

Lecture 12

For a Carnot engine, which is reversible and the most efficient engine possible, can be characterized by two temperatures, T_H and T_C . According to Carnot's theorem,

$$\text{might not be reversible} \quad \eta_{\text{any}} \leq \eta_{\text{Carnot}}$$

$$\Rightarrow 1 - \frac{Q_C}{Q_H} \leq \eta_{\text{CE}}(T_H, T_C)$$

$$\Rightarrow 1 - \frac{\cancel{Q_H} Q_C}{\cancel{Q_C} Q_H} \leq 1 - \cancel{T_H} \frac{T_C}{T_H}$$

$$\Rightarrow - \frac{Q_C}{Q_H} \leq - \frac{T_C}{T_H} \Rightarrow - \frac{Q_C}{T_C} \leq - \frac{Q_H}{T_H}$$

$$\therefore \frac{Q_H}{T_H} + \left(- \frac{Q_C}{T_C} \right) \leq 0$$

If we define ΔQ as the heat input (meaning heat entering to the system), then,

$$\sum_{\text{cycle}} \frac{\Delta Q}{T} = \frac{Q_H}{T_H} + \left(- \frac{Q_C}{T_C} \right) \leq 0$$

$$\therefore \oint \frac{\Delta Q}{T} < 0$$

If the engine is reversible, then,

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

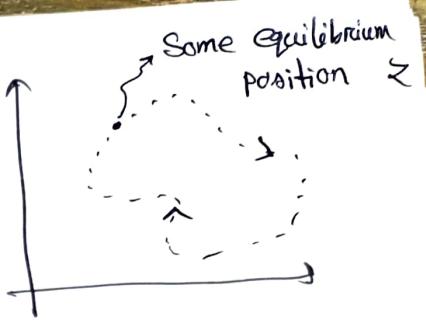
∴ For the reversible engine, $\oint \frac{dQ_{rev}}{T} = 0$.

Now, we will like to generalize this result. We have only considered engines operating between two temperatures. However, real engines can be much more complicated since their working substance changes temperature in a much more complicated way. They might operate within more than one heat reservoirs. And since you need to get the energy out of the real engine quickly, quasi-stationarity can't be maintained, so, it is pretty much obvious that reversibility is violated. So, we would like to generalize our treatment to a whole series of reservoirs and we would like the cycle to be either reversible or irreversible.

Cyclic process

We start from an equilibrium position, we make a transformation, and ultimately return to the same

point and then wait enough so that we reach to the equilibrium position.



Clausius' theorem

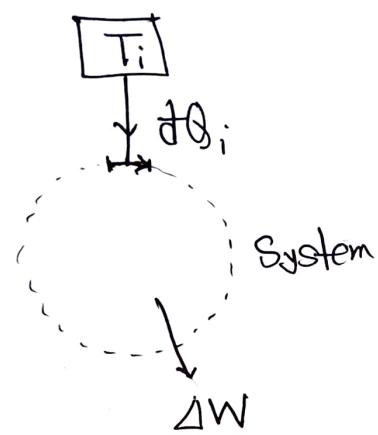


Figure 1

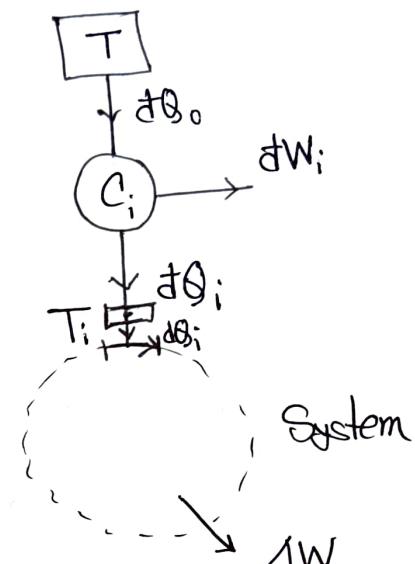


Figure 2

Our general cycle is illustrated in figure 1. For this cycle, heat dQ_i enters at a particular part of the cycle, where the system receives the heat while being connected to a reservoir that is at temperature T_i . The total work extracted from the cycle is, say, ΔW . Since the system returns to the same state after completion of the cycle, $\Delta U = 0$. So, according to first law,

$$\Delta W = \oint \cancel{dQ_i} \quad (1)$$

where the sum is taken over the whole cycle

Now, let's think about the second generalization. We imagine heat is being supplied at each point of the cycle to the system via a Carnot engine. The Carnot engine is connected between a reservoir at temperature T (there can be more than one Carnot engine as long as they are connected to the same reservoir with temperature T). The engine dumps heat dQ_i at temperature T_i to our system at some specified point ~~in~~ interval in the cycle. In the process, the Carnot engine does some work dW_i in each intervals. The system does a total of ΔW work in the whole cycle.

Now, for the i^{th} interval, for the Carnot engine,

$$\frac{dQ_o}{T} = \frac{dQ_i}{T_i}$$

$$\Rightarrow \frac{dQ_i + dW_i}{T} = \frac{dQ_i}{T_i}$$

$$\Rightarrow dW_i = dQ_i \left(\frac{T}{T_i} - 1 \right) \quad \text{--- (11)}$$

Here, the sign of dQ_i is not specified. The Carnot engine might operate in a series of

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infinitesimal cycle in either direction.

Now, after the cycle is completed, the system and the Carnot's engine return to their original state. The whole scheme seems to convert heat into work. That is, it seems the whole operation is extracting some heat $\oint \delta Q_0 = \oint \delta Q_0$ from the reservoir and converting into a total work W . Here, the work W is the ~~same~~ sum of total work elements done by Carnot's engine, and the work performed by the system in the complete cycle.

$$\therefore W = \oint \delta w_i + \Delta W$$

But this would violate second law of thermodynamics, Kelvin's statement.

\therefore Total work done in the cycle, $\Delta W + \oint \delta w_i \leq 0$
(the reverse is however possible, that some work is done on the system that produced some heat, and hence the inequality).

$$\therefore \cancel{\oint (\delta Q_0 - \delta Q_i)} + \oint \delta Q_i \leq 0$$

$$\text{Now, } \Delta W + \oint dW_i \leq 0$$

$$\Rightarrow \oint dQ_i + \oint dQ_i \left(\frac{T}{T_i} - 1 \right) \leq 0$$

↓ ↓
 from (i) from (ii)

$$\Rightarrow \oint dQ_i + \oint \frac{T}{T_i} dQ_i - \oint dQ_i \leq 0$$

$$\Rightarrow T \oint \frac{dQ_i}{T_i} \leq 0$$

$$\therefore - \oint \frac{dQ_i}{T_i} \leq 0$$

Since T is a non-zero and non-negative quantity, we can divide both sides by T .

This is known as Clausius' inequality, which is embodied in the expression of Clausius' theorem.

Clausius' theorem: For any cyclic transformation (reversible or not), $\oint \frac{dQ}{T} \leq 0$, where dQ is the heat increment supplied to the system at temperature T .

Consequences of Clausius' theorem

1. Say, heat is being introduced to the system in quasi-static manner, and we consider a reversible cycle. For a reversible cycle,

We can run the cycle in the opposite direction,



$$\therefore \oint \frac{dQ_{rev}}{T} \rightarrow - \oint \frac{dQ_{rev}}{T}$$

Since Clausius' theorem states that, $\oint \frac{dQ_{rev}}{T} \leq 0$,^①

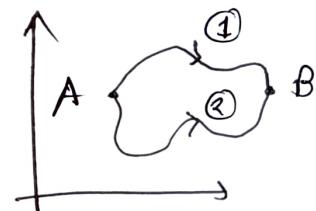
running the cycle in opposite direction implies,

$$\oint -\frac{dQ_{rev}}{T} \leq 0 \quad \text{--- (ii)}$$

Equation (i) and (ii) implies that,

$$\boxed{\oint \frac{dQ_{rev}}{T} = 0}$$

Now, consider the quantity in the cycle ABA.



$$\therefore \oint \frac{dQ_{rev}}{T} = 0$$

$$\Rightarrow \int_A^B \frac{dQ_{rev}}{T_1} + \int_B^A \frac{dQ_{rev}}{T_2} = 0$$

$$\therefore \int_A^B \frac{dQ_{rev}}{T_1} = - \int_B^A \frac{dQ_{rev}}{T_2} = \int_A^B \frac{dQ_{rev}}{T_2}$$

So, the integral is independent of the path taken from A to B.

$\int_A^B \frac{dQ_{rev}}{T}$ is the same in all paths going from A to B.

Therefore, the quantity $\frac{dQ_{rev}}{T}$ is an exact differential. This is like conservative force in mechanics, where the work done is independent of path. Since the differential is exact we can write down a new state function which we call, entropy, S , by,

$$dS = \frac{dQ_{rev}}{T}$$

$$\therefore S(B) - S(A) = \int_A^B dS = \int_A^B \frac{dQ_{rev}}{T}$$

For an adiabatic process (a reversible adiathermal process), we have $dQ_{rev} = 0$.

$\Delta S = 0$
and so, an adiabatic process involves no change in entropy (this is why this process is also called isentropic).

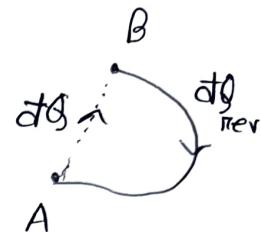
Anyways, given some reference state 0, you can define the entropy of some state A as.

$$S(A) = \int_0^A \frac{dQ_{rev}}{T}$$

Since entropy is a state function, it depends on the state variables. It doesn't matter whether you go to a state in irreversible or irreversible path. As long as the system is in some equilibrium

state, you have a well defined entropy (up to at least relative to some reference state).

Q. Reversibility; irreversible transformation: Consider an irreversible change from A to B. Then make a complete cycle by returning from B to A along a reversible path. Now, according to Clausius' theorem,



$$\oint \frac{dQ}{T} \leq 0$$

$$\Rightarrow \int_A^B \frac{dQ_{irrev}}{T} + \int_B^A \frac{dQ_{rev}}{T} \leq 0$$

$$\Rightarrow \int_A^B \frac{dQ}{T} \leq \int_A^B \frac{dQ_{rev}}{T}$$

$$\Rightarrow \int_A^B dS \geq \int_A^B \frac{dQ}{T}$$

$\therefore dS \geq \frac{dQ}{T}$

$S(B) - S(A) \geq \int_A^B \frac{dQ}{T}$

and

The equality obviously hold for a reversible process.

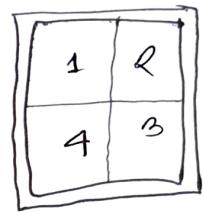
If we now stress that the irreversible path is also adiabatic, meaning isolated from the

environment, then $\oint \delta Q = 0$.

$\therefore S(B) \geq S(A)$ that is $dS \geq 0$

So, entropy of any isolated system never decreases. Moreover, if the adiathermal process is also reversible, then the resulting states have the same entropy, that is the entropy change is zero. Consider adiabatical isolating a number of subsystems, each initially separately in equilibrium. As they come to a state of joint equilibrium, since the net $\oint \delta Q = 0$, we must have $\oint dS \geq 0$. Thus, an adiabatic (isolated) system attains a maximum value of entropy in equilibrium since the entropy can only increase (irreversibly changes). The direction of increasing entropy thus points out to the thermodynamic arrow of time, the path to equilibrium. Isolated systems can only evolve to states of equal or higher entropy.

This gives us another statement of second law:
"The entropy of an isolated system always tends to



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a maximum." We can apply this idea to the universe as a whole. Assuming the universe itself is a thermally isolated system, the first two law of thermodynamics can be written as —

1. $U_{\text{universe}} = \text{constant}$

2. S_{universe} can only increase (if you disregard the impossible reversible processes).

Revisiting the first law

The first law of thermodynamics states that,

$$dU = dW + dQ$$

Now, for reversible change, $dQ = TdS$

$$\text{and } dW = -pdV$$

$$\therefore -dU = TdS - pdV$$

$$\boxed{\therefore dU = TdS - pdV} \quad \begin{array}{l} \text{(if the only work done} \\ \text{is by shrinking or expanding} \\ \text{volume).} \end{array}$$

— (1)

In general we can have generalized force J_i and generalized displacement dx_i and the first law will take the following form:

$$\boxed{dU = TdS + \sum_i J_i dx_i}$$

This result, derived by a consideration of reversible changes. However, the equation states a relationship between functions of state, since all the quantities are functions of state. We therefore make a most important range of validity of the equation, and declare it is applicable to any differential change, reversible or irreversible. There is something subtle going here. You can go from one state to another in irreversible paths. Say, you are going from A to B in irreversible path (that include not quasi-static process and friction may be). You want to use this equation. But you can always construct a reversible path from A to B, and calculate $\int_A^B dU$ - using the equation. The thing is $\int_A^B dU$ is gonna be the same whether you are going from A to B in reversible OR irreversible paths. So, the equation will correspond to the same result.

For example, for any change in fluid, $dU = dW + dQ$

$$\therefore dU = TdS - PdV \quad \text{--- ①}$$

It is only for a reversible process, $dQ = PdV$ and $dW = -PdV$

$\delta Q = TdS$ and $\delta W = -pdV$. However, equation ④ implies that, for an irreversible process,

$$\delta Q < TdS$$

In an irreversible process then, $\delta W > -pdV$, so that equation ① is valid. If $\delta Q = TdS - \epsilon$, then $\delta W = -pdV + \epsilon$ so that equation ① is still valid. This can be illustrated by an experiment where a gas expands into vacuum under isolated conditions. Interested readers of this lecture is suggested to follow chapter 3 of the book by A. B. Pippard named "Elements of Classical Thermodynamics" [Pages 19-23 and then Chapter 4 (page 42)].

Now, we have mostly solved the problem of finding expressions for δQ and δW in terms of functions of state, and so we will have to only deal with exact differentials. Equation ① is valid for all cases, and it is from this equation analytical applications of thermodynamics to physical problems stem.

Now, eqn (1) indicates that U changes whenever S or V changes. Thus, the ~~different~~ function U can be written in terms of the variable S and V , which are so called natural variables. These variables are both extensive (like all generalized displacements), where P and T are both intensive variables (like all generalized forces). We can now write $U = U(S, V)$ and hence,

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

and immediately upon comparing with (1) we can write,

$$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_V}$$

$$\text{and } \boxed{P = -\left(\frac{\partial U}{\partial V}\right)_S}$$

The ratio of P and T can also be written as-

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

Using the reciprocity theorem,

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

We can express some variables in terms of others.

$$dU = TdS + \sum_i J_i dX_i$$

$$\Rightarrow TdS = dU - \sum_i J_i dX_i$$

$$\therefore dS = \frac{1}{T} dU - \sum_i \frac{J_i}{T} dX_i$$

which implies, $S = S(U, X)$ where $X = (X_1, X_2, \dots, X_n)$
if there are n number of ways to do work. The equations imply,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_X \quad \text{and} \quad \frac{J_i}{T} = - \left(\frac{\partial S}{\partial X_i} \right)_{U, X_{j \neq i}}$$

For our case where there is only one way to do work,

$$dU = TdS - PdV$$

$$\therefore \frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V \quad \text{and} \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_U$$

Here, $\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_V$

If we recall from our tour to Statistical mechanics,

$$\frac{1}{k_B T} = \frac{d \ln \Omega}{d E} = \frac{d \ln \Omega}{d V}$$

Combining these two we get, $[S = k_B \ln Q]$, which is nothing but Boltzmann entropy. This is how, the Boltzmann entropy and thermodynamic entropy is connected to each other and imply the same thing.