**Entropy**

- For a reversible ideal gas Carnot cycle:

\[
\varepsilon = \frac{-w}{q_{\text{rev}}} = 1 + \frac{q_2^{\text{rev}}}{q_1} = 1 - \frac{T_2}{T_1}
\]

\[
\Rightarrow \quad \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \quad \Rightarrow \quad \oint \frac{dq_{\text{rev}}}{T} = 0
\]

- The efficiency of any reversible engine has to be the same as the Carnot cycle:

\[
\varepsilon = \frac{(-w)}{q_1} \quad \varepsilon' = \frac{(-w')}{q_1'}
\]

Assume \( \varepsilon' > \epsilon \) (left engine less efficient than Carnot cycle)

Since the engine is reversible, we can run it backwards. Use the work \((-w')\) out of the Carnot engine as work input \((w)\) to run the left engine backwards.

\[
\therefore \quad \text{Total work out} = 0 \quad (-w = w > 0)
\]

But \( \varepsilon' > \epsilon \) \( \Rightarrow \quad \frac{-w'}{q_1'} > \frac{-w}{q_1} \quad \Rightarrow \quad \frac{w}{q_1} > \frac{-w}{-q_1} = \frac{w}{-q_1} \quad \Rightarrow \quad q_i < -q_i' \quad \text{since} \quad q_i < 0, \quad q_i' > 0
\]

\[
\Rightarrow \quad -(q_i' + q_i) > 0
\]

This contradicts the 2\(^{\text{nd}}\) law (Clausius). This says that we have a net flow of heat into the hot reservoir, but no work is being done!

\[
\therefore \quad \text{The efficiency of any reversible engine is} \quad \varepsilon = 1 - \frac{T_2}{T_1}
\]
• We can approach arbitrarily closely to any cyclic process using a series of only adiabats and isotherms.

∴ For any reversible cycle \[ \oint \frac{dq_{\text{rev}}}{T} = 0 \]

• This defines Entropy, a function of state

\[ dS = \frac{dq_{\text{rev}}}{T} \quad \Rightarrow \quad \Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{\text{rev}}}{T} \]

Note: Entropy is a state function, but to calculate \( \Delta S \) requires a reversible path.

• An irreversible Carnot (or any other) cycle is less efficient than a reversible one.

\[ \begin{align*}
1 \rightarrow 2 \\
(\neg w)_{\text{irrev}} < (\neg w)_{\text{rev}} & \Rightarrow \ w_{\text{irrev}} > w_{\text{rev}} \\
\Delta U = q_{\text{irrev}} + w_{\text{irrev}} = q_{\text{rev}} + w_{\text{rev}} & \Rightarrow \ q_{\text{irrev}} < q_{\text{rev}}
\end{align*} \]

** An irreversible isothermal expansion requires less heat ** than a reversible one.

\[ \varepsilon_{\text{irrev}} = 1 + \frac{q_{2 \text{rev}}}{q_{1 \text{irrev}}} < 1 + \frac{q_{2 \text{rev}}}{q_{1 \text{rev}}} = \varepsilon_{\text{rev}} \quad (q_2 < 0) \]

also \[ \oint \frac{dq_{\text{irrev}}}{T} < 0 \]
 Leads to **Clausius inequality** \[ \int \frac{dq}{T} \leq 0 \] contains \[ \int \frac{dq}{T} = 0 \]

\[ \int \frac{d q_{\text{rev}}}{T} < 0 \]

The entropy of an **isolated** system **never** decreases

(A) irreversible

1 \[\xrightarrow{\text{irreversibly}}\] 2

(B) reversible

(A): The system is **isolated** and **irreversibly** (spontaneously) changes from [1] to [2]

(B): The system is brought into contact with a heat reservoir and **reversibly** brought back from [2] to [1]

Path (A): \( q_{\text{irrev}} = 0 \) (isolated)

Clausius \[ \int \frac{dq}{T} \leq 0 \Rightarrow \int_{1}^{2} \frac{dq_{\text{irrev}}}{T} + \int_{2}^{1} \frac{dq_{\text{rev}}}{T} \leq 0 \]

\[ \Rightarrow \int_{2}^{1} \frac{dq_{\text{rev}}}{T} = S_2 - S_1 = -\Delta S \leq 0 \]

\[ \therefore \Delta S = S_2 - S_1 \geq 0 \]

This gives the direction of spontaneous change!

| For isolated systems | \( \Delta S > 0 \) Spontaneous, irreversible process | \( \Delta S = 0 \) Reversible process | \( \Delta S < 0 \) Impossible |

1 \[\xrightarrow{\text{independent of path}}\] 2 \( \Delta S = S_2 - S_1 \)

But! \( \Delta S_{\text{surroundings}} \) depends on whether the process is reversible or irreversible
(a) **Irreversible:** Consider the universe as an isolated system containing our initial system and its surroundings.

\[
\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0
\]

\[
\therefore \Delta S_{\text{surr}} > -\Delta S_{\text{sys}}
\]

(b) **Reversible:**

\[
\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S'_{\text{surr}} = 0
\]

\[
\therefore \Delta S'_{\text{surr}} = -\Delta S_{\text{sys}}
\]

Examples of a spontaneous process

Connect two metal blocks thermally in an isolated system \((\Delta U = 0)\)

Initially \(T_1 \neq T_2\)

\[
dS = dS_1 + dS_2 = \frac{dq_1}{T_1} - \frac{dq_2}{T_2} = dq_1 \frac{(T_2 - T_1)}{T_1 T_2} \quad (dq_1 = -dq_2)
\]

\(dS > 0\) for spontaneous process

\[
\Rightarrow \text{ if } T_2 > T_1 \Rightarrow dq_1 > 0 \quad \text{ in both cases heat flows from hot to cold as expected}
\]

\[
\text{ if } T_2 < T_1 \Rightarrow dq_1 < 0
\]

Joule expansion with an ideal gas
$$1 \text{ mol gas } (V, T)^{\text{adiabatic}} \equiv 1 \text{ mol gas } (2V, T)$$

$$\Delta U = 0 \quad q = 0 \quad w = 0$$

$$\Delta S = -\Delta S_{\text{backwards}}$$

Compress back isothermally and reversibly

$$q_{\text{rev}} \neq 0$$

$$1 \text{ mol gas } (2V, T) = 1 \text{ mol gas } (V, T)$$

$$\Delta S_{\text{backwards}} = \int \frac{dq_{\text{rev}}}{T} = -\int \frac{dw}{T} = \int_{2V}^{V} \frac{RdV}{V} = R \ln 2$$

$$\therefore \Delta S = R \ln 2 > 0$$

spontaneous

Note that to calculate $\Delta S$ for the irreversible process, we needed to find a reversible path so we could determine $dq_{\text{rev}}$ and $\int \frac{dq_{\text{rev}}}{T}$. 
