

## Thermodynamics – Lecture 5 Recap

- Saw how the two statements of the Second Law of Thermodynamics are logically equivalent.
- Looked at a Carnot Cycle in more detail, and showed that the ratio of the heat interactions is the same as the temperatures of the reservoirs,

$$\frac{|Q_L|}{Q_H} = \frac{T_L}{T_H} \Rightarrow \eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}; \text{COP}_{L \text{ Carnot}} = \frac{T_L}{T_H - T_L}; \text{COP}_{H \text{ Carnot}} = \frac{T_H}{T_H - T_L}.$$

- Looked at the Carnot Principles, which tell us that no engine can be more efficient than a Carnot Cycle.
- Considered how real engines can be modelled, including an efficiency calculation.

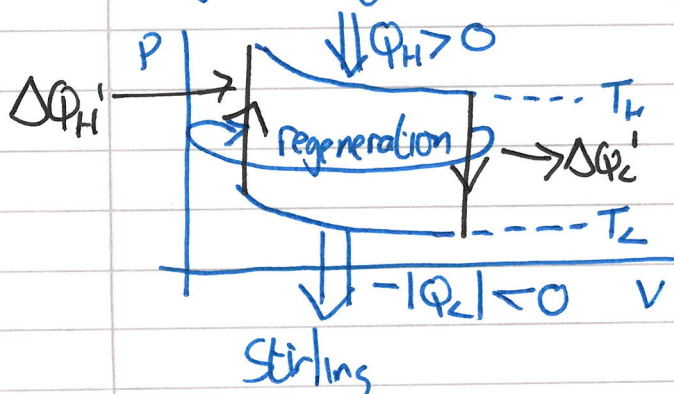
## Thermodynamics – Lecture 6 Aims

- To finish looking at real engine refrigeration cycles, including the Stirling Cycle.
- To consider the Clausius Inequality, and what it means from a thermodynamic perspective.
- To be introduced to the concept of entropy as a thermodynamic function of state.
- To see how to calculate entropy changes in standard thermodynamic processes.

### Stirling + Ericsson Cycles

Like Carnot cycle they 'totally' reversible, where only external heat is added isothermally

Isotherms are joined isochoric/isobars, but the heat interactions on the isochoric/isobaric stay within engine confines via regeneration



$$\Delta Q_L' = \int_{T_H}^{T_L} C_V dT = C_V(T_L - T_H)$$

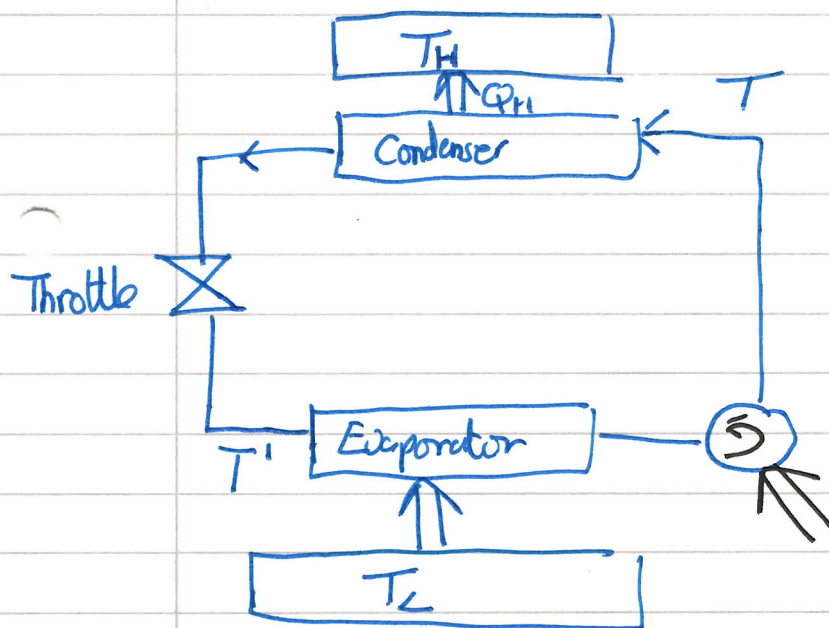
$$\Delta Q_H' = C_V(T_H - T_L)$$

Regenerator keeps  $\Delta Q_L'$  in confines of engine so output at  $\Delta Q_H'$

Only net external heat from isotherm.

Refrigeration cycle — Don't break 2nd law, work is supplied to move heat from cold to hot

Fridges — Remove heat from a cold place to hot environment  
Heat pump — Adds heat to a hot place from a cold environment



Work compresses gas until hotter than the environment  
 $T > T_H$

Heat rejected to the environment using the condenser

Throttle the gas (expansion) to cool it

Gas temp  $T' < T_L$  (lower than fridge) so heat taken by evaporation

## 12. Clausius Inequality

Mathematical representation of 2nd Law, places a direction on a process. Helps us understand heat flow in cycles

$$\oint \frac{\delta Q}{T} \leq 0$$

Integral of heat around the cycle

[ $\delta Q$  is the heat supplied/rejected to the cycle's working substance]

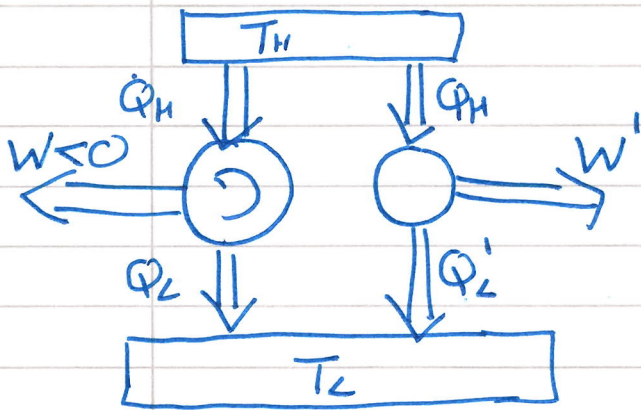
A totally reversible cycle

$$\oint \frac{\delta Q_{\text{rev}}}{T} = 0$$

$\delta Q_{\text{rev}}$  is heat added/removed reversibly



Consider two engines operating between  $T_H$  and  $T_L$



A = Carnot

B

A: Carnot, takes in heat  $|Q_H|$   
Does work  $W = -|W| < 0$   
Rejects heat  $-|Q_L| < 0$

B: Real (imperfect) engine, again  
Takes in heat  $|Q_H|$   
Does less work than A  
 $|W'| < |W|$  ;  $W' < 0$   
Reject more heat to cold  
 $|Q'_L| > |Q_L|$  ;  $Q'_L < 0$

Reversible  $\frac{|Q_L|}{Q_H} = \frac{T_L}{T_H} \Rightarrow \frac{|Q_L|}{T_L} = \frac{Q_H}{T_H}$

$$0 = \frac{Q_H}{T_H} - \frac{|Q_L|}{T_L} \quad \text{or} \quad \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$

[ $Q_L < 0$  as rejected]

Real engine  $Q_H, T_H, T_L$  as before but  $|Q'_L| > |Q_L|$

$$\therefore \frac{Q_H}{T_H} - \frac{|Q'_L|}{T_L} < 0 \quad \text{or} \quad \frac{Q_H}{T_H} + \frac{Q'_L}{T_L} < 0$$

Proof 13.1 generalise to many reservoirs  $\oint \frac{\delta Q}{T} \leq 0$

Thermodynamics – Handout 6

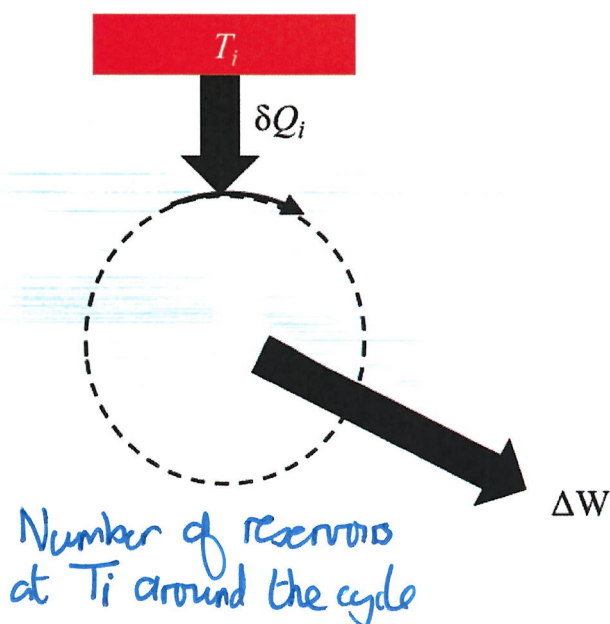


Figure 23: Heat entering through one part of an engine cycle.

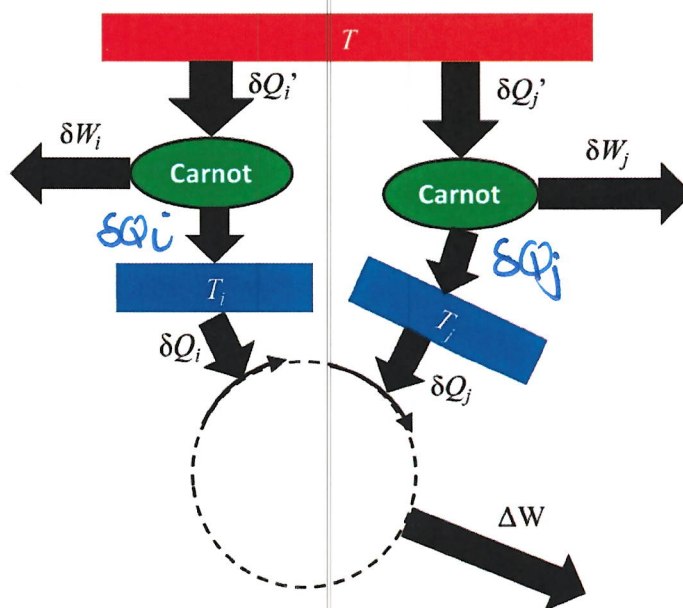


Figure 14: Heats entering a cycle from a number of Carnot cycles that are all connected to a single hot reservoir

Generalise to any cycle, operating between many heat reservoirs. Differential heat  $\delta Q_i$  enters the cycle when it interacts with reservoir at temperature  $T_i$ . The total cycle work (of left) is given by,

1st law  $dU = \delta Q + \delta W$   
 $dU = 0$  (cycle)

$$\Delta W = \sum_{\text{cycle}} \delta Q_i$$

[Differential heats, don't worry about signs]

More generally, the heat into a cycle comes from the heat rejected by a number of Carnot cycles, which all share a common hot reservoir

Add arrows on each Carnot

$$\delta Q'_i = \delta Q_i + \delta W_i \quad ; \quad \delta Q'_j = \delta Q_j + \delta W_j$$

[Differential heats so no signs]

Each Carnot

$$\frac{Q_H}{|Q_C|} = \frac{T_H}{T_C} \Rightarrow \frac{C_H}{T_H} = \frac{|Q_C|}{T_C}$$

$$\frac{\text{Heat from reservoir at } T}{T} = \frac{\text{Heat rejected to reservoir at } T_i}{T_i}$$

$$\frac{\delta Q'_i}{T} = \frac{\delta Q_i}{T_i} \Rightarrow \frac{\delta Q_i + \delta W_i}{T} = \frac{\delta Q_i}{T_i}$$

$$\delta W_i = T \frac{\delta Q_i}{T_i} - \delta Q_i$$

As shown, engine on left looks like a Kelvin violator. Not allowed

Total Work  $\leq 0$  to avoid violating Kelvin

Total Work = Cycle Work + All Carnot Works

$$W_T = \Delta W + \sum_{\text{cycle}} \delta W_i \leq 0$$

$$W_T = \sum_{\text{cycle}} \delta Q_i + \sum_{\text{cycle}} \left[ \frac{T \delta Q_i}{T_i} - \delta Q_i \right] \leq 0$$

$$\Rightarrow \sum_{\text{cycle}} \frac{T \delta Q_i}{T_i} \leq 0$$

But  $T \geq 0$  (thermodynamic temperature)

$$\therefore T \sum_{\text{cycle}} \frac{\delta Q_i}{T_i} \leq 0 \Rightarrow \sum_{\text{cycle}} \frac{\delta Q_i}{T_i} \leq 0$$

$$\text{In } \lim_{\rightarrow 0} \delta Q_i \rightarrow \oint \frac{\delta Q}{T} \leq 0$$

Example 13.1: Simple entropy calculations

Adiabatic Expansion:

$$\Delta S = \int \frac{\delta Q}{T} = 0.$$

Isothermal Expansion:

$$\Delta S = \int_A^B \frac{\delta Q_{\text{rev}}}{T} = \frac{1}{T_0} \int_A^B \delta Q_{\text{rev}} = \frac{(\Delta Q_{\text{rev}})}{T_0}.$$

Temperature change at constant volume:

$$S_B - S_A = \int dS = \int_A^B \frac{C_V dT}{T} = C_V \ln \left( \frac{T_B}{T_A} \right).$$



### 13 Entropy

For a cycle when heat added reversibly  $\oint \frac{\delta Q_{rev}}{T} = 0$

$\frac{\delta Q_{rev}}{T}$  must be a function of state (exact differential) and is called entropy, denoted  $S$

$1/T$  integrating factor of  $\delta Q$  to make it exact.

Calculate the entropy change between two states, independent of the path

$$dS = \frac{\delta Q_{rev}}{T} ; \quad \Delta S = \int_A^B dS = S_B - S_A = \int_A^B \frac{\delta Q_{rev}}{T}$$

Temperature in Kelvin. Around cycle  $\oint dS = 0$

1st law concerned with total energy,  $U$   
2nd law " " entropy,  $S$  [Quality of energy]

Entropy describes energy quality (how much work is obtainable).

As Clausius inequality (for heat interactions around cycle) becomes more negative, engine rejects more heat so does less work. This corresponds to Universe entropy increase.

Less Work  $\Rightarrow$  Lower efficiency  $\Rightarrow$  Smaller temp difference

Reduced energy quality [Better than 'disorder']

### Example 13.1: Simple entropy calculations

Adiabatic Expansion:

$$\Delta S = \int \frac{\delta Q}{T} = 0. \quad \text{Thermally isolated, } \delta Q = 0$$

Isothermal Expansion: *Constant temp,  $T_0$*

$$\Delta S = \int_A^B \frac{\delta Q_{rev}}{T} = \left( \frac{1}{T_0} \right) \int_A^B \delta Q_{rev} = \frac{(\Delta Q_{rev})}{T_0}$$

*Constant so take out*

*Heat added/removed reversibly  
at constant temperature  
[Use energy conservation to  
calculate]*

Temperature change at constant volume:

$$C_V = \left( \frac{\partial Q}{\partial T} \right)_V, \quad \delta Q = C_V dT$$

$$S_B - S_A = \int_A^B dS = \int_A^B \frac{C_V dT}{T} = C_V \ln \left( \frac{T_B}{T_A} \right)$$

*Integrate  
between two  
temperatures*

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

*If  $C_V$  not a function  
of temperature*