

## Thermodynamics – Lecture 3 Recap

- Looked at the meanings of work and internal energy and saw how they led to the first law of thermodynamics.
- Investigated the first law of thermodynamics, mathematically:

$$dU = \delta Q + \delta W \quad ; \quad dU = \delta Q - pdV.$$

- Began to consider the meaning of reversibility and quasi-static when applied to thermodynamics.

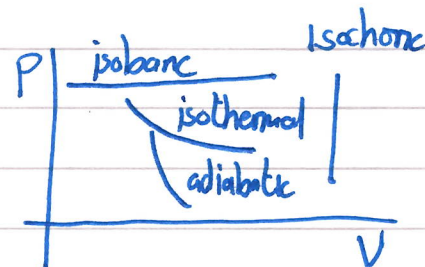
## Thermodynamics – Lecture 4 Aims

- Finish considering the meaning of reversibility and quasi-static when applied to thermodynamics and see one derivation of the adiabatic equation of state.
- To be introduced to the concept of heat engines.
- To see the various statements of the Second Law of Thermodynamics and how they are logically equivalent.

### 8 Reversibility

A process is reversible no dissipative work is done (express everything in terms of thermo coordinates)  
 Quasi-static processes happen very slowly, system always remains in an equilibrium state — there no finite temperature differences  
 No shock waves

Isobaric — constant pressure  
 Isochoric — constant volume  
 Isothermal — constant temperature  
 adiabatic — Thermally isolated (no heat)



Ideal gas:

Isothermal  
 Adiabatic

$$pV = RT_0$$

$$pV^\gamma = k$$

$$p \propto 1/V$$

$$p \propto 1/V^\gamma$$

Isobaric heating  
 Temperature  $T_1 \rightarrow T_2$



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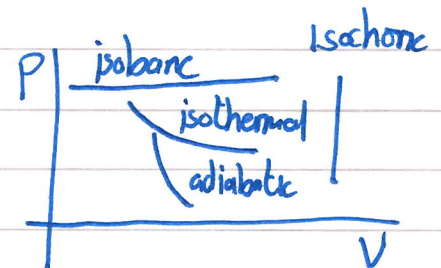
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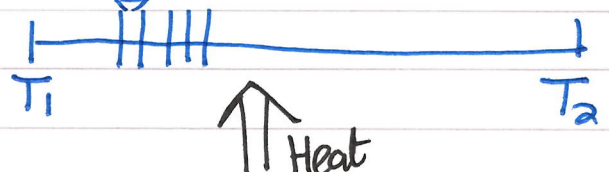
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$$\text{Heat} = \int_{T_1}^{T_2} \delta Q = \int_{T_1}^{T_2} C_p dT \quad \left[ C_p = \left( \frac{\partial Q}{\partial T} \right)_p \right]$$

Exercise 3 - Which does heat flow in a reversible isothermal expansion of an ideal gas?

1st Law  $dU = \delta Q + \delta W = \delta Q - p dV$

Ideal gas has  $U = U(T)$  only so isothermal  $U_f = U_i \Rightarrow dU = 0$   
 $\therefore Q_{if} = \int \delta W = \int p dV$   $p = RT_0/V$  for ideal gas

$$Q_{if} = \int_{V_i}^{V_f} \frac{RT_0}{V} dV = RT_0 \ln \left( \frac{V_f}{V_i} \right) \quad \text{If } V_f > V_i \ln \left( \frac{V_f}{V_i} \right) > 0$$

and  $Q_{if} > 0$  [Heat in]

Example 8.1: What is the equation of state for ideal gas on adiabatic?

The First Law of thermodynamics is,  $dU = \delta Q + \delta W = \delta Q - p dV$  &  $\delta Q = 0$ . [No heat on adiabatic]

From proof 7.1 we have that  $C_V = \left( \frac{\partial U}{\partial T} \right)_V \Rightarrow dU = C_V dT$

$$C_V dT + p dV = 0 \Rightarrow dT = -\frac{p dV}{C_V} \quad (1)$$

Using  $C_p = R + C_V$

$$C_V = C_p - R$$

$$0 = (C_p - R) dT + p dV = C_p dT - R dT + p dV \quad (2)$$

For an ideal gas,  $pV = RT$ , and the total differential of the temperature is

$$T = \frac{pV}{R} \quad dT = \frac{1}{R} d(pV) \quad \text{chain rule } d(pV)$$

$$dT = \frac{1}{R} [p dV + V dp] \quad (*)$$

Substituting (\*) into (2) (the term  $R dT$ ) gives

$$0 = C_p dT - p dV - V dp + p dV \Rightarrow dT = \frac{V dp}{C_p}$$

Two dT

Any two infinitesimal temperature changes must be equal, so  $\frac{V dp}{C_p} = -\frac{p dV}{C_V}$

Differential equation  
separate variables  
+ integrate

$$\int \frac{dp}{p} = - \int \frac{C_p}{C_V} \frac{dV}{V}$$

$$\ln p = -\gamma \ln V + C.$$

$$\ln p = \ln(V^{-\gamma} \times \text{Const}) \Rightarrow p V^\gamma = \text{Const.}$$

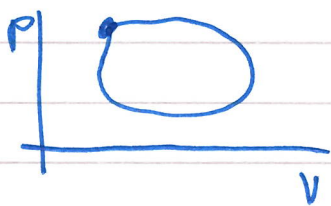
Describes ideal gas behaviour under adiabatic conditions

## 9. Heat Engines

Turning work to heat is easy. Reverse more difficult.  
Heat engine used to produce work from a temperature difference

Operate in cycle —

- Heat taken in at high temperature
- Some heat is converted to work
- Waste heat is rejected at low temperature
- Cycle returned to its initial state



Blob in thermo state  $(p, V, T)$  has its thermo coordinates changed as it moves around the cycle

Engines can run in reverse — requires work to be supplied, take heat from cold to hot.

- Refrigerator — removes heat from an enclosed cold space to the environment
- Heat pump — takes from the cold environment to a hot space.

Efficiency — how much work you get out for a given heat input  $\left[ \frac{\text{Product}}{\text{expense}} \right]$

Coefficient of performance — how much heat is moved for a given amount of work

$$\eta = \frac{\text{Product}}{\text{Expense}} = \frac{|\text{Work Done}|}{\text{Heat input}} \leftarrow \begin{array}{l} \text{Engines do} \\ \text{-ve work} \end{array}$$

$$\text{COP}_L = \frac{|\text{Heat remove from Cold}|}{\text{Work input}} \leftarrow \begin{array}{l} \text{heat out of} \\ \text{cold} \end{array}$$

$$\text{COP}_H = \frac{\text{Heat added to hot}}{\text{Work input}}$$



Thermodynamics – Handout 4

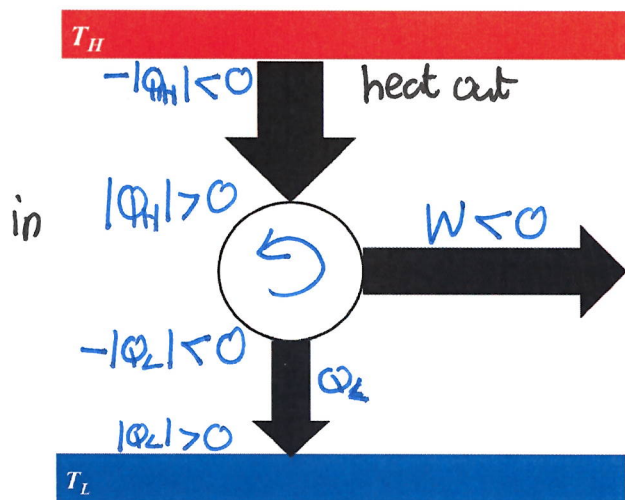


Figure 5: Efficiency of a Heat Engine.

cycle  $\oint dU = 0$  [Exact, engine returns to initial state]

1st Law  $dU = \delta Q + \delta W$   
 $0 = \oint \delta Q + \oint \delta W$

$\oint \delta W = -\oint \delta Q$   
 $W = -(Q_H - Q_L)$   
 Difference in heats

$$\eta = \frac{|Work|}{Heat\ in} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

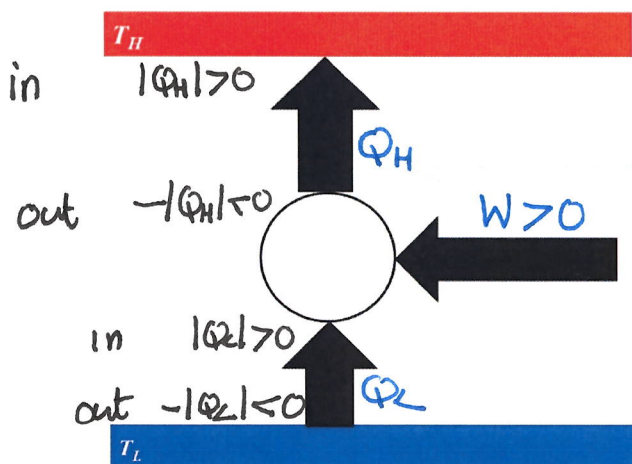


Figure 6: Coefficient of performance of a Refrigerator/Heat pump.

Exercise 4 – Determine Fridge and Heat Pump coefficients of performance (See DUO)

Fridge: heat from cold to hot

$$COP_L = \frac{Product}{Expense} = \frac{|Q_L|}{W}$$

(Work supplied removes heat)

Heat pump: heat into hot from cold

$$COP_H = \frac{Q_H}{W}$$

Example 9.1: To maintain a fridge at 4 °C, heat must be removed at 360 kJ/min using 2 kW power. The coefficient of performance is

Write as rates

$$COP_L = \frac{\dot{Q}_L}{\dot{W}_{in}} = \frac{360}{2} \left( \frac{1 \text{ kW}}{60 \text{ kJ/min}} \right) = 3$$

COP can be > 1

Heat rejected to room  $\dot{Q}_H = \dot{W} + \dot{Q}_L = 2 \text{ kJ s}^{-1} \times 60 + 360 = 480 \text{ kJ/min}$ .

Energy conservation

Heat taken from the fridge plus the work supplied show up in room's internal energy

Heat pump has  $COP_H = 2.5$  to keep house at  $20^\circ\text{C}$ . When  $-2^\circ\text{C}$  outside, the house loses  $80,000\text{ kJ/h}$ . *supply heat to house equivalent to what is lost*

*work to the heat pump*

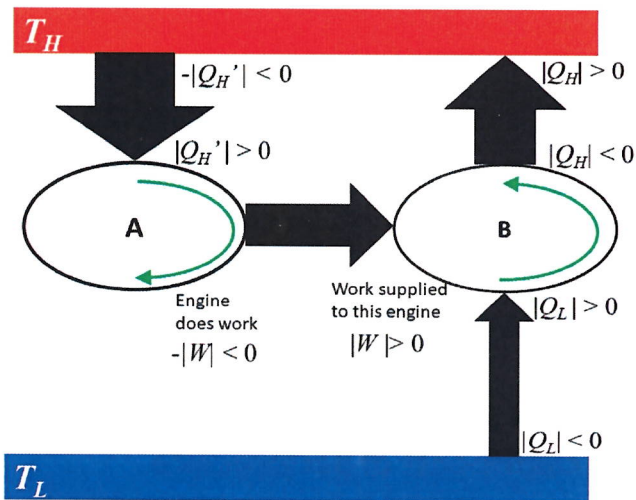
$$W_{in} = \frac{|\dot{Q}_H|}{COP_H} = \frac{80,000}{2.5} = 32,000\text{ kJ/h} \quad (8.9\text{ kW}).$$

*Energy conservation to work out heat extract from environment*

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 80,000 - 32,000 = 48,000\text{ kJ/hour.}$$

*Electricity supplied.*

*Resistive heater would require 80 kJ to warm the house*



*- See lecture 5.*

Figure 1: If the Kelvin statement of the *Second Law* is violated, so is the Clausius.



Most efficient engines are Carnot cycles - Ideal engine model in an abstract form, tells us max possible heat to work.

Considered a system passing through many equilibrium states, so is reversible (+ quasi static)

Carnot knew work from a temperature difference, and heat from hot to cold under its own action

Devised a system where only heat transfer was between bodies of near equal temperature

- Heat in at constant temp
- Adiabatic expansion
- Heat rejected at constant temp
- Adiabatic compression

Perfect engine has  $\eta = 1 - \frac{T_L}{T_H}$ ,  $COP_L = \frac{T_L}{T_H - T_L}$

$$COP_H = \frac{T_H}{T_H - T_L}$$

Perfect reversible cycles only depend on temperature.

## 10 Second Law of Thermodynamics

Encapsulates understanding of heat engines + places a direction on processes. First Law (energy conservation) even if satisfied some processes just don't happen.

Energy having quality as well as quantity.

Refrigerator Clausius - It is impossible to devise a process whose sole result is the transfer of heat from a cold to a hot reservoir

Nature is asymmetric

Heat Engine Kelvin Planck - It is impossible to construct a device that operates in a cycle, whose sole result is the transfer of heat to work  
Tie on conversion of heat to work