

PREVIOUSLY ON

...*Thermodynamics*

Heat *can* be converted to work

Reversible Carnot Engines

Carnot Heat Flows proportional to Temperatures

Second Law stated in terms of efficiency

Real Engine cycles: Otto, Sterling, Brayton

Three body heat exchange

Clausius: "What about heat transfers in an arbitrary cyclic process?"

Carnot refrigerators A and B
and Engine E.

Heat reservoirs T_0 , T_1 , T_2

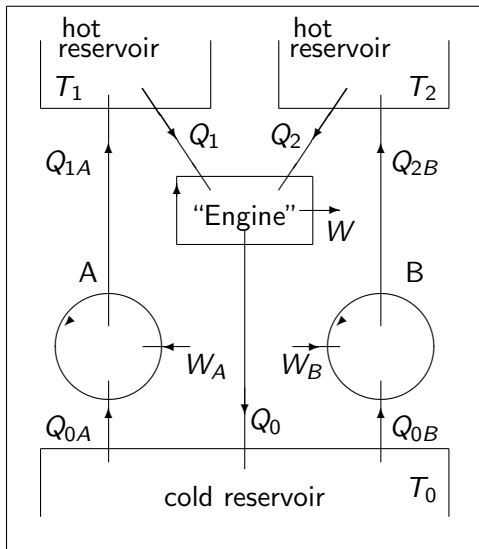
Adjust Heat flow to hot
reservoirs

$$(Q_1 = Q_{1A}; Q_2 = Q_{2A})$$

Heat flow to cold reservoir

$$Q_{0A} + Q_{0B} - Q_0.$$

(expect to be -ve)



Clausius Inequality

- **System:** both fridges and the engine
- Total work done: $W - (W_A + W_B)$.
- No net heat flows to HOT reservoirs.
- $(Q_{0A} + Q_{0B}) - Q_0 = W - (W_A + W_B)$ (1st Law).
- Kelvin-Planck violated unless...



$$W \leq W_A + W_B \quad \text{and so} \quad Q_{0A} + Q_{0B} - Q_0 \leq 0$$

- From the Carnot refrigerator efficiencies we have...
 $\frac{Q_{1A}}{Q_{0A}} = \frac{T_1}{T_0} \implies Q_{0A} = Q_1 \times \frac{T_0}{T_1}$; similarly $Q_{0B} = Q_2 \times \frac{T_0}{T_2}$.
- Thus in terms of the heat **entering the cold reservoir**,

$$Q_{0A} + Q_{0B} - Q_0 = \left(\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \right) T_0 - Q_0 \leq 0 \rightarrow \frac{Q_1}{T_1} + \frac{Q_2}{T_2} - \frac{Q_0}{T_0} \leq 0$$

Heat flows to working substance

Again...

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} - \frac{Q_0}{T_0} \leq 0$$

So far we considered heat flows Q_i for the engines and refrigerators.

Now consider heat inputs q_i to **the working substance of the engine**. The engine absorbs heat $q_1 = Q_1$ from the hot reservoirs, and *returns* heat to the cold reservoir, so there is a change of sign: $q_0 = -Q_0$.

$$\frac{q_0}{T_0} + \frac{q_1}{T_1} + \frac{q_2}{T_2} \leq 0$$

Generalised Clausius Inequality

In general

- If the number of engines and refrigerators is arbitrary,

$$\sum_i \frac{q_i}{T_i} \leq 0$$

Where T_i are from the reservoirs, not the temperature of the system.

- In the limit of $q \rightarrow 0$, the summation may be replaced by an integral:

$$\int \frac{dq}{T} \leq 0, \quad \text{Clausius inequality}$$

T is temperature of **surroundings**, not the **system**.

Clausius for Reversible cycles.

Reversible: system in equilibrium with surroundings

$$T_{\text{system}} = T_{\text{reservoirs}}$$

Clausius inequality: $\int \frac{dq}{T} \leq 0$

but since all processes can also be reversed... $\int \frac{dq}{T} \geq 0$

So for reversible cycles,

$$\int \frac{dq_R}{T} = 0, \quad \text{reversible cycle only}$$

Note that now T is the same for both the **surroundings** and the **system**.

Entropy - an existence proof from a contour integral

Consider a reversible cycle i to f
then back to i ,

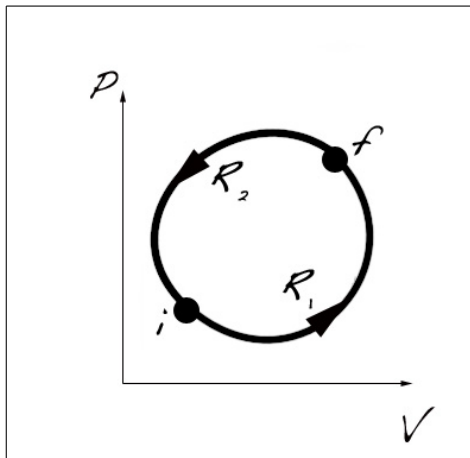
Reversibility means the equality sign
in the Clausius inequality applies:

$$\int \frac{dq_R}{T} = \int_i^f \frac{dq_R}{T} + \int_f^i \frac{dq_R}{T} = 0$$

from which

$$\int_{i|\text{path 1}}^f \frac{dq_R}{T} = \int_{i|\text{path 2}}^f \frac{dq_R}{T}.$$

Because the value of the integral is path-independent, $\frac{dq_R}{T}$ is an exact differential of some state function, we call it **entropy** S :



Entropy - a new state variable

- The integral is path-independent.
- $\frac{dq_R}{T}$ is an exact differential of some state function,
- We call it entropy S :

$$\int_i^f \frac{dq_R}{T} = \int_i^f dS = S_f - S_i = \Delta S$$

- This equation defines *changes* in entropy.
- It doesn't give a physical clue to what entropy means microscopically.
- It doesn't hint at what $S = 0$ means.

The Principle of Increasing Entropy

Reconsider the existence proof for entropy if one process (i to f) is irreversible.

The Clausius inequality leads to

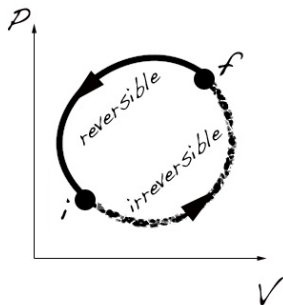
$$\int_i^f \frac{dq}{T} + \int_f^i \frac{dq_R}{T} \leq 0$$

from which

$$\int_i^f \frac{dq}{T} \leq \int_i^f \frac{dq_R}{T} = S_f - S_i$$

For an irreversible process, $S_f - S_i$, is greater than the integration of infinitesimal contributions:

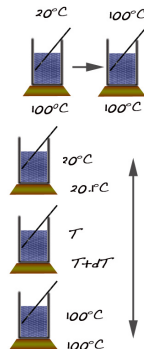
$$\int \frac{\text{heat supplied from the surroundings}}{\text{temperature of the surroundings}} = \int_i^f \frac{dq}{T} \leq \int dS_{\text{system}}$$



Example calculation of an entropy change

Water at 20°C is placed in thermal contact with a heat reservoir at 100°C ; heated **irreversibly** at constant pressure to an equilibrium state at 100°C .

- To calculate the entropy change of the water (the “system”) consider an **alternative reversible** process.
- Use as the “surroundings” a series of heat reservoirs each at slightly higher temperature from T_i to T_f .
- Each intermediate stage in the **alternative** process is the reversible transfer of heat $dQ = C_P dT$ from a reservoir at the temperature of the water.
- The change in entropy of the water is $dS = C_P dT/T$.
- For the complete process, the change in entropy of the water is $\Delta S^{SYS} = C_P \ln \frac{373}{293} = C_P \times 0.24141$.
- The change in entropy for the **system** in an irreversible process between equilibrium states can be calculated using an equivalent reversible process.



... entropy change in system

$$\Delta S^{SYS} = C_P \ln \frac{373}{293} = C_P \times 0.24141$$

Calculate change in entropy ΔS^{SURR} of the **surroundings**

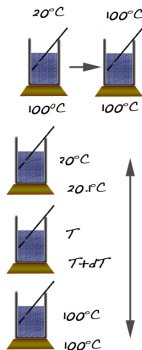
Actual surroundings: a reservoir at 100°C , delivers heat

$$C_P(T_f - T_i) = C_P(373 - 293) = C_P \times 80$$

Again, consider an alternative reversible process, delivering heat via a series of reservoirs each slightly cooler than the previous. The change in entropy of the surroundings is thus $-C_P(373 - 293)/373 = -C_P \times 0.21448$.

note that entropy increases

$$\Delta S^{TOT} = \Delta S^{SYS} + \Delta S^{SURR} = 0.02693C_P > 0$$



Changes of entropy of thermally isolated systems in adiabatic processes

A thermally isolated system exchanges no heat with the surroundings. So, for an irreversible process inside a thermally isolated system

$$dS > 0 \quad (\rightarrow S_f - S_i = \Delta S > 0 \text{ for a process})$$

It also follows that for a finite **reversible** adiabatic process $\Delta S = 0$.
Conclusion:

The entropy of a thermally isolated system increases in any irreversible process and is unaltered in a reversible process.

This is the principle of increasing entropy.

Equivalent statements of Second Law

- 1 Heat cannot flow from a cooler to a hotter reservoir.
- 2 Heat cannot be 100% converted to Work
- 3 Reversible cycles are the most efficient engines possible
- 4 Entropy cannot decrease

“Heat is the lowest form of energy”

Summary so far:

Main Postulate

⇒

Isolated systems tend to equilibrium
for which state variables exist

Irreversibility

⇒

State variables do not exist during irreversible processes

0th Law

⇒

Temperature defines Thermal Equilibrium;
 $T_{Equilibrium} = T_{IdealGas} = T_{Carnot}$

1st Law

⇒

Energy is conserved; $\Delta U = \Delta Q + \Delta W$

2nd Law

⇒

Entropy of System + Surroundings cannot decrease;

Third Law

⇒

(not covered yet) Absolute zero T and S exist

Important corollaries so far:

Equilibrium

⇒ Nonequilibrium systems exist.

Work, Heat

⇒ Integrals are Path Dependent

State Function

⇒ Can get by integrating along *any* path; $\oint dX = 0$

Clausius

⇒ Heat can't flow from cold to hot

Kelvin-Planck

⇒ Cannot convert all heat energy to work

Carnot

⇒ Most efficient possible engine has $\eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$

Clausius Inequality

⇒ Heat flow into a system: $\oint \frac{dQ}{T} < 0$

Clausius Equality

⇒ State variable Entropy exists for *system* $\Delta S = \int \frac{dQ}{T}$

Time

⇒ Defined by direction of increase in Entropy