



**Lecture TOPIC 6** (Finn: 5.1, 5.2, 5.3, 5.5)

**Synopsis:** The Clausius inequality. Entropy, and principle of increase in entropy.

**INTRODUCTION TO THE THERMODYNAMIC FUNCTION ENTROPY**

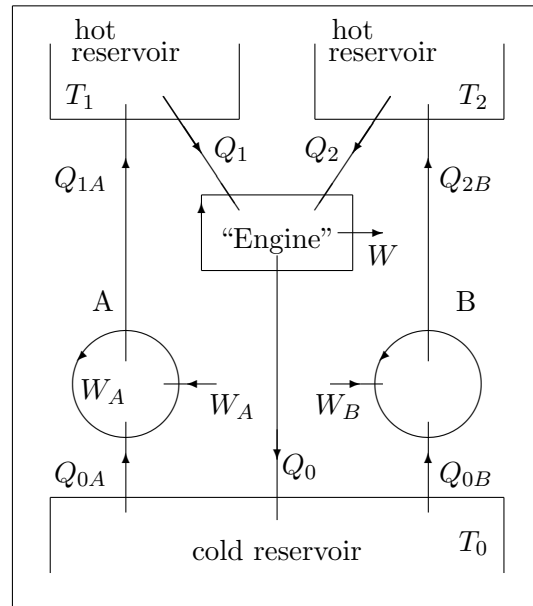
**The Clausius inequality**

This considers the heat transfers to a substance as it is taken round an arbitrary cyclic process exchanging heat with any number of surrounding bodies. It can be derived by breaking down the process into equivalent interactions with a large number of Carnot engines and refrigerators.

**Heat exchange with 3 bodies**

We look at this procedure for a system exchanging heat with 3 different bodies (diagram) and then generalise the result. Consider two Carnot refrigerators A and B and an Engine. The refrigerators are adjusted to exactly the same amount of heat to their hot reservoirs as is taken from those reservoirs by the Engine: ( $Q_1 = Q_{1A}$ ;  $Q_2 = Q_{2A}$ ) No such restriction can be put on the heat transfers to and from the cold reservoir and therefore heat flowing from it is  $Q_{0A} + Q_{0B} - Q_0$ . (We'll see later that this is negative)

Now consider the complete ensemble as a composite **system** with the Engine driving the refrigerators. The net work done *by* the composite system is  $W - (W_A + W_B)$ .



No net heat flows into/out of the hot reservoirs. The balance of heat flow and mechanical work for the composite **system** is  $(Q_{0A} + Q_{0B}) - Q_0 = W - (W_A + W_B)$  (1st Law). Since the heat flow is from a single reservoir, the Kelvin-Planck statement of the Second Law would be contradicted if  $W > W_A + W_B$ . Therefore we must have  $W \leq W_A + W_B$  and  $Q_{0A} + Q_{0B} - Q_0 \leq 0$

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

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

So far we considered heat flows  $Q_i$  around a system of 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:  $q_0 = -Q_0$ .

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

The above argument can be generalised and refined as follows.

1. If the number of engines and refrigerators is arbitrary,

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

Note that the  $T_i$  are the temperatures of the reservoirs with which heat is exchanged rather, not the temperature of the system.

2. In the limit where the amounts of heat entering the working substance are very small at each step, but the number of steps is very large, the summation may be replaced by an integral:

$$\oint \frac{\delta q}{T} \leq 0, \quad \text{Clausius inequality}$$

Note that  $T$  is still the temperature of the reservoirs, which may or may not be equal to that of the system.

3. **Reversible cycles.** For the special case where the device operates entirely reversibly,  $T_{\text{system}} = T_{\text{reservoirs}}$  during each heat exchange. Since all processes can also be reversed, an equivalent conclusion is  $\oint \frac{\delta q}{T} \geq 0$

For both inequalities to be valid simultaneously, they must be restricted to the “=” case, so for reversible cycles,

$$\oint \frac{\delta q_R}{T} = 0, \quad \text{reversible cycle only}$$

Note in this last expression  $T$  is also the temperature of the system.

## Entropy - a new state variable

Consider a system performing a reversible cycle from initial state  $i$  to an intermediate state  $f$  then back to  $i$ , as shown in the indicator diagram (think of it as a sample of gas). Since the cycle is reversible the equality sign in the Clausius inequality applies giving,

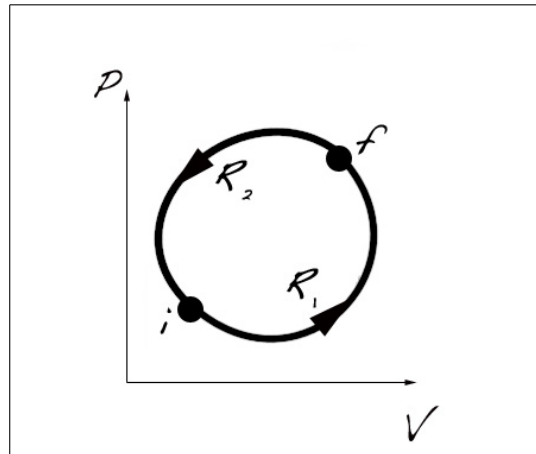
$$\int \frac{\delta q_R}{T} = \int_i^f \frac{\delta q_R}{T} + \int_f^i \frac{\delta q_R}{T} = 0$$

from which

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

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

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



## The Principle of Increasing Entropy

Now reconsider the existence proof for entropy if one part ( $i$  to  $f$ ) is irreversible.

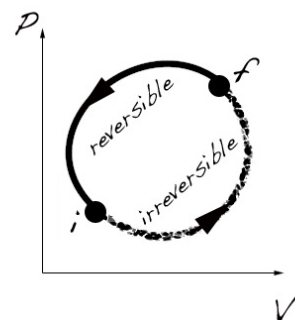
The Clausius inequality leads to  $\int_i^f \frac{dq}{T} + \int_f^i \frac{dq_R}{T} \leq 0$

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

(note the change in sign when inverting the limits on the integral).

This means that in an irreversible process, the change in entropy,  $S_f - S_i$ , is greater than the integration of infinitesimal contributions:

$$\left( \text{“heat supplied from the surroundings”} \right) / \left( \text{“temperature of the contributing part of the surroundings”} \right).$$



Also, consider heat being measured by the heat capacity. If the heat capacity was *negative* all the signs would change and the entropy would decrease. This doesn't happen: the Second Law requires heat capacities to be positive.

## Changes of entropy of thermally isolated systems in adiabatic processes

When a system is thermally isolated no heat is exchanged with the surroundings. Then for an irreversible process undergone by a thermally isolated system

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

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

*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.*

### Example calculation of an entropy change

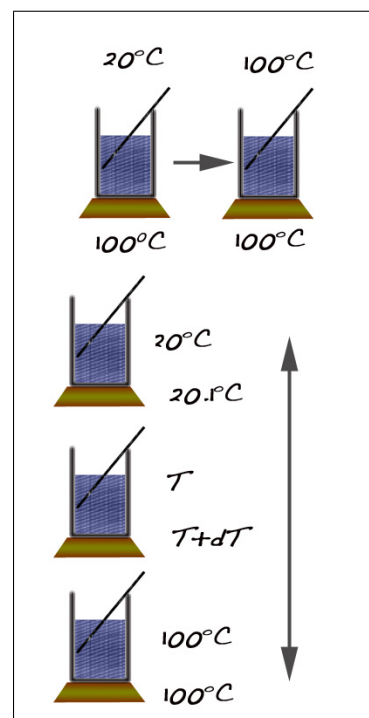
A sample of water at  $20^\circ\text{C}$  is placed in thermal contact with a heat reservoir at  $100^\circ\text{C}$ . The sample, of heat capacity  $C_P$ , is thereby heated **irreversibly** at constant pressure from its initial equilibrium state at  $20^\circ\text{C}$  to a final equilibrium state at  $100^\circ\text{C}$ . What is the entropy change?

Define the system to be the water. Consider an **alternative reversible** process, between its initial and final equilibrium states.

Specifically, use as the “surroundings” a series of a large number of heat reservoirs each at a infinitesimally higher temperature  $T + \delta T$  than the one before it, starting at  $T_i$  and ending at  $T_f$ . Each stage in this **alternative** process is a **reversible** transfer of heat  $C_P dT$  from a reservoir at the same temperature as the water at that stage. The change in entropy of the water is  $C_P dT/T$ , and the change in entropy of the reservoir is  $-C_P dT/T$ . Integrating over the complete process,  $\Delta S^{System} = C_P \ln \frac{373}{293} = C_P \times 0.24141$ . Since entropy is a state variable, this is the same as the change in entropy for the *irreversible* process between equilibrium states.

Now calculate the change in entropy  $\Delta S^{Surr}$  of the actual surroundings. This consists of a reservoir at  $100^\circ\text{C}$  which delivers the same amount of heat  $C_P(373 - 293) = 80C_P$  as arrives in the water. In the **alternative, reversible** process this is done by transfer to an imaginary reservoir at  $373 - \delta T$ . The change in entropy of the surroundings is thus  $-C_P(373 - 293)/373 = -C_P \times 0.21448$ .

n.b. total entropy increases:  $\Delta S^{Sys} + \Delta S^{Surr} = 0.02693C_P > 0$



## Summary of Laws

<b>Main Postulate</b>	$\Rightarrow$	Isolated systems tend to equilibrium for which state variables exist
<b>Irreversibility</b>	$\Rightarrow$	State variables do not exist during irreversible processes
<b>0th Law</b>	$\Rightarrow$	Temperature defines Thermal Equilibrium; $T_{Equilibrium} = T_{IdealGas} = T_{Carnot}$
<b>1st Law</b>	$\Rightarrow$	Energy is conserved; $\Delta U = \Delta Q + \Delta W$
<b>2nd Law</b>	$\Rightarrow$	Entropy of System + Surroundings cannot decrease;
<b>Third Law</b>	$\Rightarrow$	(not covered yet) Absolute zero T and S exist

## Key Corrolaries

<b>Equilibrium</b>	$\Rightarrow$	Nonequilibrium systems exist.
<b>Work, Heat</b>	$\Rightarrow$	Integrals are Path Dependent
<b>Clausius</b>	$\Rightarrow$	Heat can't flow from cold to hot
<b>Kelvin-Planck</b>	$\Rightarrow$	Cannot convert all heat energy to work
<b>Carnot</b>	$\Rightarrow$	Most efficient possible engine has $\eta = 1 - T_{cold}/T_{hot}$
<b>Clausius Inequality</b>	$\Rightarrow$	Heat flow into a system: $\oint \frac{dQ}{T} < 0$
<b>Clausius Equality</b>	$\Rightarrow$	State variable Entropy exists for <i>system</i> ; $\Delta S = \int \frac{dQ}{T}$
<b>State Function</b>	$\Rightarrow$	Can be calculated by integration along any path; $\oint dX = 0$
<b>Time</b>	$\Rightarrow$	Defined by direction of increase in Entropy

## Some notes about integrals

Often we break partial differentials in order to integrate them. There's no standard notation for the "path dependent" integral, here I use  $dV_T$  to indicate that the integral is along a path of constant  $T$ . For example given the ideal gas relation:

$$\left(\frac{\partial P}{\partial V}\right)_T = -RT/V^2$$
$$\int dP_T = -RT \int dV_T/V^2 \implies P = RT/V + f(T)$$

We can do these integrals because T is constant, but it also means that if we have an indefinite integral the constant of integration can be T-dependent. n.b. for the ideal gas,  $f(T)$  turns out to be zero, but that's not generally true.

By contrast  $\left(\frac{\partial P}{\partial V}\right)_S = f_0(T, V)$  is much more troublesome, because T isn't constant and isn't an independent variable. Before integrating we would need to use the equation of state in the form  $T(S, V)$  to eliminate T.