Entropy

The two definition of second law, ie Kelvin Planck & Clausius, only apply to a cyclic process. Of course there are processes, both in Engineering or nature that are not cyclic eg. Combustion process in IC engine or cooling of cup of coffee.

As the application of the first law to non-cyclic processes led to the new property "Energy", the application of Second Law will lead to the new property Entropy. We proved the existence of energy by applying the First law an arbitrary cyclic process undergoing different routes. To do the same for the second law we need to combine the two definition of the second law in a more general way. This has been done by Clausius and is known as "The inequality of Clausius".

Clausius' Theorem

"Whenever a system executes a complete cyclic process the integral of $\frac{dQ}{T}$ is less than zero or in the limit is equal to zero;"

\[ \int \frac{dQ}{T} \leq 0 \]

![Diagram of Clausius' Theorem](image)

Proof:
Consider a direct Carnot cycle ie reversible heat engine operating between temperatures TH & TL:

\[ \int dQ = Q_H - Q_L > 0 \]

For this cycle,
But from definition of absolute temperature scale (and since TH and TL are constant) and the cycle is reversible:
\[ \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0 \quad \text{(For absolute temperature)} \]

In the limit when \( \delta Q \rightarrow 0 \) (i.e., \( T_H \rightarrow T_L \)), \( \int \frac{\delta Q}{T} \) remains zero.

Thus we can conclude that for a reversible heat engine:
Now consider an irreversible process between \( T_H \) & \( T_L \):

\[ W_i < W_f \text{ (from second law)} \]

Since \( W = Q_H - Q_L \), then:

\[ Q_H - Q_{Li} < Q_H - Q_{Li} \]

\[ Q_H > Q_{Li} \]

\[ \int \delta Q = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} > 0 \]

\[ \int \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} > 0 \]

Suppose we make the engine more and more irreversible while keeping \( T_H \), \( T_L \) and \( Q_f \) the same. Then:

\( W_i \rightarrow 0 \)

And

\[ \int \delta Q \rightarrow 0 \]

And becomes more negative

Thus for all irreversible heat engine cycles:

To complete the proof we must also consider refrigeration (reversed) cycles i.e:

**Reversed Carnot Cycle**

\[ \int \delta Q = -Q_H + Q_L < 0 \]
And
\[
\oint \frac{\delta Q}{T} = -\frac{Q_H}{T_H} + \frac{Q_B}{T_B} = 0
\]

Thus we can conclude that for all cycles:
\[
\oint \frac{\delta Q}{T} \leq 0
\]

Where equality holds for reversibly cycles and inequality for irreversible cycles.

**Entropy**

Consider a system which undergoes a reversible process from state 1 to state 2 along path A, and let cycle be completed along path B, which is also reversible. Since the cycle is reversible we can write:

\[
\oint \frac{\delta Q}{T} = 0 = \frac{2}{1} \left( \frac{\delta Q}{T} \right)_A + \frac{1}{2} \left( \frac{\delta Q}{T} \right)_B
\]

Now let cycle be completed along path C

\[
\oint \frac{\delta Q}{T} = 0 = \frac{2}{1} \left( \frac{\delta Q}{T} \right)_A + \frac{1}{2} \left( \frac{\delta Q}{T} \right)_C
\]

But paths B and C represent arbitrary reversible processes. So \[ \oint \frac{\delta Q}{T} \] is the same for all reversible paths between states 1 and 2.

Thus it must be independent of path and depend only on the end-states, i.e. it must be a property. This property is called Entropy, S.

Notes:
(i) Entropy is an extensive property
(ii) Entropy is here defined for only a reversible process. But since entropy is a property, the change in the entropy of a substance in going from one state to another is the same for all processes, both reversible and irreversible. From above we can find change in entropy along a reversible path but once this is evaluated it gives the magnitude of entropy change in all processes between states 1 and 2.
(iii) The definition only tells us about changes in entropy and so as in the case of energy its absolute value is not known. The third law says that at absolute zero entropy approaches zero. In practice, usually an arbitrary selected reference state is used e.g. triple point of water.

**Principle of increase in entropy**
The entropy of any system which is thermally isolated from the surroundings either increases, or in the limit (when the process is reversible) remains constant.

**Proof:**

For reversible cycle 1-A-2-B-1:
\[
\int \frac{\delta Q}{T} = \int_1^A \left( \frac{\delta Q}{T} \right)_A + \int_A^B \left( \frac{\delta Q}{T} \right)_B = 0
\]

For irreversible cycle 1-A-2-C-1:
\[
\int \frac{\delta Q}{T} = 0 = \int_1^A \left( \frac{\delta Q}{T} \right)_A + \int_A^C \left( \frac{\delta Q}{T} \right)_C < 0 \, \text{(clausius)}
\]

Thus
\[
\int_1^B \left( \frac{\delta Q}{T} \right)_B > \int_1^C \left( \frac{\delta Q}{T} \right)_C
\]

But path B is reversible and entropy is a property so that:
\[
\int_1^B \left( \frac{\delta Q}{T} \right) = \frac{1}{2} \int dS_B = \frac{1}{2} dS_C
\]

Or in general:
\[
S_2 - S_1 \geq \int \frac{\delta Q}{T}
\]

Example: Conduction with finite temperature difference

\[T_H \quad Q \quad T_C\]

\[\text{Isolated System}\]

\[\delta S \text{ for high temperature reservoir} = -Q/T_H\]
\[\delta S \text{ for low temperature reservoir} = +Q/T_C\]

Therefore: \[\delta S_{\text{isolated system}} = -Q/T_H + Q/T_C > 0 \quad (T_H > T_C)\]

i.e. the process is irreversible.

Entropy change for some standard processes:

Adiabatic and reversible process:
\[ S_2 - S_1 \geq \frac{2}{1} \frac{dQ_{\text{rev}}}{T} = 0 \]

Therefore i.e. entropy remains constant in an adiabatic reversible process, i.e. isentropic

Adiabatic and irreversible process:

\[ S_2 - S_1 \geq \frac{2}{1} \frac{dQ_{\text{rev}}}{T} = 0 \]

So \( S_2 > S_1 \) i.e. not isentropic

Isothermal process

\[ dS = \frac{dQ_{\text{rev}}}{T} \]

Therefore \( Q_{\text{rev}} = T(S_2 - S_1) \)

**Entropy and disorder**

On a microscopic scale the motion of molecules is random i.e. not in a particularly orderly direction. But work involves orderly motion. Whenever work is dissipated into internal energy, the disorderly motion of molecules is increased (i.e. temperature goes up and therefore the motion becomes more random) i.e. an **irreversible process increases disorder on a microscopic scale**. We said before that all spontaneous natural processes are **irreversible**. Thus we can say that: "There is a tendency on the part of nature to proceed toward a state of greater disorder" e.g.

Because for this to be possible the molecules should have an order motion.

**Nb. It is therefore impossible to go back in time because this will decrease the entropy**

To learn more on reading entropy property diagrams, click [here](#).

The theory of entropy also leads us onto \( TdS \) equations, click [here](#) to read more.

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