Thermodynamics Entropy

by Tony Shing

Overview:

− Reversible Process v.s. Irreversible Process

− Related history of Thermodynamics entropy (anything before Boltzmann)

　− Carnot's engine

　− Kelvin's temperature

　− Clausius' entropy function

1 Reversible v.s. Irreversible

In thermodynamics, a system is undergoing a "reversible" process only if

− No energy loss out of system (i.e. satisfy thermal 1$^{\text{st}}$ law), and

− The process is quasi-static.

1.1 Quasi Static Process

The term "**quasi-static**" literally describes the system as looking like static, but at the same time is also changing, like in a "half-equilibium-half-transititioning" state. For example, we can look at the reality during the process of a gas compression.

1. <u>Before Compression</u>, we can assume the gas being evenly distributed. The particles' speeds are mostly the same everywhere in the container, and so we can assign a well-defined single value as the pressure in the container.

<p style="color:red; text-align:center">(add figure here: gas compress 1)</p>

2. <u>Right at the beginning of the push</u>, only the gas particles near the piston can feel the piston pushing. So region near the piston has a different pressure from region far away from the piston. The pressure in the container becomes ambiguous.

<p style="color:red; text-align:center">(add figure here: gas compress 2)</p>

3. <u>When piston just comes to stop</u>, particles pushed by piston start to mix with the rest of the gas particles. The pressure in the container is still ambiguous.

<p style="color:red; text-align:center">(add figure here: gas compress 3)</p>

4. <u>After some time</u>, the particles become well-mixed and kinetic energy becomes even distributed among particles. We can again assign a well-defined single value as the pressure in the container.

<p style="text-align:center">(add figure here: gas compress 4)</p>

So now comes the question: we found that we cannot use a single value to represent the pressure during the compression. Is it really correct to represent a process with a single line in the PV diagram?

<p style="text-align:center">(add figure here: ambiguous PV)</p>

In reality, this is indeed <u>incorrect</u>. But in order to use the derived results (those we have seen in the last note), physicists theorize the process to be "infinitestimal" in order to apply them in thermodynamics:

– The piston is moving extremely slow, only compress a very tiny volume at each step.

– Time allowed for the gas to fully mix is extremely long. So we can assure the KE are even distributed.

Then such step is repeated for many many times, we can "approximate" the state parameters to be well-defined and changing continuously along the process.

<p style="text-align:center">(add figure here: doted to continuous)</p>

Such process is called "Quasi-Static" process:

$$\text{Quasi-static } = \underline{\text{Half Equilibrium }} + \underline{\text{ Half transitioning}}$$

Made of infinitely many intermediate states so its state parameters are always well-defined Made of infinitely many processes so state parameters are always smoothly changing

Quasi-static processes are the ideal processes in thermodynamics because they are <u>reversible</u>.

<p style="text-align:center">(add figure here: quasi static reversible)</p>

1.2 Irreversible Process

However, quasi-static process is impractical because

– it takes an extremely long waiting time (ideally, infinite long).

– only very small change at each step (ideally, infinitestimally small).

All thermodynamics processes, when carried out in reality, are irreversible. The lines in the P-V diagram shall not be as well-defined as we have seen,

<p style="text-align:center">(add figure here: ideal PV cycle vs reality PV cycle)</p>

<p style="text-align:center">P.2</p>

Adapting this reality to what we have learnt in the last note,

1. Formula to δW and δQ are only for the ideal reversible case. An irreversible process does not have a not well-defined path, so integration is not analytically comput-able.

$$\int_{\substack{\text{Irreversible} \\ \text{process}}} \delta W = \int_{\substack{\textcolor{red}{\text{No exact}} \\ \textcolor{red}{\text{path}}}} \mathrm{d}W = (\text{Uh oh...})$$

2. A real engine cannot be run as a refridgerator by inverting its cycle, because its processes are no longer reversible.

3. Efficiency of real engines must be less than the theoretical limit (Carnot's theorem).

Note: Such irreversibility only happens in thermodynamics system. In the mechanical perspective, the state parameters are positions and velocities of the particles (x_i, v_i). If we can compute the equation motion of the particles, we can predict when the particles return to their initial positions and velocities. So every process is reversible as long as energy is conserved.

In the next note, we shall discuss more the differences between mechanical and thermodynamics perspectives, and how do these lead to irreversibility of a system.

The following sections present several important discoveries within the early period of thermodynamics researches.

- (1824) Carnot's theorem and Carnot's engine.

- (1848) Kelvin temperature scale.

- (1850-1851) First two statements of thermodynamics 2$^{\text{nd}}$ law by Kelvin and Clausius.

- (1854) First mathematical formulation of entropy by Clausius.

The era of classical thermodynamics ended around 1860s, when *statistical mechanics* started taking place.

---

2 Historical Development of Thermodynamics 2$^{\text{nd}}$ Law

2.1 Carnot's Engine & Carnot's Theorem

Nicolas Léonard Sadi Carnot was the first person who suggested the concepts of **heat engine**:

- one can extract energy for our use, via the process when heat flow from hot object to cold object. It is just like we can extract KE from objects that fall from a high place to low place.

- A heat engine is a operator that runs cyclic processes which can extract energy to do work, from the natural heat flow between hot and cold objects.

– As long as the temperature difference between hot/cold objects is maintained, a heat engine can run a cycle of processes indefinitely.

(add figure here: first carnot engine = piston transfer back and forth)

He also proposed one of the foundation in thermodynamics: **Carnot's theorem**.

Among any heat engines that operate between 2 heat reservoirs of fixed temperature, the engine that runs reversible processes is the most efficient in converting heat to work done.

The reversible engine that he proposed was the Carnot cycle, which gives the theoretical maximum of engine efficiency. Any other engines that run reversible cycles would also have the same maximum efficiency.

(add figure here: Carnot cycle)

	Process
$\boxed{1} \rightarrow \boxed{2}$	iso. T
$\boxed{2} \rightarrow \boxed{3}$	Adiabetic
$\boxed{3} \rightarrow \boxed{4}$	iso. T
$\boxed{4} \rightarrow \boxed{1}$	Adiabetic

Unfortunately, Carnot did not prove his theorem correctly - his arguments were based on thermal 1st law and involved circular reasoning. Carnot passed away in 1832 and did not live long enough to see his work being recognized. It was until around 1850s, scientists realized that Carnot's theorem shall not be proven by 1st law. It must be described as an independent law - the thermodynamics 2nd law.

Side note:

– Theorem = Consequences that can be logically derived from known facts.

– Law = Rules that are concluded based on observations (like common sense).
Such observations may be explainable with deeper theories,
but we do not know yet.

2.2   The First 2 statements of Thermodynamics 2nd Law

Lord Kelvin and Rudolf Clausius independently formulated their own statement about the law of irreversibility:

– Kelvin: No W.D. $\Rightarrow$ No reverse heat flow

– Clausius: Cannot convert 100% Heat flow to W.D.

Note that their statements are still "laws" - they were written down based on common sense, without explanation.

We can prove that they are logically equivalent to Carnot's theorem by contradiction (If one fails, the other must also fail.)

1. <u>Clausius fails $\Rightarrow$ Kelvin fails</u>
   Suppose Clausius' statement is wrong - *there exists an engine that can convert 100% of a heat flow to W.D.*

   (add figure here: wrong cla)

   Then we can operate it together with a refridgerator that runs Carnot cycle:

   (add figure here: cla to kel)

   By energy conservation, we have

   $$Q_1' = Q_2' + W = Q_2 + Q_1 > Q_1$$

   which is equivalent to a cycle with net heat flow of Q_2' from colder reservoir to hotter reservoir, without any external W.D. supply. *This is a contradiction to Kelvin's statement.*

   (add figure here: cla logic wrong)

2. <u>Kelvin fails $\Rightarrow$ Clausius fails</u>
   Suppose Kelvin's statement is wrong - *heat can flow from a colder reservoir to a hotter reservoir without needing any external W.D.*

   (add figure here: wrong kel)

   Then we can operate it together with an engine that runs Carnot cycle:

   (add figure here: kel to cla)

   If we maintain the heat flow out of colder reservoir (Q) equal to the heat flow into the colder reservoir (Q_2), such that T_2 is kept constant, by energy conservation we writes

   $$Q = Q_2 = Q_1 - W$$

   which is equivalent to having 100% of the heat extracted from hot reservoir to be converted into W.D.. *This is a contradiction to Clausius' statement.*

3. <u>Carnot fails $\Rightarrow$ Kelvin fails</u>
   Suppose Carnot's theorem is wrong - *there is a hypothetical engine that runs irreversible process but has a higher efficiency than a Carnot engine.*

   $$\begin{pmatrix} \text{Efficiency of} \\ \text{Hypothetical engine} \end{pmatrix} = \eta_1 > \eta_2 = \begin{pmatrix} \text{Efficiency of} \\ \text{Carnot engine} \end{pmatrix}$$

   Then we can operate it together with a Carnot refridgerator.

If we look at the net heat flow into the hot reservoir,

$$\frac{\eta_1}{\eta_2}Q - Q > 0 \quad \text{if} \quad \eta_1 > \eta_2$$

which is equivalent to having heat flowing from cold reservoir to hot reservoir spontaneously. *This is a contradiction to Kelvin's statement.*

<u>Note</u>: Because an irreversible engine cannot be reverted to become an irreversible refridgerator, It is not logical to operate an irreversible engine side by side with an irreversible refridgerator to keep the heat balance.

---

3 Kelvin's Temperature Scale

3.1 Temperature Measurement Before 19$^{\text{th}}$ Century

Some oldest temperature scales were defined using expansion/contraction of material under heat. For example, the Celsius scale was defined by the change in length of mercury/alcohol in a thin glass tube, using water's freezing and boiling as reference points and divide the expansion into 100 grids.

(add figure here: Celsius thermometer)

Meanwhile, thermodynamics properties of ideal gas were already well-investigated through experiments. For example, scientists already knew that the P-T relation is linear, i.e. it can be plotted as a straight line.

(add figure here: PT graph)

However, data were limited by the freezing point of material being used to measure temperature. Without experimental support, it was impossible to tell if there were new physics beyond $-273.15°$C.

3.2 Thermodynamics Temperature Scale

The Kelvin temperature scale is not just naively shifting the 0 point from $0°$C to $-273.15°$C, but is a derived scale based on the efficiency of Carnot engine.

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{\text{Heat input to colder reservoir}}{\text{Heat output from hotter reservoir}}$$

$$\sim 1 - \frac{T_C}{T_H} = 1 - \frac{\text{How hot is the colder reservoir}}{\text{How hot is the hotter reservoir}}$$

$$= \left(\begin{matrix}\text{Some function of "Relative hottness"} \\ \text{between hotter and colder reservoir}\end{matrix}\right)$$

The idea is that in a reversible engine, the engine efficiency is purely determined by how hot the hotter reservoir relative to the colder reservoir. If we can measure the engine efficiency, we can create a scale of hottness between reservoirs.

(add figure here: same cold reservoir -¿ run with hot reservoir 1 gives eta1, run with hot reservoir 1 gives eta2 -¿ res1 is hotter than res2 if eta1¿eta2)

Let's say the hottness/coldness of 2 heat reservoirs H and C are measured using some scale θ, assigned with a "relative hottness" of θ_H and θ_C respectively.

1. Operate a Carnot engine between the two reservoirs. Let the efficiency be written as a function of θ_H and θ_C.

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - f(\theta_C, \theta_H)$$

(add figure here: carnot engine)

2. We can insert a warm reservoir W in between them, whose relative hottness is in between. i.e. $\theta_H > \theta_W > \theta_C$.

(add figure here: middle engine)

3. We also have these mathematical relations:

$$- \frac{Q_C}{Q_H} = \frac{Q_C}{Q_W} \cdot \frac{Q_W}{Q_H} \quad \Rightarrow \quad f(\theta_C, \theta_H) = f(\theta_C, \theta_W) \cdot f(\theta_W, \theta_H)$$

$$- \frac{Q_C}{Q_H} = \frac{1}{\frac{Q_H}{Q_C}} \quad \Rightarrow \quad f(\theta_C, \theta_H) = \frac{1}{f(\theta_H, \theta_C)}$$

4. What kinds of function $f(\cdot, \cdot)$ satisfy these relations? There are infinitely many choices, for example,

   – Taking $f(\theta_C, \theta_H) = \dfrac{\theta_C}{\theta_H}$, then

$$f(1, 10) = \frac{1}{10} = \frac{10}{100} = f(10, 100)$$

   An engine working between reservoirs with "hottness" 1 and 10 yield the same efficiency as working between reservoirs with "hottness" 10 and 100.

(add figure here: exp scale)

   This scale of hottness is a logarithmic scale relative to efficiency.

   – Taking $f(\theta_C, \theta_H) = e^{\theta_C - \theta_H}$, then

$$f(0, 10) = e^{10-0} = e^{20-10} = f(10, 20)$$

   An engine working between reservoirs with "hottness" 0 and 10 yield the same efficiency as working between reservoirs with "hottness" 10 and 20.

This scale of hottness is a linear scale relative to efficiency.

5. Finally, which scale was chosen in history? Because the Celcius scale already existed at that time and was in used in thermodynamics experiment and theories, such as deriving the efficiency of Carnot engine,

$$\begin{matrix} \text{Carnot engine's} \\ \text{efficiency} \end{matrix} = 1 - \frac{T_L + 273.15}{T_H + 273.15}$$

where T_H, T_L are values of temperature measured under the Celcius scale. It is just convenient to choose $f(\theta_1, \theta_2) = \dfrac{\theta_1}{\theta_2}$ so that our new scale of hottness is

$$\boxed{\theta = (\text{Celsius temperature}) + 273.15}$$

which is now known as the **Kelvin temperature scale**.

3.3   The Consequence: Absolute Zero

Through the Kelvin scale, we can relate temperature with engine efficiency to explain why the absolute zero temperature cannot be reached. Consider a Carnot engine working between two reservoirs, with the colder side at absolute zero ($\theta = 0$). Then the efficiency of this engine becomes

$$\eta = 1 - \frac{0}{\theta_H} = 1$$

This is equivalent to having heat 100% converted into work done, which is a violation to the Clausius statement.

In addition, if we choose a different temperature scale

– Choose $f(\theta_C, \theta_H) = \dfrac{\theta_C}{\theta_H}$ $\Rightarrow$ the point of 100% efficiency corresponds to $\theta_C = 0$.

– Choose $f(\theta_C, \theta_H) = e^{\theta_C - \theta_H}$ $\Rightarrow$ the point of 100% efficiency corresponds to $\theta_C = -\infty$.

So you may also claim that negative temperature is not physical because of our choice of scale.

4   Clausius's Entropy Function

The term "**entropy**" was named by Rudolf Clausius to a special state function S

$$\mathrm{d}S \overset{\text{def}}{=\!=} \frac{\delta Q_{\text{in}}}{T}$$

Here the Q are labeled Q_{in} only to emphasize that Q is the heat <u>input</u> to each object, the same sign convention as in thermal 1st law.

Following the definition, we can derive the formula of $\mathrm{d}S$ for the 4 common thermodynamics processes. (Leave to you as an exercise.)

	Iso. V	Iso. P	Iso. T	Adiabetic
S	$= \boxed{\int \frac{\mathrm{d}U}{T} + 0}$ $= \boxed{\int \frac{C_V}{T}\,\mathrm{d}T}$ $= \boxed{\underbrace{\frac{i}{2}Nk}_{C_V} \ln\left(\frac{T_2}{T_1}\right)}$	$= \boxed{\int \frac{\mathrm{d}U}{T} + \int \frac{\delta W}{T}}$ $= \boxed{\int \frac{C_P}{T}\,\mathrm{d}T}$ $= \boxed{\underbrace{\frac{i+2}{2}Nk}_{C_P} \ln\left(\frac{T_2}{T_1}\right)}$	$= \boxed{\int \frac{\mathrm{d}U}{T} + \int \frac{\delta W}{T}}$ $= \boxed{\frac{1}{T}\left(\int \mathrm{d}U + \int \delta W\right)}$ $= \boxed{Nk \ln\left(\frac{V_2}{V_1}\right)}$	0

Formula in $\boxed{\text{red box}}$ are universal, and formula in $\boxed{\text{blue box}}$ are for ideal gas only.

4.1 Entropy as a state function

Like the other state functions U, P, V, T, etc, change in entropy between states is independent of the process (as long as the process is reversible).

$$\Delta S = \int_{\substack{\text{Any reversible process} \\ (P_1,V_1,T_1) \to (P_2,V_2,T_2)}} \frac{\delta Q_{\text{in}}}{T} = S(P_2, V_2, T_2) - S(P_1, V_1, T_1)$$

Although the definition of S contains a δQ which is path dependent, we can show that S is indeed a state function by computing its line integral along a loop.

$$\text{If } S \text{ is a state function} \quad \Leftrightarrow \quad \begin{pmatrix} \text{Total change of } S \\ \text{in reversible cycle} \end{pmatrix} = \oint_{\substack{\text{Any} \\ \text{reversible} \\ \text{cycle}}} \mathrm{d}S = 0$$

1. First we show that $\oint \mathrm{d}S = 0$ in a Carnot engine. Recall that a Carnot cycle consists of 2 isothermal paths and 2 adiabetic paths,

$$\oint_{\text{Carnot}} \mathrm{d}S = \sum_{\substack{\text{all process} \\ \text{in a cycle}}} \int \frac{\mathrm{d}Q}{T}$$

$$= \int_{\text{Isothermal 1}} \frac{\mathrm{d}Q_{\text{in}}}{T} + \int_{\text{Adiabetic 1}} \frac{\mathrm{d}Q_{\text{in}}}{T}^{\,0} + \int_{\text{Isothermal 2}} \frac{\mathrm{d}Q_{\text{in}}}{T} + \int_{\text{Adiabetic 2}} \frac{\mathrm{d}Q_{\text{in}}}{T}^{\,0}$$

(add figure here: Carnot cycle)

Denote the heat exchange:

- Along $\boxed{1} \rightarrow \boxed{2}$: $Q_{H,\text{in}}$ = the amount of heat flow into the engine in one cycle.
- Along $\boxed{3} \rightarrow \boxed{4}$: $Q_{L,\text{out}}$ = the amount of heat flow out of the engine in one cycle.

The efficiency formula of Carnot engine tells that

$$\eta = 1 - \frac{Q_{L,\text{out}}}{Q_{H,\text{in}}} = 1 - \frac{T_L}{T_H}$$

$$\frac{Q_{H,\text{in}}}{T_H} = \frac{Q_{L,\text{out}}}{T_L}$$

Therefore

$$\begin{aligned}
\oint_{\text{Carnot}} \mathrm{d}S &= \int_{\text{Isothermal 1}} \frac{\mathrm{d}Q_{\text{in}}}{T} + \int_{\text{Isothermal 2}} \frac{\mathrm{d}Q_{\text{in}}}{T} \\
&= \frac{Q_{H,\text{in}}}{T_H} + \frac{Q_{L,\text{in}}}{T_L} \\
&= \frac{Q_{H,\text{in}}}{T_H} + \frac{(-1)Q_{L,\text{out}}}{T_L} \\
&= 0
\end{aligned}$$

2. Second we show that any arbituary cycle can be cut into many Carnot cycle.

(add figure here: cut arbituary cycle)

By the property of line integral, integrating along the same path but in opposite direction yields negative of the original value, just like $\int_a^b f \, \mathrm{d}x = - \int_b^a f \, \mathrm{d}x$.

(add figure here: loop cancel)

So we can conclude that S is a state function.

$$\oint_{\substack{\text{Any} \\ \text{reversible} \\ \text{cycle}}} \mathrm{d}S = \sum_{\substack{\text{many many} \\ \text{Carnot cycle}}} \left(\oint_{\text{Carnot}} \mathrm{d}S \right) = 0$$

Example 4.1. Consider a simple cycle of ideal gas that only involves 3 states

1. Iso. P (expansion)

2. Iso. V

3. Iso. T (contraction)

(add figure here: cycle of 3 process)

We can demonstrate that the entropy change after one cycle is indeed 0. First write down the relations of P, V, T between initial/final states of each process:

	Process	Relation
$\boxed{1} \to \boxed{2}$	Iso. P	$P_1 = P_2$
$\boxed{2} \to \boxed{3}$	Iso. V	$V_2 = V_3$
$\boxed{3} \to \boxed{1}$	Iso. T	$T_3 = T_1$

And the entropy change along each process:

	Process	$\mathrm{d}S$	
$\boxed{1} \to \boxed{2}$	Iso. P	$\dfrac{i+2}{2} Nk \ln\left(\dfrac{T_2}{T_1}\right)$	> 0
$\boxed{2} \to \boxed{3}$	Iso. V	$\dfrac{i}{2} Nk \ln\left(\dfrac{T_3}{T_2}\right)$	< 0
$\boxed{3} \to \boxed{1}$	Iso. T	$Nk \ln\left(\dfrac{V_1}{V_3}\right)$	< 0

Using the state parameters relation and ideal gas property $P_1 = P_2 \Rightarrow \dfrac{T_1}{T_2} = \dfrac{V_1}{V_2}$,

$$\begin{aligned}
\Delta S &= \frac{i+2}{2} Nk \ln\left(\frac{T_2}{T_1}\right) + \frac{i}{2} Nk \ln\left(\frac{T_3}{T_2}\right) + Nk \ln\left(\frac{V_1}{V_3}\right) \\
&= \frac{i+2}{2} Nk \ln\left(\frac{T_2}{T_1}\right) + \frac{i}{2} Nk \ln\left(\frac{T_1}{T_2}\right) + Nk \ln\left(\frac{V_1}{V_2}\right) \\
&= \frac{i+2}{2} Nk \ln\left(\frac{T_2}{T_1}\right) + \frac{i}{2} Nk \ln\left(\frac{T_1}{T_2}\right) + Nk \ln\left(\frac{T_1}{T_2}\right) \\
&= 0
\end{aligned}$$

4.2   Clausius Theorem

Entropy is a special state function that when we consider a <u>closed system</u> (Energy conserved within) - no matter how the objects interact (thermal, mechanical, etc.), the total change in their entropy is always ≥ 0.

- Equality holds if all the interaction processes are reversible.

- Becomes inequality if there involve irreversible processes.

$$\boxed{\Delta S_{\text{irrev}} \;>\; \Delta S_{\text{rev}} \;=\; \sum_{\substack{\text{All objects} \\ \text{involved in} \\ \text{energy exchange}}} \int_{\substack{\text{Any} \\ \text{reversible} \\ \text{process}}} \frac{\delta Q_{\text{in}}}{T} \;=\; \underline{0}}$$

This is the **Clausius theorem**. The theorem origins from a simple fact - thermal interactions (i.e. heat exchange) between two objects occurs only if they have a temperature difference.

1. Let the hotter object be at temperature T_H and the colder temperature be at temperature T_C. We must always have $T_H > T_C$ in order to have heat exchange.

2. By energy conservation, heat flowing out of the hotter object, $Q_{H,\text{out}}$, must equal to heat flowing into the colder object $Q_{C,\text{in}}$.

Combining the two conditions,

$$\frac{Q_{H,\text{out}}}{T_H} < \frac{Q_{C,\text{in}}}{T_C}$$

$$\underbrace{\frac{Q_{H,\text{in}}}{T_H}}_{\substack{\Delta S \text{ of} \\ \text{Hotter object}}} + \underbrace{\frac{Q_{C,\text{in}}}{T_C}}_{\substack{\Delta S \text{ of} \\ \text{Colder object}}} > 0$$

$$\Rightarrow \underbrace{\sum_{\substack{\text{All objects} \\ \text{involved in} \\ \text{energy exchange}}}}_{} \left(\frac{Q_{\text{in}}}{T}\right) > 0$$

As told by Kelvin's statement of 2$^{\text{nd}}$ law, heat flow from hot objects to cold objects are not reversible unless work done is applied. To reduce the change in entropy, we can connect the two objects by a Carnot engine, splitting the heat transfer process into two steps:

1. Heat flow from hot object to engine. Because $Q'_{H,\text{out}} = Q'_{E,\text{in}}$ and it requires $T_H > T_{E,H}$ for heat transfer to occur,

$$\frac{Q'_{H,\text{out}}}{T_H} < \frac{Q'_{E,\text{in}}}{T_{E,H}}$$

(add figure here: hot res to engine)

2. Heat flow from engine to cold object. Because $Q'_{E,\text{out}} = Q'_{C,\text{in}}$ and it requires $T_{E,C} > T_C$ for heat transfer to occur,

$$\frac{Q'_{E,\text{out}}}{T_{E,C}} < \frac{Q'_{C,\text{in}}}{T_C}$$

(add figure here: engine to cold res)

The total entropy change is still > 0, but it would be smaller than that when engine does not exist:

$$0 < \underbrace{\frac{Q'_{H,\text{in}}}{T_H}}_{\substack{\Delta S \text{ of} \\ \text{Hotter object}}} + \underbrace{\frac{Q'_{E,\text{in}}}{T_{E,H}} + \frac{Q'_{E,\text{in}}}{T_{E,C}}}_{\substack{\Delta S \text{ of} \\ \text{Engine}}} + \underbrace{\frac{Q'_{C,\text{in}}}{T_C}}_{\substack{\Delta S \text{ of} \\ \text{Colder object}}} < \frac{Q_{H,\text{in}}}{T_H} + \frac{Q_{C,\text{in}}}{T_C}$$

Because the engine converts part of the heat transfer into W.D., this W.D. can be "saved up" and used to revert the heat flow later. The system is "less irreversible".

Ideally, if

- The heat engine is a reversible engine (So $\Delta S = 0$ for the engine), and

- $T_H - T_{E,H}$ and $T_{E,C} - T_C$ are infinitestimally small (≈ 0),

then the total $\Delta S = 0$ and the work done extracted by the engine can be used to invert the heat flow completely. Only then we can say the system is reversible.

Example 4.2. Water can enter a supercool phase under certain condition. In this phase, the water is below 0°C but remains in liquid state.

Supercooled water can exist in atmospheric pressure but it is "quasi-stable". If received a shock, the water will freeze into ice spontaneously. We can demonstrate that this freezing process is an irreversible process by computing the the entropy change.

Given the following data:

- Both the supercooled water and ice are at $-10°C = 263.15$ K.

- Heat capacity under constant pressure of ice $C_{P,I} = 2100$ J/K/kg.

- Heat capacity under constant pressure of water $C_{P,W} = 4184$ J/K/kg.

- Latent heat of fusion of water $L = 334000$ J/kg.

We can form a cycle with two processes:

- <u>Ice to Supercooled water</u> : With the help of a refridgerator. Reversible.

- <u>Supercooled water to ice</u> : Spontaneously freezing.

Note that in the melting/freezing process, heat exchange occurs between the ice/supercooled water and <u>the envirnoment</u>. When calculating total entropy change, we must also consider the change in the environment.

1. The reversible path from ice to supercooled water involving using a refridgerator, which absorb energy from the environment to do work on the ice. The change in entropy of the ice is

$$\Delta S_{\text{ice, rev}} = \Delta S_{\text{heat up}} + \Delta S_{\text{melting}} + \Delta S_{\text{cool to water}}$$
$$= \int_{263.15}^{273.15} \frac{C_{P,I}}{T} \, dT + \frac{L}{273.15} + \int_{273.15}^{263.15} \frac{C_{P,W}}{T} \, dT$$
$$\approx 1145$$

Because this is a reversible process, the total change in entropy of (ice + environment) must be 0.

$$\Delta S_{\text{envr, rev}} = -\Delta S_{\text{ice, rev}} = -1145$$

2. After spontaneous freezing, the ice/supercooled water has returned to its original state. Because entropy is a state function, we know that the entropy must also return to its original value. So the change in this process is

$$\Delta S_{\text{ice, irrev}} = -\Delta S_{\text{ice, rev}} = -1145$$

However, the process of energy exchange with the environment is not the same as when operating a refridgerator. All because there is no W.D. involve. Temperature of the environment remains at 263.15 K throughout the process.

$$\Delta S_{\text{envr, irrev}} = \frac{C_{P,I} \times 10 + L - C_{P,W} \times 10}{263.15}$$
$$\approx 1190$$

So there is a net gain of entropy $1190 - 1145 \approx 45$ J/K/kg after a cycle of "ice $\xrightarrow{\text{refridgerator}}$ supercooled water $\xrightarrow{\text{spontaneous freezing}}$ ice".

— The End —