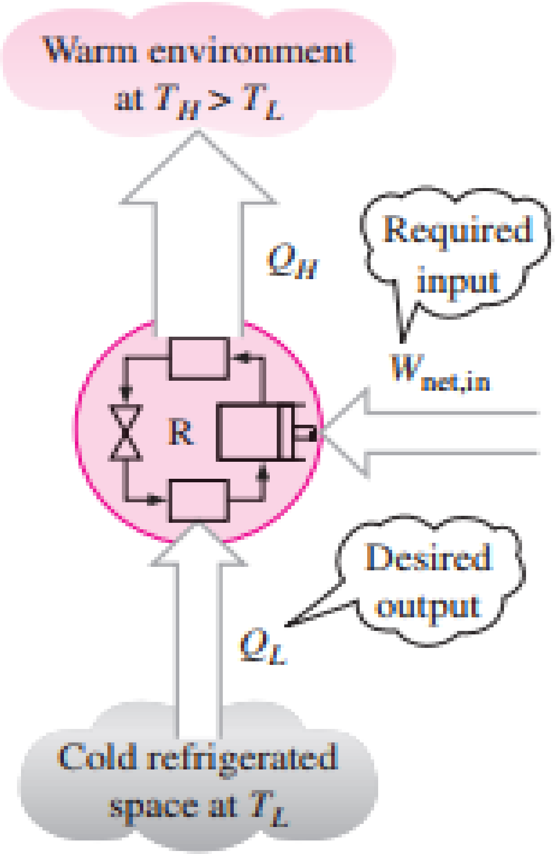
$$Q_L \frac{T_H}{T_L} = W + Q_L \Rightarrow \frac{T_H}{T_L} = \frac{W}{Q_L} + 1$$

$$\frac{W}{Q_L} = \frac{T_H - T_L}{T_L}$$

Or, finally, the coefficient of performance of the Carnot refrigerator, c_R, is:

$$c_R = \frac{Q_L}{W} = \frac{T_L}{T_H - T_L} = \frac{1}{\frac{T_H}{T_L} - 1}$$

Notice! value of c_R can be greater than unity which means the amount of heat removed from the refrigerated space can be greater than the amount of work input. It is in contrast to the thermal efficiency, which is always less than 1.



Example 3.2

A Carnot engine operates between 400 K and 300 K.

a. If this engine receives 1200 J from the high temperature reservoir in each cycle, how much energy does it exhaust to the low temperature reservoir as heat in each cycle?

b. Take this same engine but operate it now as a refrigerator. Each cycle of the operation of the refrigerator it extracts 1200 J from the 300 K reservoir. How much energy does it exhaust as heat to the high temperature reservoir? Where did the difference between heat input and heat output came from?

c. What is the work done by the engine and what the work done on the refrigerator?

Heat Pump

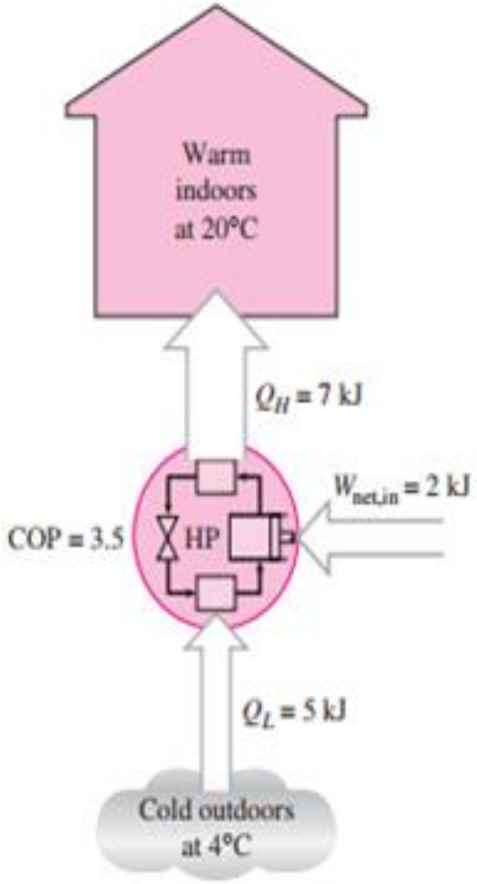
Another device that transfer heat from lower temperature of medium to high-temperature is **heat pump**. The coefficient of performance of a heat pump in a cycle is

$$c_{HP} = \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - \frac{Q_L}{Q_H}}$$

We find that

$$C_{HP} = \frac{Q_L + |W|}{W} \Rightarrow c_{HR} = c_R + 1$$

We can see that coefficient of performance of a heat pump is always greater than unity.



Heat Pump

- In practice, some of the delivered heat Q_H is lost to the outdoor environment through piping, ductwork, and other system components.
- When the outdoor air temperature becomes very low, the heating coefficient of performance (COP_H) can drop below unity. Under these conditions, the system typically activates electric resistance heating to maintain indoor comfort.
- Heat pumps are therefore often evaluated using a seasonal average COP, rather than instantaneous performance.
- Most existing residential systems use outside air as the heat source during winter; these systems are known as air-source heat pumps.

Heat Pump

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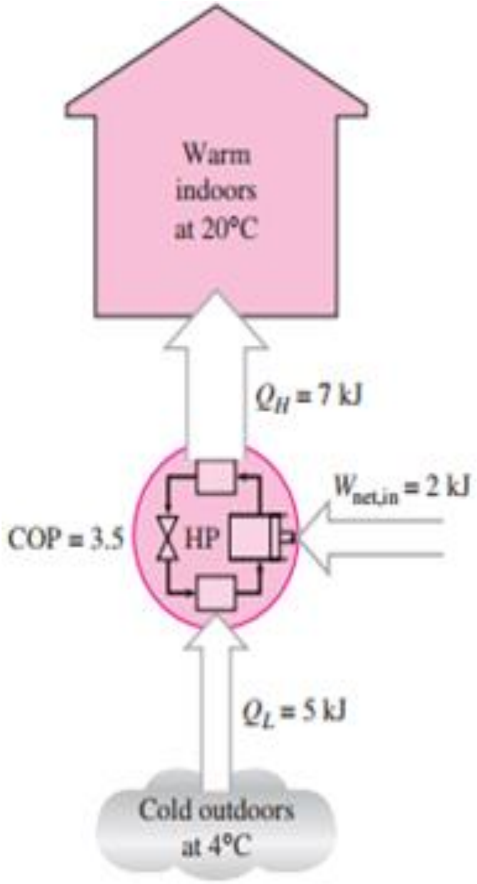
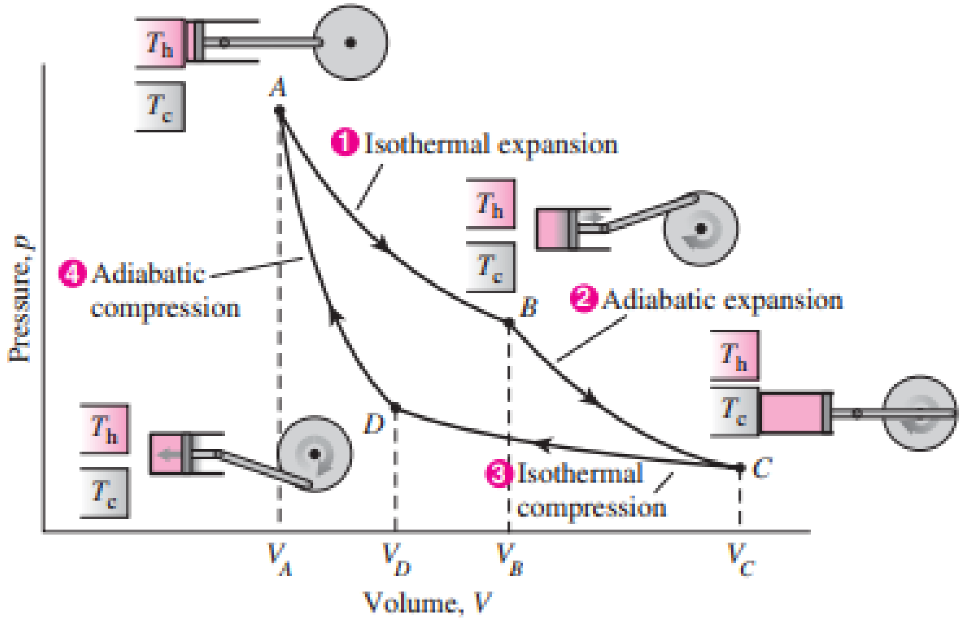


Carnot Cycle for Heat Engine: PV Path

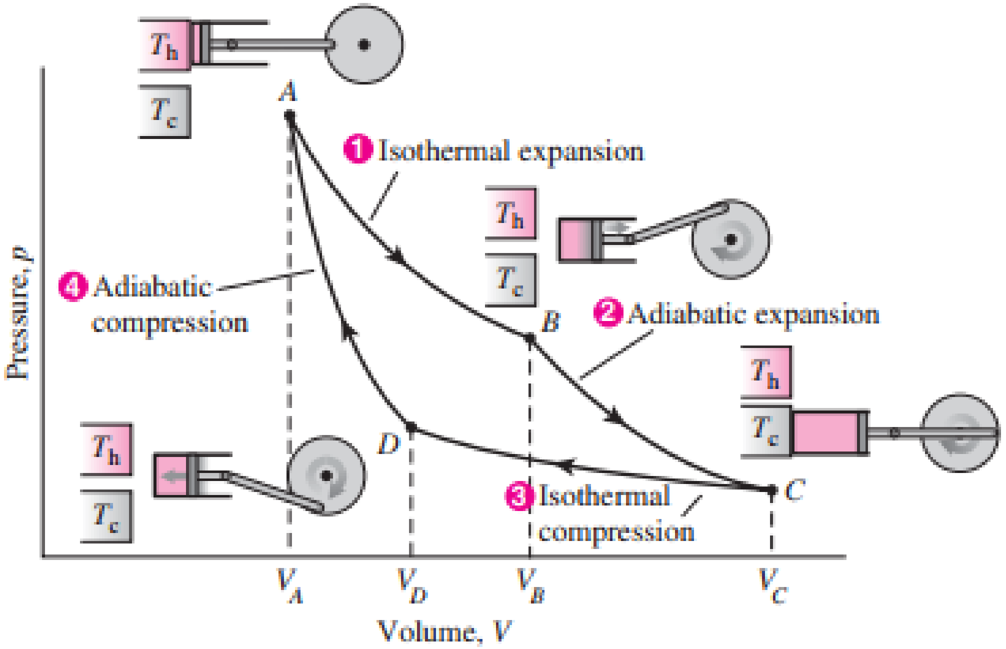
A Carnot engine is a series of reversible processes that run in a cycle, operating between two (heat reservoirs at) temperatures $T_H > T_C$. It can operate as a heat engine or a refrigerator.

It consist of two isotherms and two adiabatic processes.



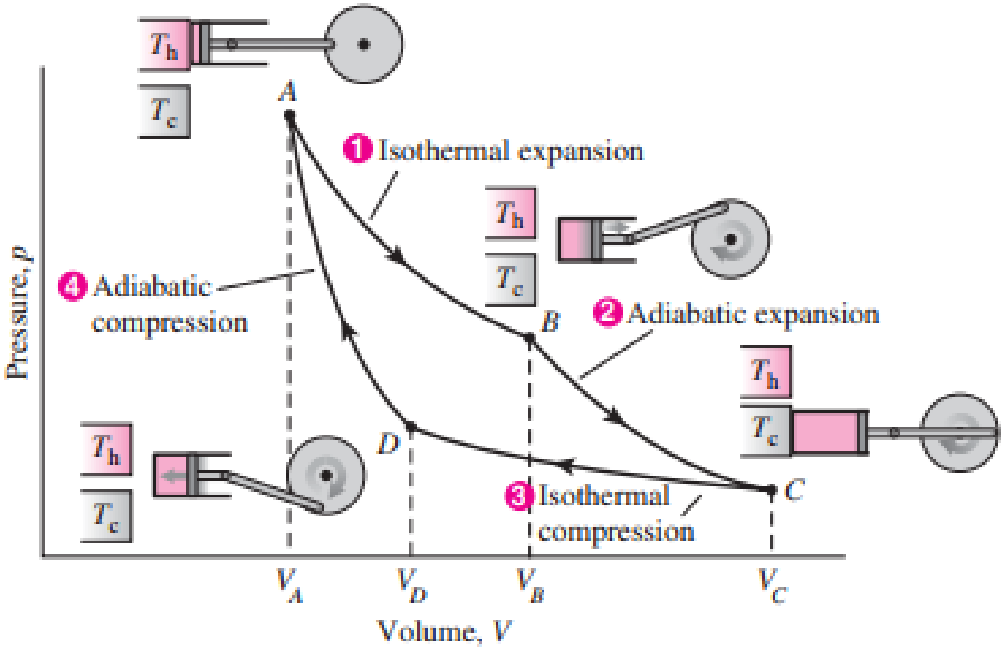
Carnot Cycle for Heat Engine: PV Path

1. An isothermal expansion at temperature T_H from an initial volume V_A to a volume V_B. An amount of heat Q_H flows into the system during this isothermal step (system absorb an amount of heat Q_H from surroundings).
2. An adiabatic expansion (Q=0) from of the gas from volume V_B to volume V_C. During this adiabatic expansion the temperature of the gas decreases from T_H to T_L and pressure (*in an adiabatic expansion the expanding gas does work on the surroundings at the expense of its internal energy, hence the internal energy of the gas decreases, and so does the temperature.)*



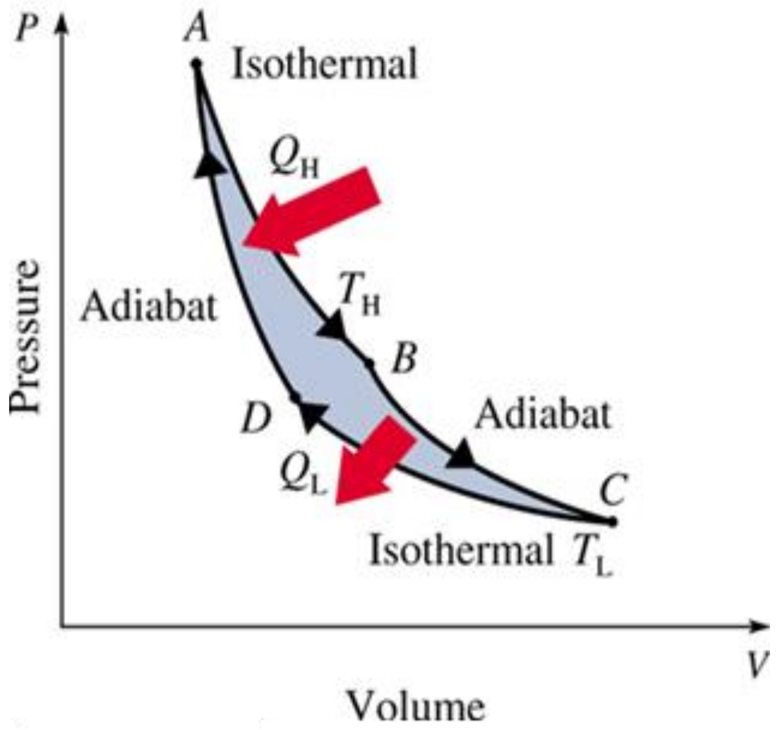
Carnot Cycle for Heat Engine: PV Path

3. An isothermal compression of the gas, from V_C to V_D in which heat Q_L is exhausted at temperature T_L. (Work is done on the gas, compressing it and the step is isothermal, hence energy has to be released to the surrounding to keep the temperature constant).
4. Finally, an adiabatic compression of the gas, in which the temperature increases from T_L back to T_H and the volume goes from V_D back to V_A, completing the cycle.



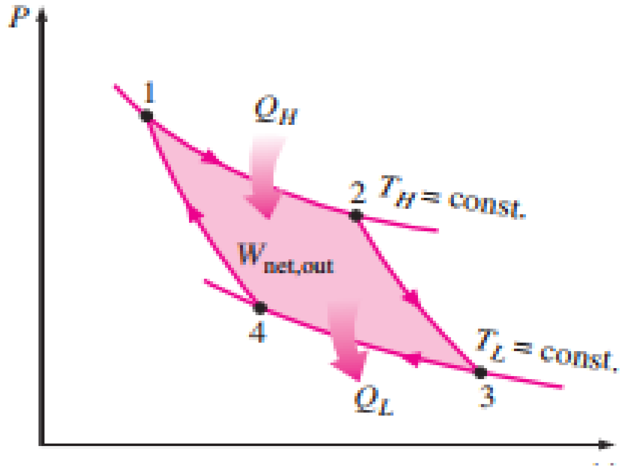
Carnot Cycle for Heat Engine

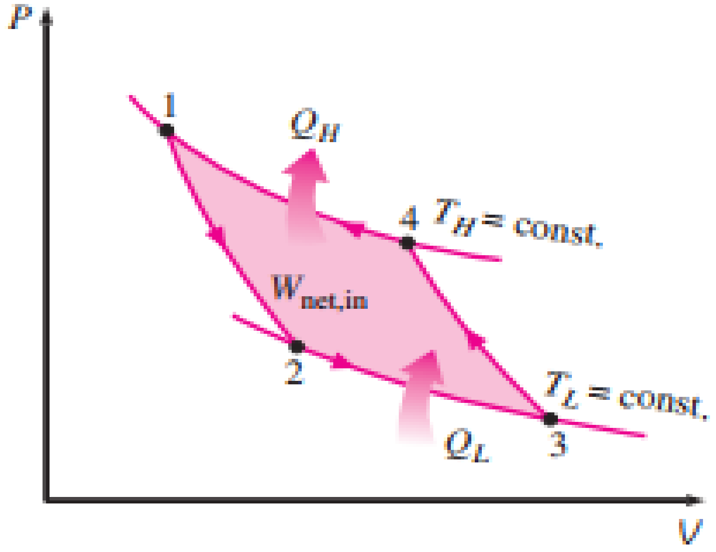
1. Work done by the gas (positive), PdV, is the area underneath curves $A \Rightarrow B$ and $B \Rightarrow C$.
2. The work done on the gas (is the area under the curves $C \Rightarrow D$ and $D \Rightarrow A$.
3. Area enclosed by the curves defining the Carnot engine cycle.



Carnot Cycle Heat pump and Refrigerator

- The Carnot heat-engine cycle is a totally reversible cycle. Therefore, all the processes that comprise it can be reversed, in which case it becomes the Carnot refrigeration cycles.
- The net work done is given by area inside the loop.





Carnot Cycle for Heat Engine

1. Let us look at the step $A \Rightarrow B$, the isothermal expansion at T_H. Since isothermal, internal energy of gas doesn't change:

$$\Delta U_{A \Rightarrow B} = 0$$

From, 1st law of thermodynamics states

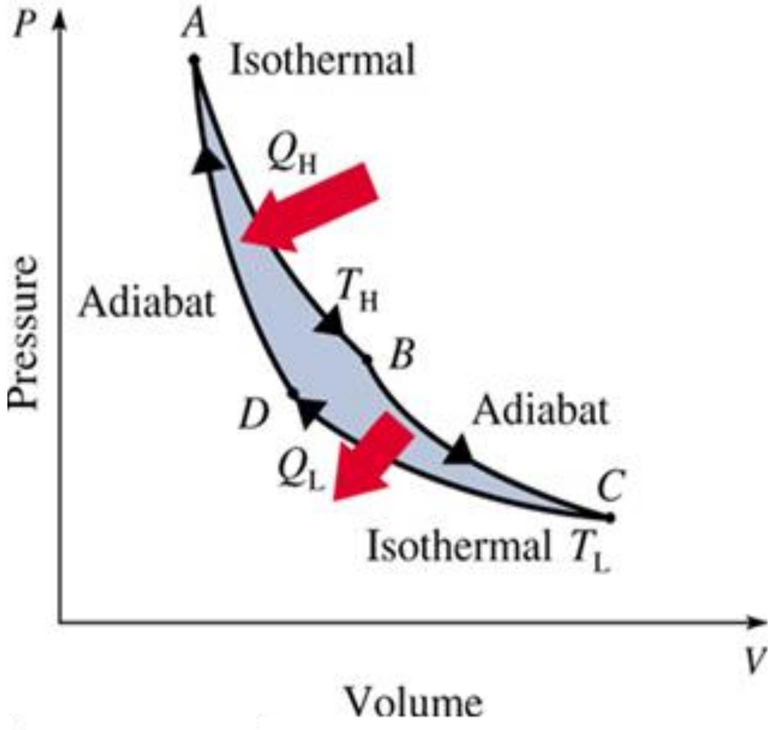
$dQ = dU + dW_{by}$:

$$Q_H = W_{A \Rightarrow B}$$

where $\Delta U = 0$

Work done by a classical ideal gas in an isothermal expansion: $dW = PdV$

$$W_{A \Rightarrow B} = \int_{V_A}^{V_B} dW = Nk_B T_H Log\left(\frac{V_B}{V_A}\right)$$



Carnot Cycle for Heat Engine

Step $B \Rightarrow C$ we note that, since it is an adiabatic step, $\Delta Q = 0$

since, $dQ = dU + dW_{by}$

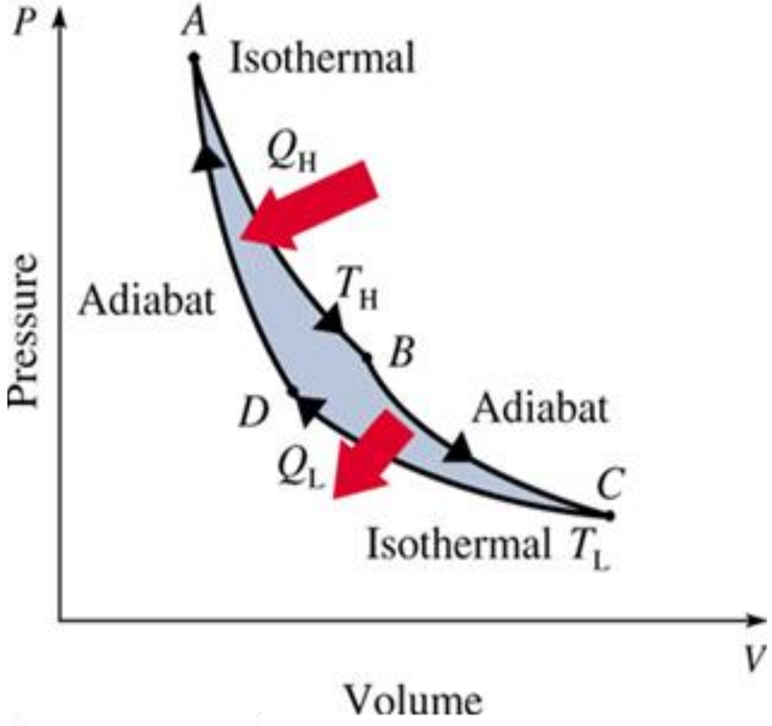
$$-\Delta U_{B\to C} = W_{B\to C}$$

But

$$\Delta U_{B\to C} = \frac{f}{2} N k_B (T_L - T_H)$$

We find that,

$$W_{B\to C} = \frac{f}{2} N k_B (T_H - T_L)$$

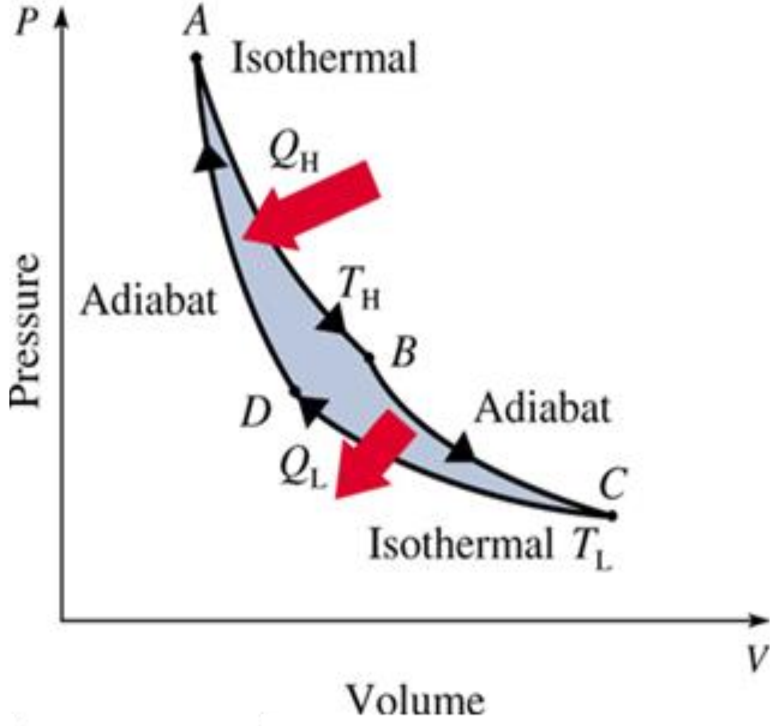


Carnot Cycle for Heat Engine

i. **Isothermal compression,** from C to D, we can obtain, like what we did for A to B:

$$W_{C\to D} = \int_{V_C}^{V_D} \frac{Nk_BT_L}{V}\,dV$$

$$W_{C\to D} = Nk_BT_L Log\left(\frac{V_D}{V_C}\right) = Q_L$$



Carnot Cycle for Heat Engine

Last step, adiabatic compression (D→ A). Just like B to C, but only with a compression instead of an expansion.

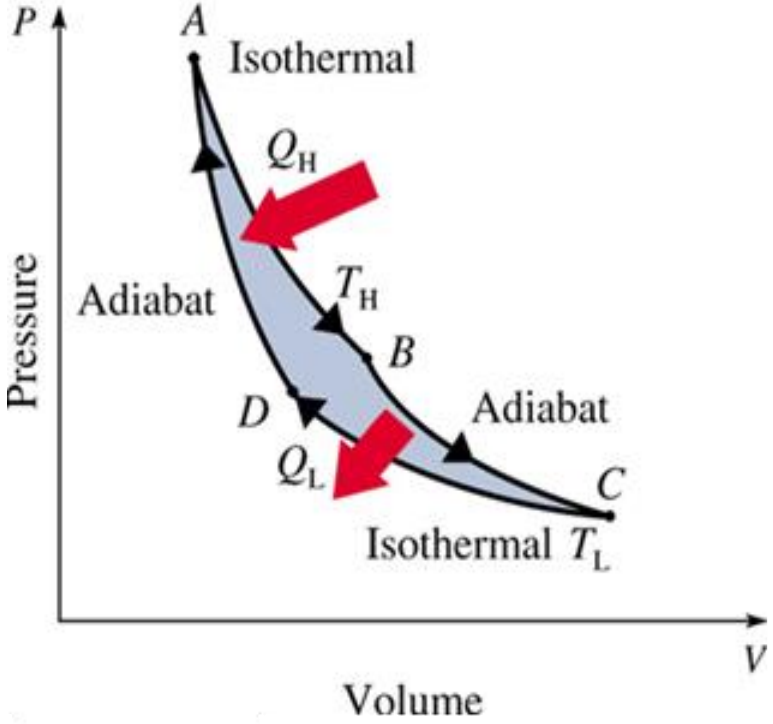
Since, adiabatic process, Q =0, and $dQ = dU + dW$

$$-\Delta U_{D\to A} = W_{D\to A}$$

Where

$$\Delta U_{D\to A} = \frac{f}{2} N k_B (T_H - T_L)$$

$$W_{D\to A} = -\frac{f}{2} N k_B (T_H - T_L)$$



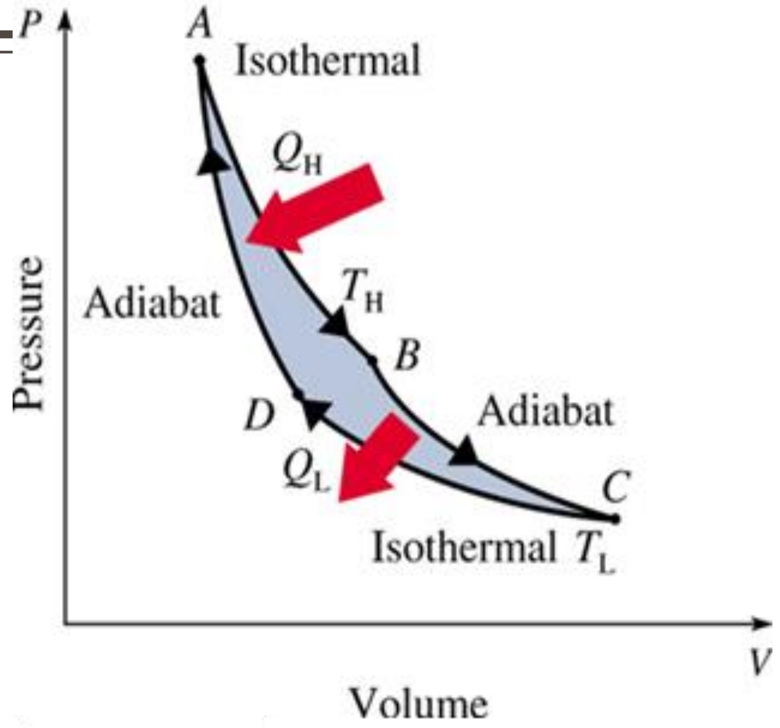
Carnot Cycle for Heat Engine

We can now compute the net work done by the gas:

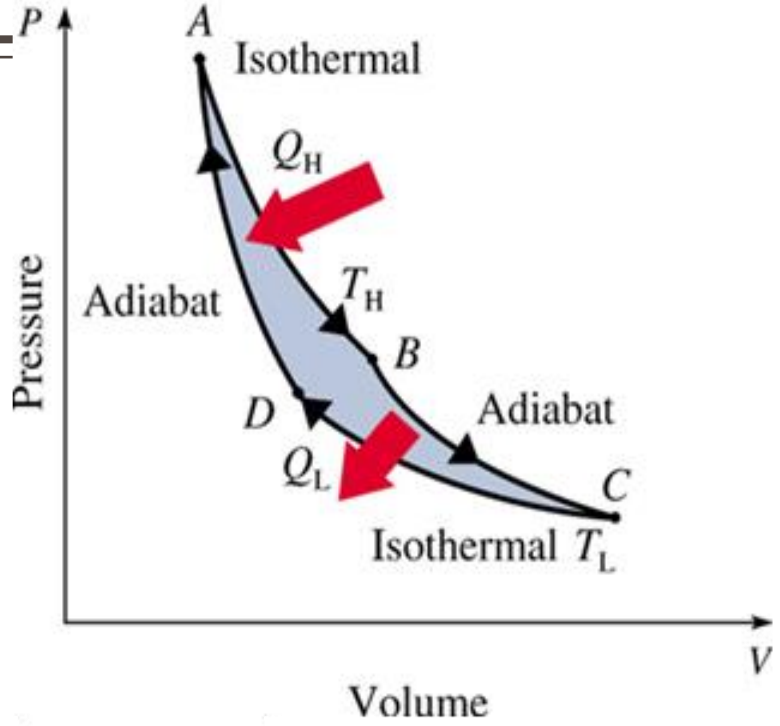
$$W_{net} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$W_{net} = Nk_B T_H Log\left(\frac{V_B}{V_A}\right) + Nk_B(T_H - T_L)$$
$$+Nk_B T_L Log\left(\frac{V_D}{V_C}\right) - Nk_B(T_H - T_L)$$

$$W_{net} = Nk_B T_H Log\left(\frac{V_B}{V_A}\right) + Nk_B T_L Log\left(\frac{V_D}{V_C}\right)$$



Carnot Cycle for Heat Engine



To move a bit further, let's recall the expressions for an adiabatic expansion or compression. In particular:

$$T\,V^{\gamma-1} = const$$

Where ideal gas $\gamma = 3/2$.

In this case, for the adiabatic expansion:

$$T_B(V_B)^{\gamma-1} = T_C(V_C)^{\gamma-1} \Rightarrow T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1}$$

And for the adiabatic compression we have:

$$T_D(V_D)^{\gamma-1} = T_A(V_A)^{\gamma-1} \Rightarrow T_L V_D^{\gamma-1} = T_H V_A^{\gamma-1}$$

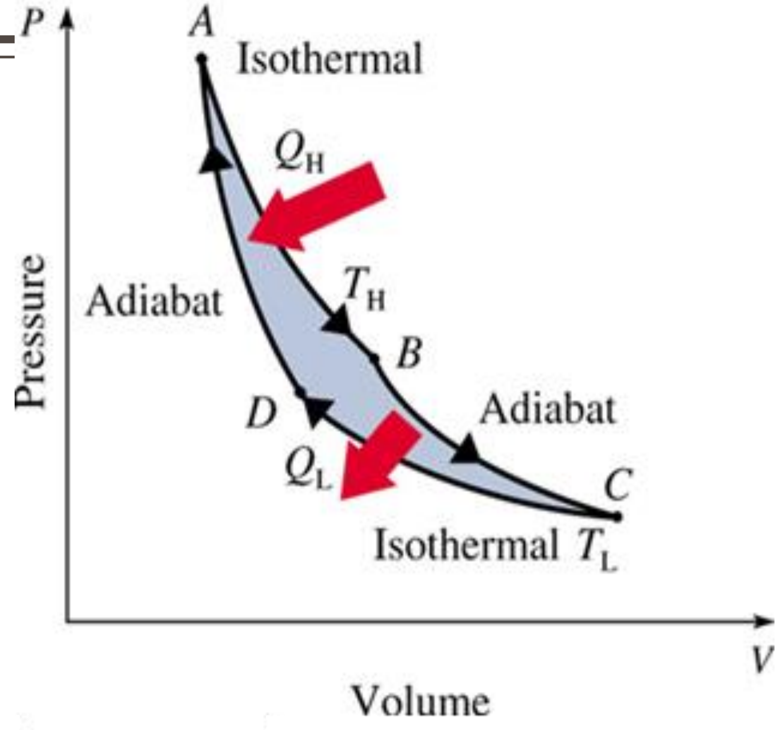
Carnot Cycle for Heat Engine

Divide one equation by the other, we get:

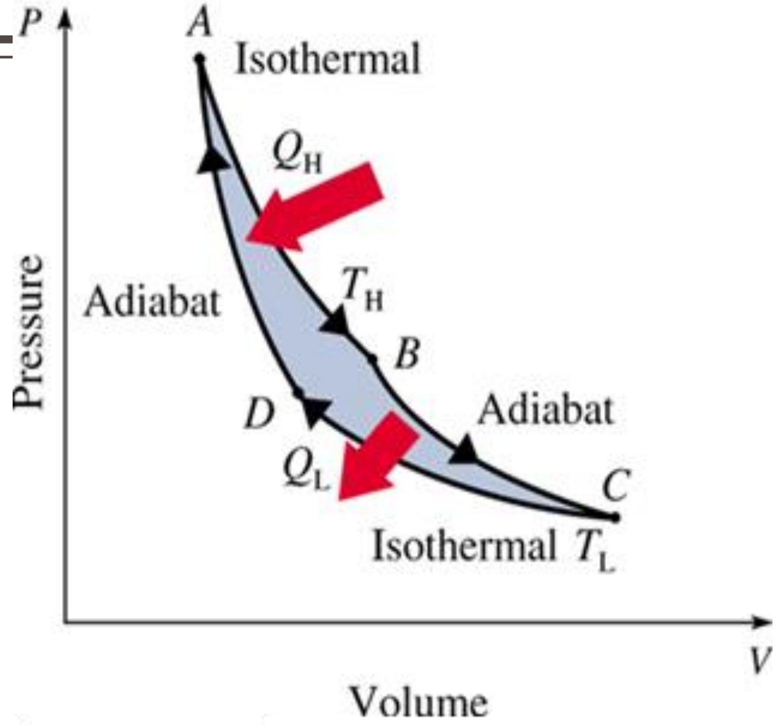
$$\frac{V_B}{V_A} = \frac{V_C}{V_D}$$

We end up

$$W_{net} = Nk_B Log\left(\frac{V_B}{V_A}\right)[T_H - T_L]$$



Carnot Cycle for Heat Engine



Let us compute directly from the definition the efficiency of this Carnot engine:

$$\eta = \frac{W}{Q_H} = \frac{Nk_B Log\left(\frac{V_B}{V_A}\right)[T_H - T_L]}{Nk_B Log\left(\frac{V_B}{V_A}\right)T_H}$$

$$\eta = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H} = \eta_C$$

Note: if $T_L = 0$ give efficiency of Carnot engine, $\eta = 1$ where absolute zero temperature is impossible.

Just as we had expected, for this reversible engine we obtain the Carnot expression for the maximum efficiency possible for an engine operating between T_H and T_L.

Carnot Cycle with T-S Diagram

Sometimes the Carnot cycle is plotted using temperature (T) and entropy (S) axes. This representation is especially useful because it gives an immediate physical interpretation of heat transfer. Recall,

$$dQ = TdS$$

So, along an isotherm (T = constant):

$$Q = \int dQ = \int_{S_1}^{S_2} TdS = T\int_{S_1}^{S_2} dS = T(S_2 - S_1)$$

And, along an adiabatic,

$$dQ = 0 \Rightarrow TdS = 0$$

Entropy, S is constant because $T \neq 0$

Carnot Cycle with T-S Diagram

Isothermal expansion ($A \rightarrow B$ at T_H): Heat absorbed from the hot reservoir

$$Q_H = T_H (S_B - S_A)$$

Adiabatic expansion ($B \rightarrow C$):

$$Q = 0 \rightarrow S = Constant \Rightarrow S_C = S_B$$

Isothermal Compression (C$\rightarrow$ D at T_L): Heat rejected to the cold reservoir

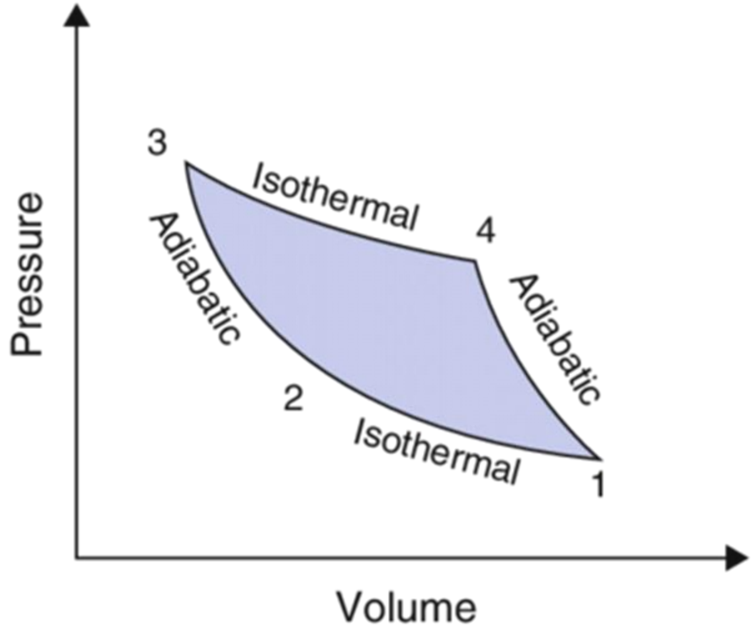
$$Q_L = T_L (S_D - S_C) \ (where\ Q_L < 0)$$

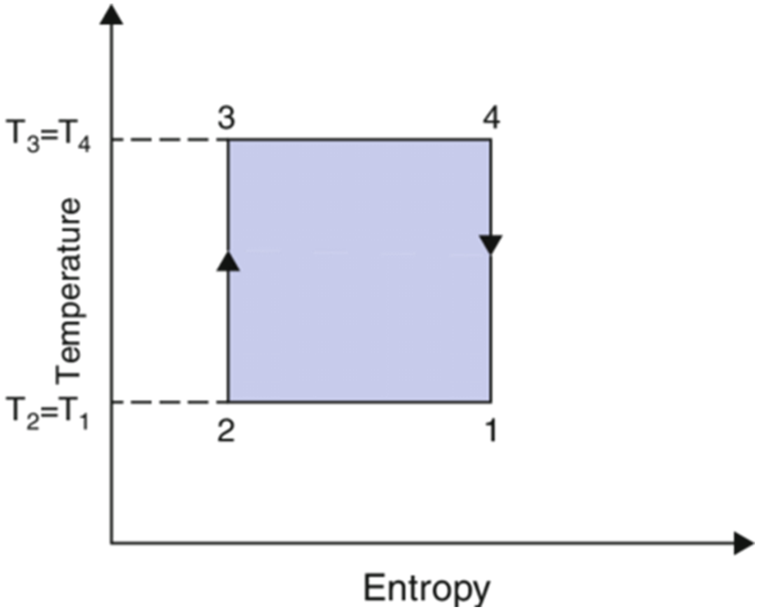
Adiabatic Compression (D$\rightarrow$ A):

$$Q = 0 \rightarrow S = Constant \Rightarrow S_A = S_D$$

$$Q_{net} = |Q_H| - |Q_L|$$

Carnot Cycle with T-S Diagram





Net Heat Transfer (Area Enclosed in T-S Plane)

$$Q_{net} = Q_H + Q_L$$

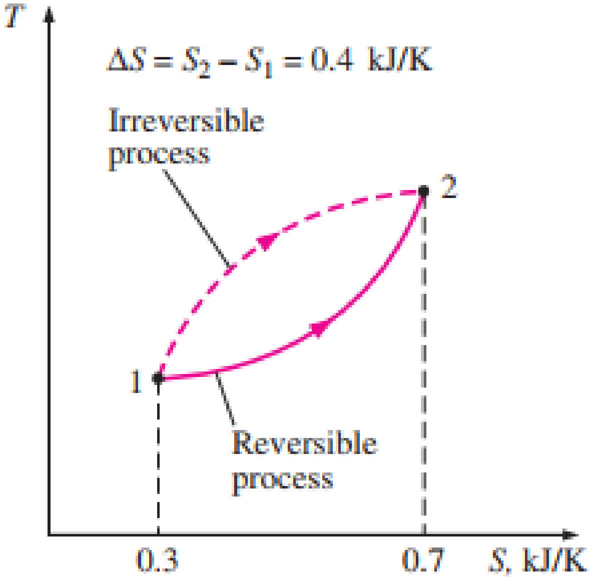
$$Q_{net} = |Q_H| - |Q_L| \ (using\ magnitude)$$

$$\text{Since for a complete cycle } \Delta U = 0$$

$$W_{net} = Q_{net}$$

Entropy

The German physicist Rudolf Julius Emanuel Clausius (1822–1888) introduced the concept of a new thermodynamic property in 1865. He named this property **entropy**, derived from the Greek word (meaning "transformation"), and symbol **S.** unit of S is kJ/K.



For an internally reversible process.

$$dS = \left(\frac{\delta Q}{T}\right)_{int\,rev}$$

For isothermal process

$$\Delta S = \int_1^2 \left(\frac{\delta Q}{T_o}\right)_{int\,rev} \rightarrow \Delta S = \frac{Q}{T_0}$$

Note: Entropy is a property of the system. (ΔS) depends only on the initial and final states, regardless of whether the path taken is reversible or irreversible.

Clausius Inequality and Entropy Generation

Clausius Inequality. For any cyclic process

$$\oint \frac{\delta Q}{T} \leq 0$$

- Equality holds for a reversible cycle
- Inequality holds for an irreversible cycle

Clausius inequality leads directly to the definition of entropy and shows that:

$$\Delta S \geq \int \frac{\delta Q}{T}$$

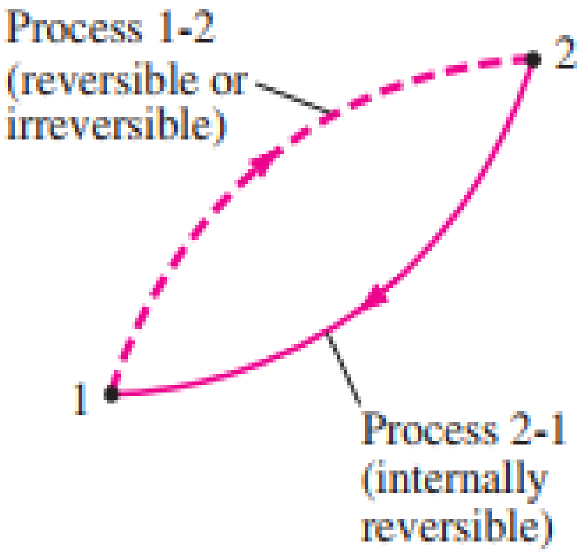
So, entropy increases whenever irreversibilities occur.

Entropy Generation

Consider a process (figure) from state 1 to state 2, and return from 2 to 1 along an internally reversible path

$$\oint \frac{\delta Q}{T} \leq 0 \rightarrow \int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T}\right)_{int\,rev} \leq 0$$

$$\int_1^2 \frac{\delta Q}{T} + S_1 - S_2 \leq 0 \Rightarrow S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$



The entropy increases always for a closed system during with irreversible process which is called **entropy generation**, S_{gen}.

$$\Delta S_{sys} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}$$

Increasing Entropy

S_{gen} is always positive or zero. It is not a property of the system. Now we can say that for an isolated system

$$\Delta S_{isolated} \geq 0$$

$$S_{gen}\begin{cases} > 0 \; Irreversible\ Process \\ = 0 \; Reversible\ Process \\ < 0 \; Impossible\ Process \end{cases}$$

Entropy and 2nd Law of Thermodynamics

- The Second Law of Thermodynamics introduces a new thermodynamic property called entropy (S).
- Entropy can seem abstract because its physical meaning is best understood from a microscopic (molecular) viewpoint.
- At the molecular level, particles and energy naturally rearrange toward states with the largest number of possible microscopic arrangements (maximum multiplicity), which corresponds to the most probable state.
- Entropy is not conserved; it can be generated during real (irreversible) processes.

$$\Delta S_{universe} \geq 0$$

For an isolated system, entropy tends to increase until thermodynamic equilibrium is reached.

Real Heat Engines

- So far, we have treated heat engines and refrigerators in an idealized way.
- We found that the theoretical limits of performance (such as the maximum efficiency of a heat engine) depend only on the operating temperatures of the hot and cold reservoirs.
- How are real engines and refrigerators actually designed and built?

Gasoline Engine (Spark-Ignition Engine) and the Otto Cycle

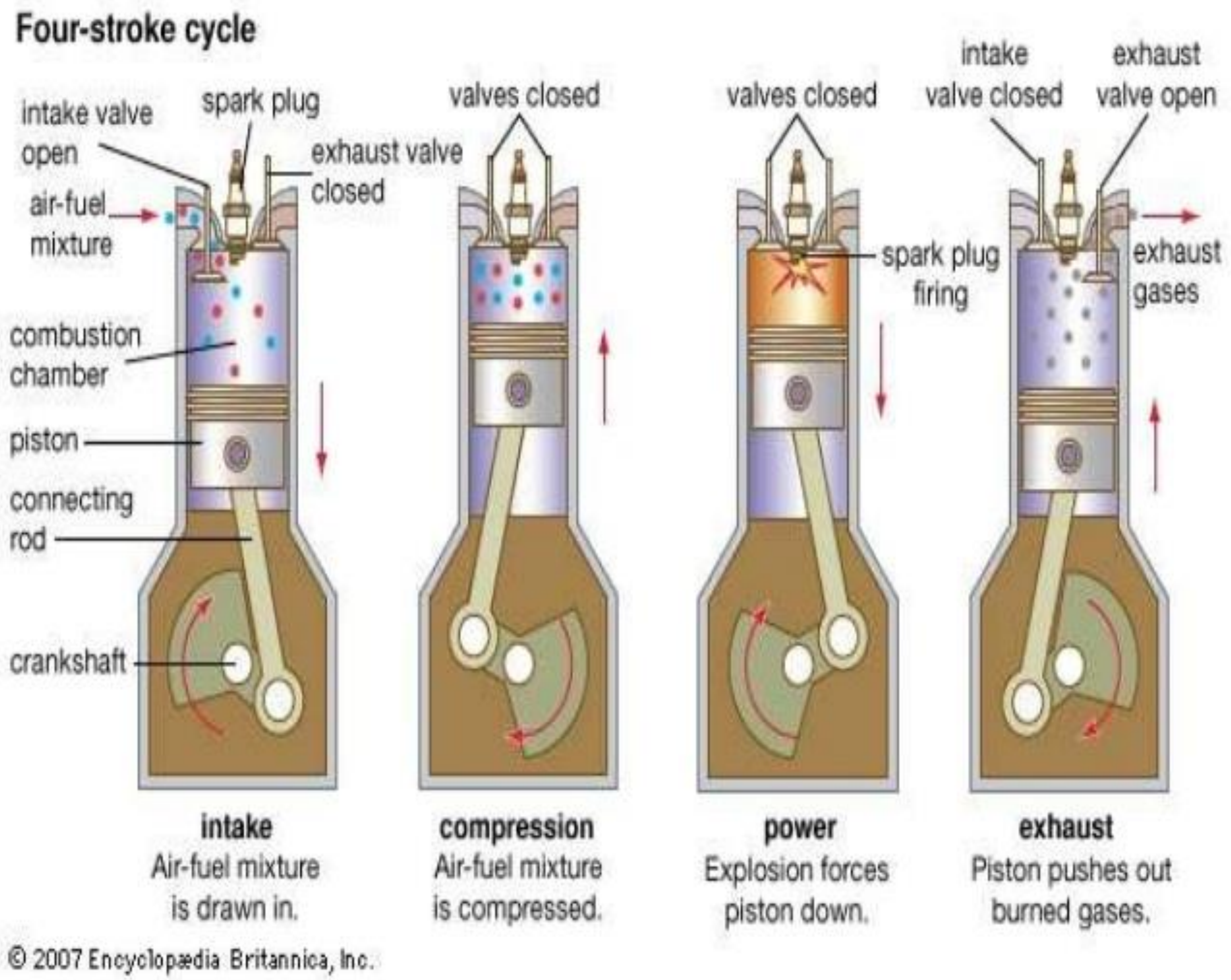
- A familiar gasoline engine is found in most automobiles and operates using the Otto cycle model.
- The working substance is a gas mixture, initially air mixed with vaporized gasoline.
- A spark plug ignites the air–fuel mixture, causing rapid combustion that greatly increases the temperature and pressure (approximately at constant volume).
- The high-pressure gas then pushes the piston outward, undergoing an expansion stroke that produces mechanical work (often approximated as adiabatic expansion).
- Finally, the hot exhaust gases are expelled and replaced by a fresh air–fuel mixture at lower temperature and pressure.

Gasoline Engine (Spark-Ignition Engine) and the Otto Cycle

- This idealized cycle is called the Otto cycle, named after the German inventor Nikolaus August Otto, who built a successful four-stroke engine in 1876.
- The cycle concept was earlier proposed by the French engineer Alphonse Beau de Rochas in 1862.

- The ideal Otto cycle is treated as internally reversible.
- A real gasoline engine is irreversible due to friction, turbulence, finite-rate combustion, and heat losses..

Internal Combustion Engines

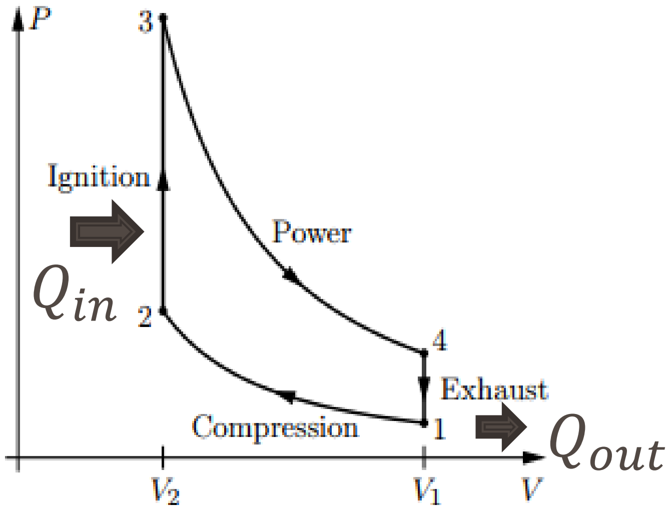


Otto Cycle (Gasoline Engine Model)

The figure shows the ideal Otto cycle, which is a simplified thermodynamic model of a spark-ignition (gasoline) engine.

Process Descriptions:

- 1 → 2: Reversible adiabatic (isentropic) compression
- 2 → 3: Constant-volume (isochoric) heat addition
- 3 → 4: Reversible adiabatic (isentropic) expansion
- 4 → 1: Constant-volume (isochoric) heat rejection



Otto Cycle (Gasoline Engine Model)

In the ideal Otto cycle, all four processes are treated as internally reversible.

The heat-transfer steps (2 → 3 and 4 → 1) occur at constant volume, but they are not the cause of irreversibility in the ideal cycle.

Real gasoline engines are irreversible due to friction, turbulence, finite-rate combustion, and heat loss.

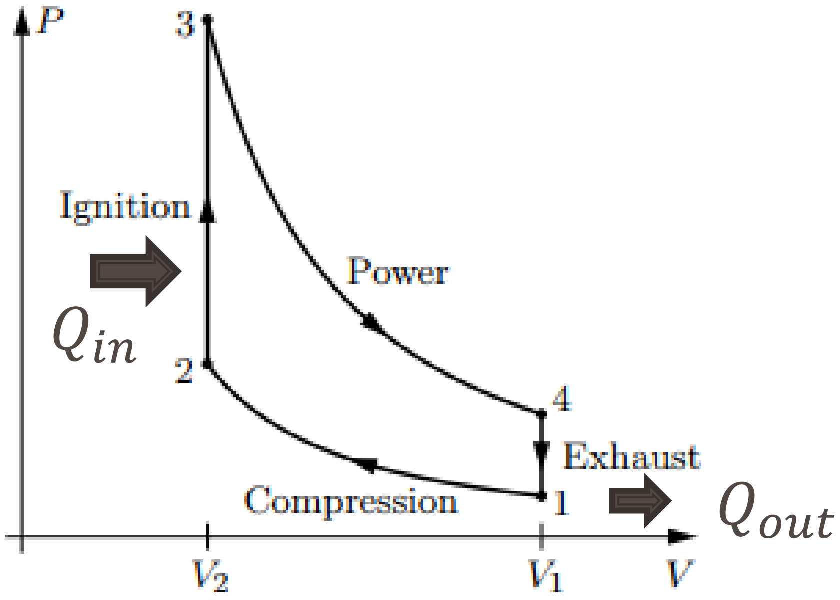
For the ideal Otto cycle, the working fluid returns to its initial state each cycle:

$$\Delta S_{system} = 0$$

In a real Otto engine, entropy is generated:

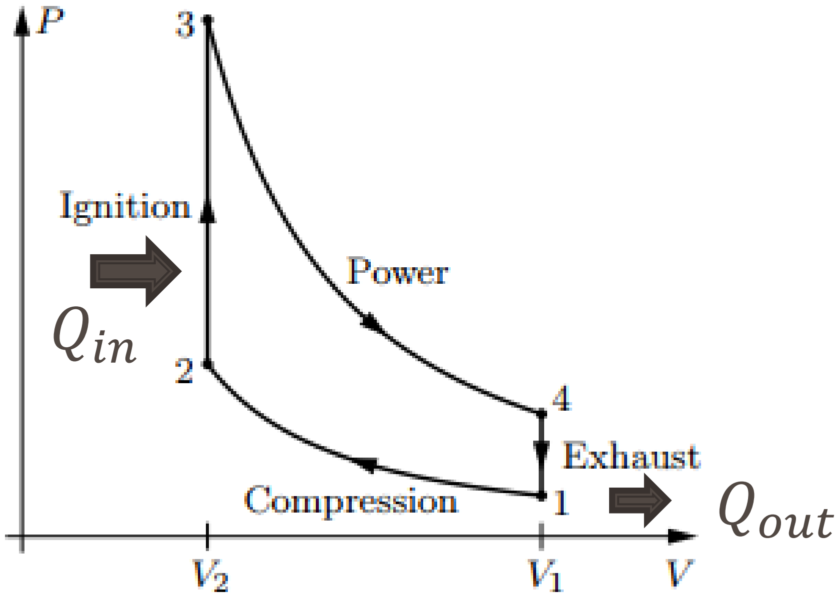
$$S_{\text{gen}} > 0$$

so the entropy of the surroundings (universe) increases.



Otto Cycle (Gasoline Engine Model)

Increase in the entropy of the surroundings, Because the engine has to return to its original at the completion of every cycle, consists of four internally reversible processes.



Otto Cycle

How much heat is added in step 2 ⇒ 3?

$$C_V = \left(\frac{dQ}{dT}\right)_V \Rightarrow dQ = C_V dT$$

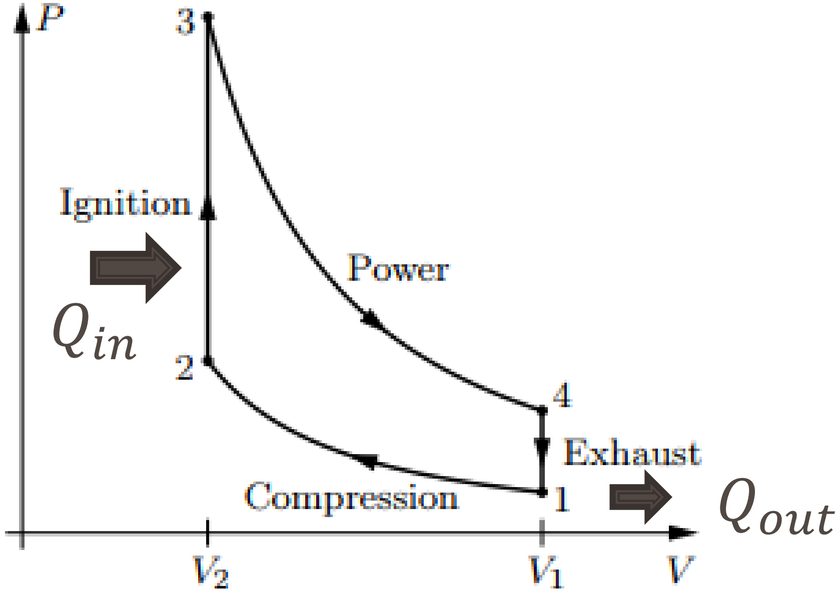
$$Q_H = \int_{T_2}^{T_3} C_V dT \rightarrow |Q_H| = |C_V(T_H - T_2)|$$

Where $T_3 = T_H$

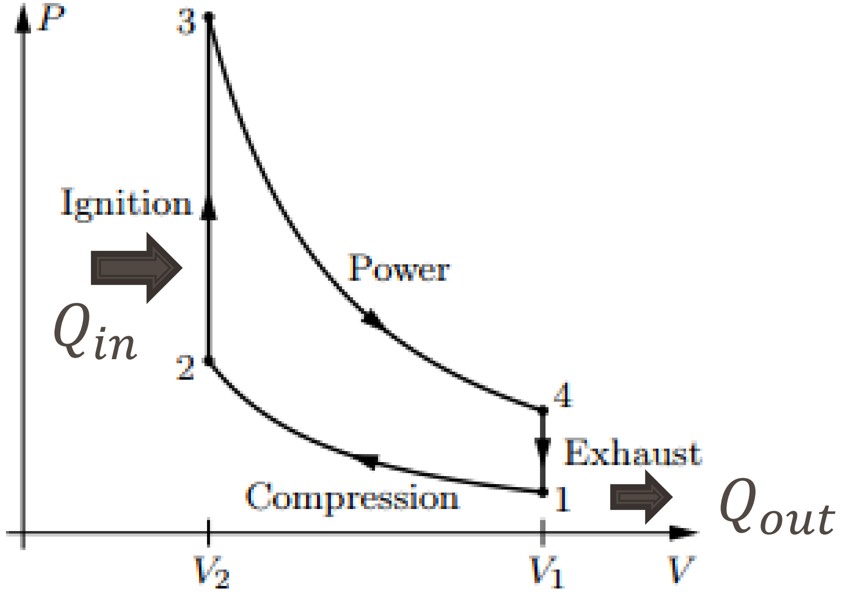
Similarly, step 4⇒ 1:

$$|Q_C| = |C_V(T_C - T_4)|$$

Where $T_1 = T_C$



Otto Cycle



First law of thermodynamics to one cycle of the Otto engine:

$$\Delta Q = \Delta U + W_{by}$$

Since U is a function of state, in a cycle $\Delta U = 0$

$$\Delta Q = W_{by} \rightarrow |Q_H| - |Q_C| = W_{by}$$

The efficiency of Otto cycle η is defined as:

$$\eta = \frac{W_{by}}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{T_4 - T_C}{T_H - T_2}$$

Unfortunately, we only are given $T_3 = T_H \; and \; T_1 = T_C$

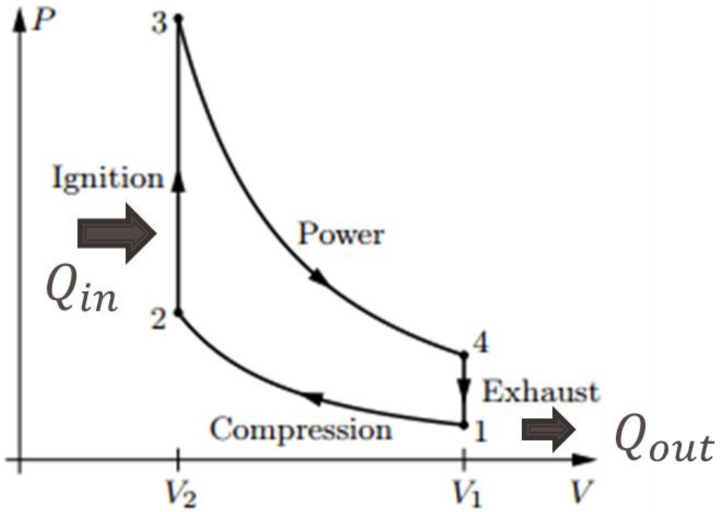
Otto Cycle

For adiabatic steps $1\Rightarrow 2$ and $3\Rightarrow 4$: applying

$$T_i V_i^{\gamma-1} = const$$

We find that

$$T_2 = T_C \left(\frac{V_1}{V_2}\right)^{\gamma-1} \text{and } T_4 = T_H \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$



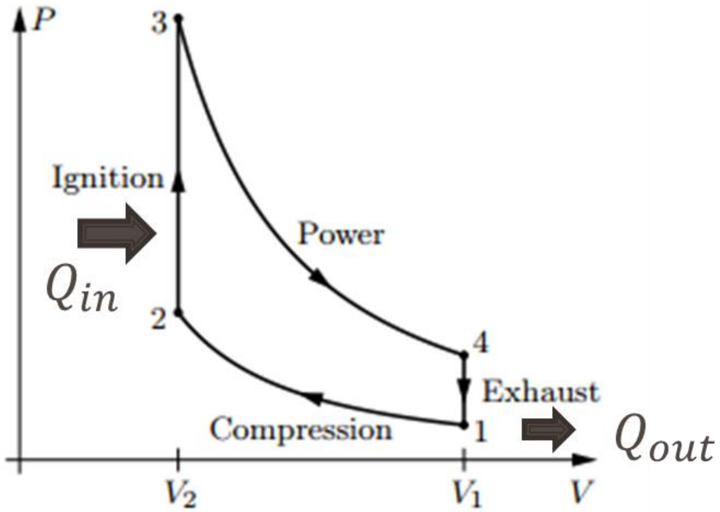
The efficiency we get:

$$\eta = 1 - \frac{\left(T_H \left(\frac{V_2}{V_1}\right)^{\gamma-1} - T_C\right)}{\left(T_H - T_C \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right)}$$

Otto Cycle

$$\eta = 1 - \frac{1}{\left(\frac{V_1}{V_2}\right)^{\gamma-1}}$$

$$\eta = 1 - \frac{1}{r^{(\gamma-1)}}$$



r = (V_1/V_2) is the "compression ratio" of the engine.

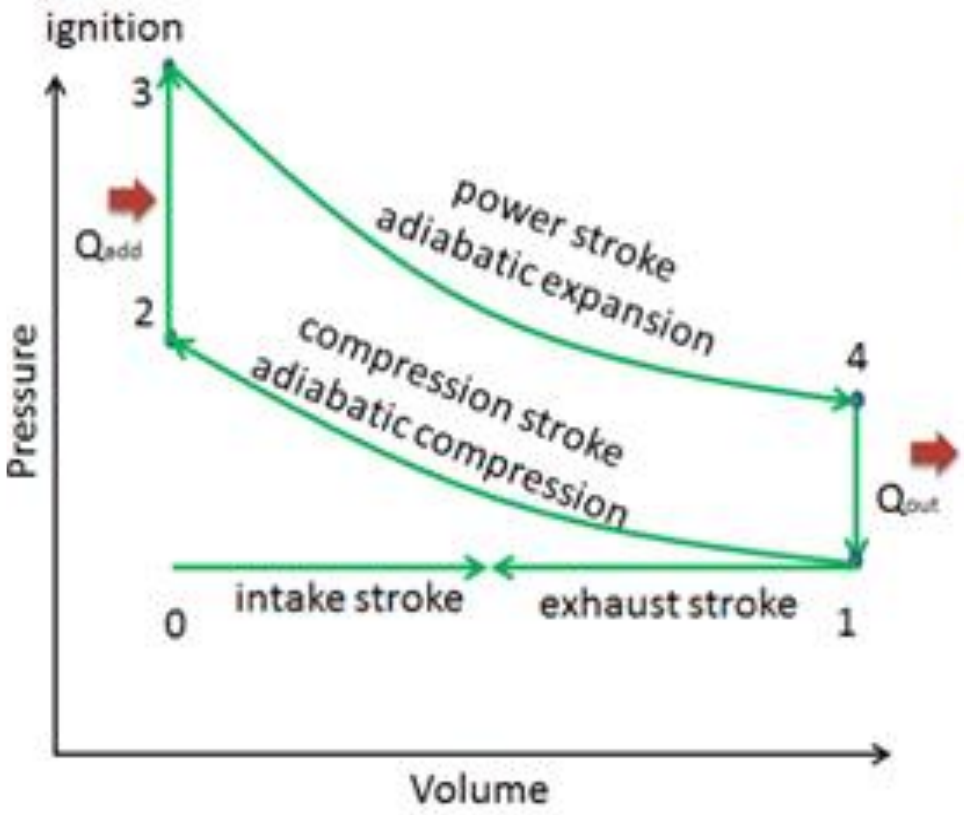
we have the efficiency in terms of the compression ratio.

Otto Cycle

We add steps 1 ⇒ 5 and 5 ⇒ 1 to the Otto cycle. A real engine, of course, does not run on an ideal gas. It lets a mixture of air and fuel in. This would be the new step 5 ⇒ 1 (this is the “intake” stroke on the engine).

In the real engine the combusted mixture is exhausted. In the model system this corresponds to the rapid cooling, step 4⇒ 1 and the new step 1 ⇒ 5.

The cycle begins all over again with the intake step, 5 ⇒ 1.



Summary of Last Class (Entropy Changes in Reversible Process)

i. **Isothermal Process**

$$\Delta S_T = \frac{Q}{T}$$

ii. **Isochoric Process (Constant Volume):**

$$\Delta S_V = C_V Log\left(\frac{T_f}{T_i}\right)$$

iii. **Isobaric Process (Pressure Constant):**

$$\Delta S_P = C_P Log\left(\frac{T_f}{T_i}\right)$$

iii. **General Case:**

$$\Delta S_{rev} = C_V Log\left(\frac{T_f}{T_i}\right) + Nk_B Log\left(\frac{V_f}{V_i}\right)$$

Entropy from Statistical Mechanics View

Statistical mechanics definition of entropy (we proof later while statistical mechanics):

$$S = k_B Log(\#\ of\ accessible\ States)$$

We will do next is to motivate the thermodynamic definition of entropy using the statistical mechanic version of the concept given above. We will reproof

$$\Delta S = \frac{Q_{rev}}{T}$$

Free Energy and Thermodynamics Potentials

The name “Thermodynamic Potential” refers to a set of state functions that depend on different independent variable. These variables in some way act as the constraints on the system.

We have already seen internal energy $U = U(V, T)$ or $U = U(N, V, T)$ thermodynamic identity (or at the combined first and second laws, or at the TdS equation) we have:

$$dU = TdS - PdV$$

from which we conclude that the natural variables for U are: $U = U(S, V)$. Or more generally, $U = U(N, S, V)$

Legendre transformation

What we will present here is a way to go from one set of independent variables to another. The process is called Legendre transformation.

Let's consider an-energy-like function $Z = Z(x, y)$ of extensive variables x and y. we write the differential as:

$$dZ = Xdx + Y\,dy$$

we already knew that:

$$\frac{\partial Z}{\partial x} = X \text{ and } \frac{\partial Z}{\partial y} = Y$$

where X and x are a conjugate pair; and Y and y are another conjugate pair.

Legendre transformation

Suppose we want to change our independent variables from x, y to X and Y.

Let’s define a function $M = M(X,Y)$ as constructed:

$$M(X,Y) = Z(x,y) - xX - yY$$

Let us compute the differential dM:

$$dM = dZ - xdX - Xdx - ydY - Ydy$$

But $dZ = Xdx + Ydy$

$$dM = Xdx + Ydy - xdX - Xdx - ydY - Ydy$$

$$dM = -xdX - ydY$$

With this we get:

$$\frac{\partial M}{\partial X} = -x \quad \text{and} \quad \frac{\partial M}{\partial Y} = -y\ ;$$

Maxwell Relations

we already knew that:

$$\frac{\partial Z}{\partial x} = X \ \text{ and } \ \frac{\partial Z}{\partial y} = Y$$

The transformation from $Z(x, y) \Rightarrow \ M(X, Y)$ is a **Legendre transformation**.

Maxwell Relations

Now suppose that we wanted to go from (x, y) as independent variables to (x, Y) as independent variables

We define a function:

$$\mathrm{N} = N(x, Y) = Z(x, y) - yY$$

and we get the differential dN:

$$dN = dZ(x, y) - ydY - Ydy = Xdx + Ydy - ydY - Ydy$$

So,

$$dN = Xdx - ydY$$

Now, with this we can write:

$$\frac{\partial N}{\partial x} = X \quad \text{and} \quad \frac{\partial N}{\partial Y} = -\mathrm{y}$$

Example 3.4

Given a function of two variables: $df = \frac{\partial f}{\partial x} \partial x + \frac{\partial f}{\partial y} \partial y \quad \equiv u\, dx + v\, dy$

Change the differential from (x, y) to (u, y) using Legendre transformation.

Quiz-3-1

A power plant operates by converting water into steam to drive turbines. In this idealized cycle, heat is drawn from a boiler and exhausted into a nearby river. Using the typical operating temperatures provided, calculate the maximum theoretical efficiency (η_{max}) of the plant (in percentage %).

Given Data:

- High-Temperature Reservoir (T_H): $500^o F$
- Low-Temperature Reservoir (T_L): $55^o F$

Entropy in Statistical Mechanics View

In statistical mechanics, entropy is defined by the Boltzmann equation: (we proof later while statistical mechanics):

$$S = k_B Log(\Omega)$$

where Ω is number of accessible microstates (possible microscopic arrangements)

Connecting Statistical and Thermodynamics Entropy

In the next section, we will use this microscopic definition to motivate the thermodynamic definition of entropy. We will show that for a reversible process:

$$dS = \frac{\delta Q_{rev}}{T}$$

And for an isothermal reversible process

$$\Delta S = \frac{Q_{rev}}{T}$$

Entropy Changes in Reversible Process

There is a reversible process between a system and its surroundings (temperature of system is equal to surrounding) in every process. **Let us look at some calculations of entropy changes.**

i. **Isothermal Process**

$$\Delta S_T = \int \frac{dQ}{T} = \frac{1}{T}\int dQ = \frac{Q}{T}$$

Entropy Changes in Reversible Process

ii. **Isochoric Process (Constant Volume):**

$$\mathrm{d}Q_V = (dU + PdV)_V = dU_V$$

we know that heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_V \rightarrow dU_V = C_V dT$

$$dS_V = \frac{dQ_V}{T} = \frac{dU_V}{T} = \frac{C_V dT}{T}$$

By assuming $\mathrm{C_V}$ is independent of temperature:

$$dS_V = \frac{C_V dT}{T} \rightarrow \Delta S_V = \int_{T_i}^{T_f} \frac{C_V dT}{T} = C_V Log\left(\frac{T_f}{T_i}\right)$$

Entropy Changes in Reversible Process

iii. Isobaric Process (Pressure Constant):

Heat capacity at constant pressure,

$$\delta Q_P = C_P dT_P$$

With this we can write (assuming C_P is independent of temperature):

$$dS_P = \frac{C_P dT_P}{T}$$

$$\Delta S_P = C_P \int_{T_i}^{T_f} \frac{dT_P}{T} = C_P Ln\left(\frac{T_f}{T_i}\right)$$

General Reversible Process of Ideal Gas

$$dQ_{rev} = dU + dW = dU + PdV$$

For an ideal gas, there is no volume dependence in the energy.

$$U(V,T) = U(T) \Rightarrow dU = C_V dT$$

$$\mathrm{d}Q_{rev} = C_V dT + PdV = C_V dT + \frac{Nk_B T}{V} dV$$

$$\frac{dQ_{rev}}{T} = C_V \frac{dT}{T} + Nk_B \frac{dV}{V}$$

$$\Delta S_{rev} = \int_{T_i}^{T_f} C_V \frac{dT}{T} + Nk_B \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S_{rev} = C_V Log\left(\frac{T_f}{T_i}\right) + Nk_B Ln\left(\frac{V_f}{V_i}\right)$$

This is the change in entropy in processes that take place for an ideal gas when there are both changes in temperature and changes in volume.

Entropy Changes in Irreversible Process

Entropy change of the penny using the reversible path.

$$dQ = dU + PdV = dU = C_V(T)dT$$

Here we are writing C_V as $C_V(T)$ to make it explicit that the heat capacity of the penny may well be a function of the temperature. For the reversible process:

$$dS = \frac{C_V(T)dT}{T} \rightarrow \Delta S = \int_{T_i}^{T_f} \frac{C_V(T)dT}{T}$$

Entropy Changes in Irreversible Process

Change of entropy of reservoir (Lake) is (recall that the process is isothermal for the lake):

$$dS_{lake} = -\frac{dQ_{penney}}{T_L} \quad \rightarrow \quad \Delta S_{lake} = -\frac{1}{T_L}\int_{T_H}^{T_L} dQ_{penny}$$

$$\Delta S_{lake} = -\int_{T_H}^{T_L} \frac{dQ_{penny}}{T_L} = -\frac{\Delta Q_{penny}}{T_L} = -\frac{C_P\left(T_{lake} - T_{penny}\right)}{T_L} = \frac{C_P(T_H - T_L)}{T_L}$$

Entropy Changes in Irreversible Process

Total entropy change:

$$\Delta S_{total} = \Delta S_{lake} + \Delta S_{penny} = -\int_{T_H}^{T_L} \frac{dQ_{penny}}{T_L} + \int_{T_H}^{T_L} \frac{C_p dT}{T}$$

Now, changing the order of the integration limits in both integrals, we can re-write this as.

$$\Delta S_{total} = \int_{T_L}^{T_H} \left[\frac{C_p dT}{T_L} - \frac{C_p dT}{T}\right]$$

since $T_H > T_L$, for every point along the integral:

$$\left[\frac{C_p dT}{T_L} - \frac{C_p dT}{T}\right] > 0$$

Hence,

$$\Delta S_{total} = \Delta S_{lake} + \Delta S_{penny} > 0$$

Entropy Changes in Irreversible Process

- Entropy increases as a result of the irreversible process. In this process the entropy of the penny decreases, the entropy of the lake increases, and because the process that was followed was not quasi-static, and hence irreversible, the overall entropy change of the Universe is an *increase* in entropy.
- It does not matter whether $T_{penny} > T_{lake}$, or $T_{penny} < T_{Lake}$. In either case the entropy of the Universe increases. What matters is that, with the temperature difference in either direction, the process is irreversible. Irreversible processes create entropy.

Legendre transformation

If we take: $U = U(S, V)$, then

$$dU = TdS - PdV$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - PdV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \ \ \& \ \ \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Partial Derivatives

Let’s consider a volume change path 1-2-3 constant pressure 1-2 and constant temperature 2-3:

$$dV_{1,2,3} = \left(\frac{\partial V}{\partial T}\right)_{P1} dT + \left(\frac{\partial V}{\partial P}\right)_{T2} dP$$

Let’s consider a volume change path 1-4-3 constant Temperature 1-4 and constant pressure 4-3:

$$dV_{1,4,3} = \left(\frac{\partial V}{\partial P}\right)_{T1} dP + \left(\frac{\partial V}{\partial T}\right)_{P3} dT$$

Since same volume change:

$$\frac{\left[\left(\frac{\partial V}{\partial T}\right)_{P3} - \left(\frac{\partial V}{\partial T}\right)_{P1}\right]}{dP} = \frac{\left[\left(\frac{\partial V}{\partial P}\right)_{T2} - \left(\frac{\partial V}{\partial P}\right)_{T1}\right]}{dT}$$

Partial Derivatives

When dP and dT approach zero. It is mixed second partial derivative of V with respect to P and T

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right]_T = \frac{\partial^2 V}{\partial P \partial T} = \left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right]_P = \frac{\partial^2 V}{\partial T \partial P}$$

So

$$\frac{\partial^2 V}{\partial P \partial T} = \frac{\partial^2 V}{\partial T \partial P}$$

So just proofed that mixed second partial derivative is independent of the order of differentiation.

Partial Derivatives

$$\left(\frac{\partial\left(\frac{\partial U}{\partial S}\right)_V}{\partial V}\right)_S = \left(\frac{\partial\left(\frac{\partial U}{\partial V}\right)_S}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Where $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -P$

Clearly the quantities on the left-hand side (T and V) are readily accessible to measurement; the condition of adiabaticity is readily met by a reversible process with no heat flow involved. On the other hand, the dependence of pressure on entropy is not a readily accessible quantity.

These relations between second cross derivatives of the thermodynamic potentials are called are called the Maxwell's relations.

Legendre transformation $(S, V) \Rightarrow (S, P)$

we have obtained $H = H(S, P)$.

$$H = U + PV \Rightarrow dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

So:

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

With this we can write:

$$\left(\frac{\partial \left(\frac{\partial H}{\partial S}\right)_P}{\partial P}\right)_S = \frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial \left(\frac{\partial H}{\partial P}\right)_S}{\partial S}\right)_P$$

Legendre transformation $(S, V) \Rightarrow (S, P)$

This becomes:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

Again, the left-hand side is readily measurable while the right-hand side is difficult to obtain experimentally.

Enthalpy (H)

Enthalpy is a state function that describes the total heat content of a system. It accounts for both the internal energy and the energy required to "make room" for the system by pushing against the surrounding pressure.

The formal definition is:

$$H = U + PV$$

Feature	**Heat (q)**	**Enthalpy (H)**
Definition	Energy in transit due to ΔT.	Total heat content of a system.
Type	Path Function (depends on the route).	State Function (depends only on start/end).
Measured as	A flow of energy (J).	A property of the substance (J/mol).
Context	What is moving between objects.	What is stored within the chemical bonds/system.

Legendre transformation $(S,V) \Rightarrow (T,V)$

We do next the Legendre transformation (S,V) => (T,V)

or, alternatively, from $U(S,V)$ => $F(T,V)$

We have:

$$dU = TdS - PdV,$$

With the transformation is from: $Z(x,y)$ to $N(X,y)$

$$N = Z - xX = U - TS = F$$

$$F = U - TS$$

$$dF = dU - SdT - TdS = TdS - PdV - SdT - TdS = -SdT - PdV$$

So, with this we can identify:

Legendre transformation $(S, V) \Rightarrow (T, V)$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \text{and} \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

And we can get the corresponding Maxwell’s relations from the cross derivatives:

$$\left(\frac{\partial\left(\frac{\partial F}{\partial T}\right)_V}{\partial V}\right)_T = \left(\frac{\partial\left(\frac{\partial F}{\partial V}\right)_T}{\partial T}\right)_V \rightarrow -\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

Again, the change of the entropy as a function of volume is very difficult to measure experimentally, when compared to the change in pressure as a function of temperature at constant volume, which is something very readily measurable with a thermometer and a manometer.

Legendre transformation U$(S,V) \Rightarrow G(T,P)$

Finally, we look at the Legendre transformation from $U(S,V) \; => \; G(T,P)$

Recalling that:

$$dU = TdS - PdV$$

$$M = Z - xX - yY \Rightarrow G = U - TS + PV$$

$$N = U - TS + PV \Rightarrow G$$

$$dG = dU - SdT - TdS + PdV + VdP$$

$$dG = TdS - PdV - SdT - TdS + PdV + VdP = -SdT + VdP$$

For the Maxwell's relation for this one we have:

$$\left(\frac{\partial\left(\frac{\partial G}{\partial T}\right)_P}{\partial P}\right)_T = \left(\frac{\partial\left(\frac{\partial G}{\partial P}\right)_T}{\partial T}\right)_P \rightarrow -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

Maxwell Relations

Thermodynamic Potential	Independent Variables	Maxwell's Relations
Internal Energy U	S, V dU = TdS - PdV	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
Enthalpy H = U + PV	S, P dH = TdS + VdP	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
Helmholtz free energy F F = U-TS	T, V dF = -SdT-PdV	$-\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$
Gibbs free energy, G = U-TS + PV G = F + PV	P, T dG = -SdT+VdP	$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

Thank you very much for your attention