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5.60 Thermodynamics & Kinetics
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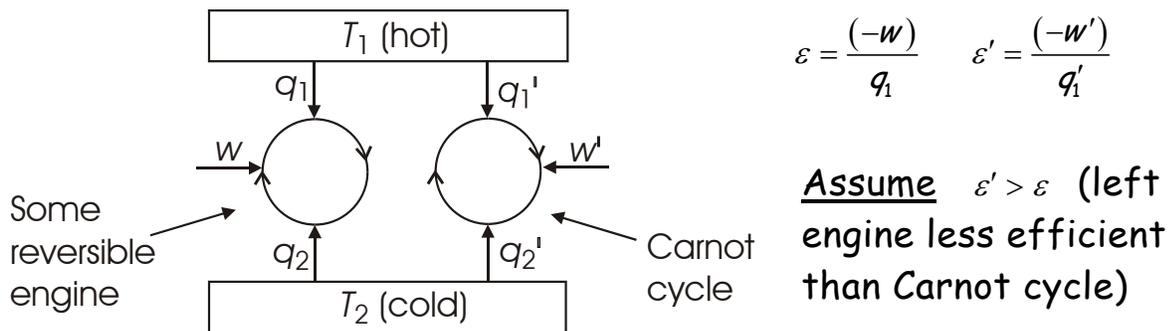
Entropy

- For a reversible ideal gas Carnot cycle:

$$\text{Efficiency} \quad \varepsilon = \frac{-w}{q_{rev}} = 1 + \frac{q_2^{rev}}{q_1^{rev}} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \Rightarrow \oint \frac{dq_{rev}}{T} = 0$$

- The efficiency of any reversible engine has to be the same as the 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.

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

$$\text{But } \varepsilon' > \varepsilon \Rightarrow \frac{-w'}{q_1'} > \frac{-w}{q_1} \Rightarrow \frac{w}{q_1'} > \frac{-w}{q_1} = \frac{w}{-q_1} \Rightarrow q_1 < -q_1' \text{ since } q_1 < 0, q_1' > 0$$

$$\Rightarrow -(q_1' + q_1) > 0$$

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

$$\therefore \text{The efficiency of any reversible engine is } \varepsilon = 1 - \frac{T_2}{T_1}$$

- We can approach arbitrarily closely to any cyclic process using a series of only adiabats and isotherms.

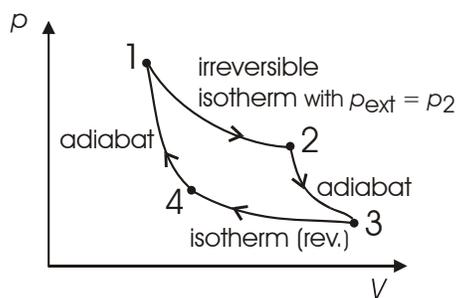
∴ For any reversible cycle $\oint \frac{\delta q_{rev}}{T} = 0$

- This defines Entropy, a function of state

$$dS = \frac{\delta q_{rev}}{T} \Rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{\delta q_{rev}}{T}$$

Note: Entropy is a state function, but to calculate ΔS requires a reversible path.

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



1 → 2

$$(-w)_{irrev} < (-w)_{rev} \Rightarrow w_{irrev} > w_{rev}$$

$$\Delta U = q_{irrev} + w_{irrev} = q_{rev} + w_{rev}$$

$$\therefore q_{irrev} < q_{rev}$$

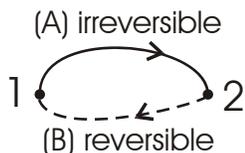
** An irreversible isothermal expansion requires less heat than a reversible one. **

$$\varepsilon_{irrev} = 1 + \frac{q_2^{rev}}{q_1^{irrev}} < 1 + \frac{q_2^{rev}}{q_1^{rev}} = \varepsilon_{rev} \quad (q_2 < 0)$$

also $\frac{\delta q_{irrev}}{T} < \frac{\delta q_{rev}}{T} \Rightarrow \oint \frac{\delta q_{irrev}}{T} < 0$

- Leads to Clausius inequality $\oint \frac{\dot{d}q}{T} \leq 0$ contains $\begin{cases} \oint \frac{\dot{d}q_{rev}}{T} = 0 \\ \oint \frac{\dot{d}q_{irrev}}{T} < 0 \end{cases}$

The entropy of an isolated system never decreases



(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): $q_{irrev} = 0$ (isolated)

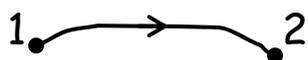
Clausius $\oint \frac{\dot{d}q}{T} \leq 0 \Rightarrow \int_1^2 \frac{\dot{d}q_{irrev}}{T} + \int_2^1 \frac{\dot{d}q_{rev}}{T} \leq 0$

$$\Rightarrow \int_2^1 \frac{\dot{d}q_{rev}}{T} = s_1 - s_2 = -\Delta S \leq 0$$

$$\therefore \Delta S = s_2 - s_1 \geq 0$$

This gives the direction of spontaneous change!

For isolated systems	$\left\{ \begin{array}{l} \Delta S > 0 \\ \Delta S = 0 \\ \Delta S < 0 \end{array} \right.$	Spontaneous, irreversible process
		Reversible process
		Impossible



$$\Delta S = s_2 - s_1 \quad \text{independent of path}$$

But! $\Delta S_{surroundings}$ 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.

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

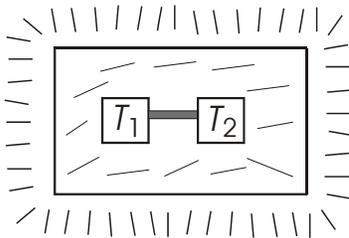
$$\therefore \Delta S_{\text{surr}} > -\Delta S_{\text{sys}}$$

- (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



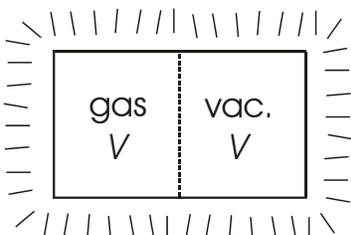
Connect two metal blocks thermally in an isolated system ($\Delta U = 0$)

Initially $T_1 \neq T_2$

$$dS = dS_1 + dS_2 = \frac{\dot{d}q_1}{T_1} - \frac{\dot{d}q_2}{T_2} = \dot{d}q_1 \frac{(T_2 - T_1)}{T_1 T_2} \quad (\dot{d}q_1 = -\dot{d}q_2)$$

$dS > 0$ for spontaneous process

\Rightarrow if $T_2 > T_1 \Rightarrow \dot{d}q_1 > 0$ } in both cases heat flows
 $T_2 < T_1 \Rightarrow \dot{d}q_1 < 0$ } from hot to cold as expected



Joule expansion with an ideal gas

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

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

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

Compress back isothermally and reversibly

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

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

$$\Delta S_{\text{backwards}} = \int \frac{\dot{d}q_{\text{rev}}}{T} = -\int \frac{\dot{d}w}{T} = \int_{2V}^V \frac{RdV}{V} = R \ln \frac{1}{2}$$

$$\therefore \boxed{\Delta S = R \ln 2 > 0} \quad \text{spontaneous}$$

Note that to calculate ΔS for the *irreversible* process, we needed to find a reversible path so we could determine $\dot{d}q_{\text{rev}}$ and $\int \frac{\dot{d}q_{\text{rev}}}{T}$.