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Second Law

- There exists a function \((S)\) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

- Another way of looking at it:

![Equilibrium State Diagram]

Figure 1: Second Law

- Entropy is additive. And...

\[
\left( \frac{\partial S}{\partial U} \right)_{V,N} > 0
\]

- \(S\) is an extensive property: It is a homogeneous, first order function of extensive parameters:

\[
S (\lambda U, \lambda V, \lambda N) = \lambda S (U, V, N)
\]

- \(S\) is not conserved.

\[
dS_{sys} \geq \frac{\delta Q}{T_{sys}}
\]

For an Isolated System, (i.e. Universe)

\(\Delta S > 0\)

 Locally, the entropy of the system can decrease. However, this must be compensated by a total increase in the entropy of the universe. (See 2)

\[
\Delta S_1 = -\frac{Q}{T_1} \quad \Delta S_2 = +\frac{Q}{T_2}
\]

\[
\Delta S_{Total} = Q \left( \frac{1}{T_2} - \frac{1}{T_1} \right) > 0
\]

Quasi-Static Processes

A Quasi-static thermodynamic process is defined as the trajectory, in thermodynamic space, along an infinite number of contiguous equilibrium states that connect to equilibrium states, \(A\) and \(B\).
**Irreversible Process**
Consider a closed system that can go from state $A$ to state $B$. The system is induced to go from $A$ to $B$ through the removal of some internal constraint (e.g. removal of adiabatic wall). The systems moves to state $B$ only if $B$ has a maximum entropy with respect to all the other accessible states. $S_B > S_A$. This kind of process is irreversible.

**Reversible Process**
In the limit, when a quasi-static process is such that the entropy increase is vanishingly small, this process can be considered reversible. The initial and final entropies of the process are the same. $\Delta S = 0$.

**Entropy and Reversible Processes**
An example of a reversible process is the heat exchange among two systems, in diathermal contact, that are at the same temperature, $T$. For the first system, the change in entropy would be given by (first law), $-\delta Q/T$. While the second system would increase its entropy by an amount $\delta Q/T$.

For a reversible process, thus,

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

**Entropy for irreversible Processes??**
According to the second law, for irreversible processes,

$$dS > \frac{\delta Q}{T}$$

When two thermodynamic states are connected through an irreversible path, we still can calculate the entropy change in the system, since $S$ is a state function and is path independent. What we need to do is to find a sequence of reversible processes that have the same end result.

**Maximum Work Theorem**
For all processes leading from a specified initial state to a specified final state, the delivery of work is maximum for a reversible system. Consider a process that goes from state 1 to state 2. Consider two possible trajectories, a reversible and an irreversible one.

Write the first law for the process.

\[ dU_R = dU_I \]
\[ \delta Q_R + \delta W_R = \delta Q_I + \delta W_I \]

The second law states that:

\[ dS = \frac{\delta Q_R}{T} \quad dS > \frac{\delta Q_I}{T} \]

Therefore,

\[ TdS + \delta W_R < TdS + \delta W_I \]

If you want to produce work, \( W_R < 0 \), therefore, \(|W_R| > |W_I|\). The Maximum work theorem has been proved.

**Limits of Q and W**

In a cyclic process, at one temperature, \( T \):

\[ \Delta S = \oint \frac{\delta Q}{T} = \frac{Q}{T} = 0 \]

Since it is a cyclic process, with initial and final states being the same, \( \Delta U = 0 \). Since \( Q = 0 \), \( W = 0 \). This proves the Kelvin-Planck Statement of the Second Law.

How do we produce work then?

We make the process operate at two distinct temperatures.

The fact that

\[ \Delta S = \oint \frac{\delta Q}{T} = \frac{Q}{T} = 0 \]

Does not mean that \( Q_H \) and \( Q_L \) have to be zero. The only condition that has to hold is:

\[ \Delta S = \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \]

**Combined First and Second Laws:**

\[ dU = \delta Q + \delta W \]
\[ dU = TdS - PdV \]
\[ dU = TdS + \sum_i Y_i dX_i \]
\[ dS = \frac{1}{T} dU + \sum_i \frac{Y_i}{T} dX_i \]
Problem 1

An ideal monoatomic gas undergoes a constant pressure, reversible expansion. During this expansion, it absorbs 6236 $J$ of heat and its entropy changes by $\Delta S = 14.41 J/K$. Calculate the initial and final temperatures of the gas.

Problem 2

When an ideal gas undergoes a Joule-Thompson expansion its temperature remains constant. Show that this expansion is irreversible by showing that entropy of the universe (system + environment) increases. The Joule-Thompson expansion is an adiabatic flow through an insulated valve, i.e. the gas comes out a lower pressure than it goes in. For an ideal gas the temperature of the gas going out is identical to the temperature of the incoming gas, i.e. $T_f = T_o$. 