

Recall:

Overview of Part II [Energy] Material

Split into three related sections

✓ 5. Basic Physics of Energy (~4/5 lectures)

- Sources & consumption of energy
- Forms of energy, units etc
- Basic balance calculations

Here! →
 ==

6. Basics of Energy Transfer (~6/7 lectures)

- Thermodynamics
- More sophisticated balance calculations etc.

7. Basics of Biological Energetics (~4 lectures)

- How do animals, cells etc store & use energy

Lecture 08

TOPICS

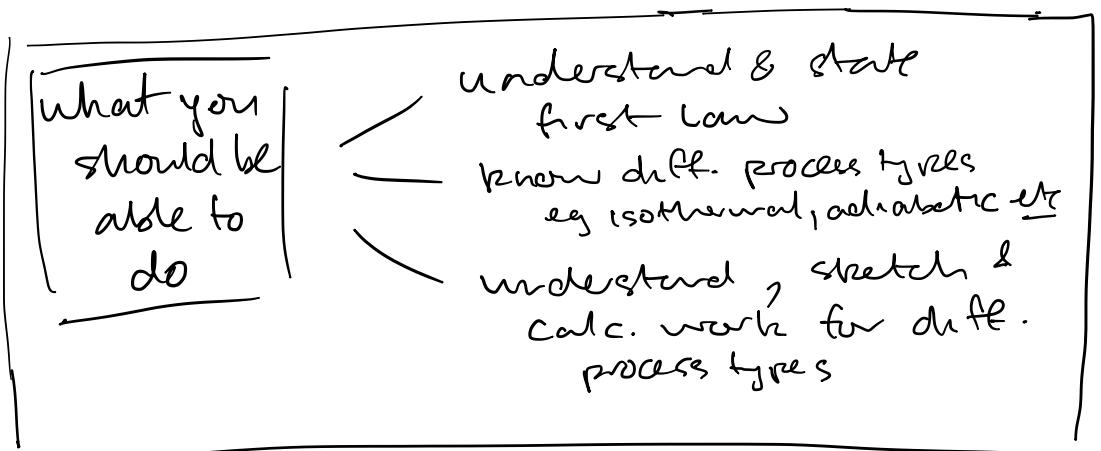
First law of thermodyn.

Work from heat

PV diagrams

Types of process

6.5



Example Qs (practice sheets & their slides)

What is the relationship between internal energy, heat and work?
(i.e. the first law of thermodynamics)

For an ideal gas, what does the internal energy (ΔU) represent?

What is the total change in internal energy (ΔU) for a heat engine undergoing a Carnot cycle?

What is meant by the terms 'isothermal' and 'adiabatic' with regard to a thermodynamic process?

How much work is done by a gas expanding against a piston from 46 L to 65 L at a constant external pressure of 101,325 Pa (1 atmosphere)?

Consider a gas in a cylinder at room temperature ($T = 293 \text{ K}$), with a volume of 0.065 m^3 . The gas is confined by a piston with a weight of 100 N and an area of 0.65 m^2 . The pressure above the piston is atmospheric pressure. What is the pressure of the gas?

The gas is heated, expanding it and moving the piston up. If the volume occupied by the gas doubles, how much work has the gas done?

First law of thermodynamics

Short version: energy is conserved

Longer: • change in internal energy
equals sum of energy
transferred

- Energy can be transferred via both
(macroscopic) mechanical work W
& 'thermal work' ie 'heat' Q
(macroscopic result of
microscopic mechanical work)

Key:

$$\Delta U = W^{\text{on}} + Q^{\text{in}}$$

+ /
state var process vars

(e.g. change in
bank balance
=
sum of transfers
& withdrawals)

Signs?

$$U \quad \left. \begin{array}{l} \nearrow w^{\text{on}} \\ \uparrow \\ Q^{\text{in}} \end{array} \right\} \begin{array}{l} \text{work on system} \\ \text{by environment} \end{array}$$

Other versions:

we often use this →

$$\Delta U = Q^{\text{in}} - W^{\text{by}} \quad \left. \begin{array}{l} \\ \end{array} \right\} \begin{array}{l} \text{common for} \\ \text{engineers} \end{array}$$

⇒ how much can we get out

$$U \quad \left. \begin{array}{l} \nearrow w^{\text{by}} \\ \uparrow \\ Q^{\text{in}} \end{array} \right\} \begin{array}{l} \text{work by system} \\ \text{on environment} \end{array}$$

(etc).

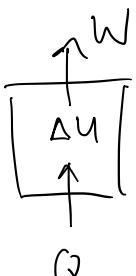
Work from thermal energy

- We can convert stored thermal energy to 'useful' work
- &
- We can add heat to a system & use this to do work.

$$\boxed{\text{KEY: } \Delta U = Q - W^{\text{by}} \quad | \quad \text{1st law}}$$

$$\text{by} \Rightarrow \boxed{W^{\text{by}} = Q - \Delta U \quad |}$$

Consider:



get work by
 - adding heat &/or
 - using stored
energy

$$\boxed{\text{Suppose } \Delta U = 0 \quad \left\{ \begin{array}{l} \text{no extra is stored} \\ \text{or used} \end{array} \right. \quad (\text{as an example})}$$

$$\text{then} \Rightarrow \boxed{W^{\text{by}} = Q}$$

\Rightarrow can 'convert' heat to work

BUT NOTE: In real processes, there are efficiency limitations on the conversion of heat to work!

(deci: "once energy becomes micro/thermal energy,
 can't completely recover/re-use it for
macroscopic mechanical work")

\rightarrow see later (2nd law)

[Heat engines have efficiency limits]

Sign Conventions

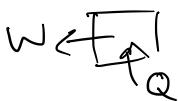
Work on vs work by system

→ different people use diff. conventions

→ if in doubt, be explicit

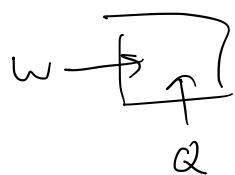
- 'Engineering' often use 'by system'

$$\underline{\Delta u = Q^m - W^{\text{by}}}$$



- Fundamental principle probably easier to remember in 'on system' form

$$\underline{\Delta u = Q^m + W^{\text{on}}}$$



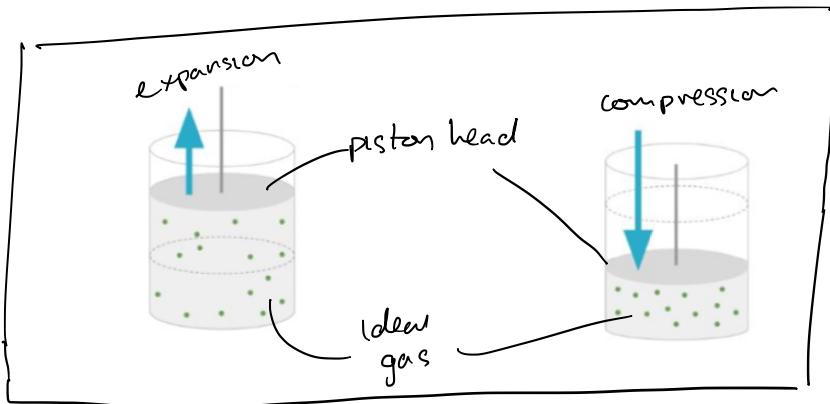
Often use 'by' convention for analysing engineering examples e.g. pistons with ideal gas

Pistons, ideal gases & PV diagrams

Very common, basic model:



Piston containing an ideal gas:



Key Equations:

work

reversible/quasi-equil. work:

$$\underline{W = P \Delta V}$$

ideal state eq'n:

$$\underline{PV = nRT}$$

state

Subtle point: external/actual work W , vs
internal/quasi-equil. work eg $P \cdot \Delta V$

→ not equal in real, irreversible processes

→ are equal in ideal, reversible/quasi-equil. processes



W vs P.ΔV ?



P.ΔV: change in state of system (internal)
 - pressure, temp, vol. etc are state vars/ properties of system

W: transfer energy to system (external)
 - Work, heat are process quantities/actual transfers between system & env.

Only equal for reversible, quasi-equil. work:

$$\boxed{\underbrace{W_{\text{ext}}}_{\substack{\text{external} \\ \text{work} \\ \text{seen}}} = \underbrace{P \cdot \Delta V}_{\substack{\text{internal} \\ \text{work of ideal} \\ \text{system}}}} \quad | \quad \text{reversible, quasi-equil.}$$

For non-ideal/inversible:

$$\boxed{\underbrace{W_{\text{ext}}}_{\text{imperfect transfer}} \neq \underbrace{P \cdot \Delta V}_{\text{2nd law}}} \quad | \quad \text{irreversible/} \\ \text{non-equil.}$$

→ For now, assume reversible, quasi-equilibrium:

$$\text{ie } \boxed{W = P \cdot \Delta V} \quad |$$

Note:

$$P \cdot \Delta V [=] \frac{\text{Force} \times \cancel{\text{area}} \times \text{distance}}{\text{Area}}$$

$$= \text{Force} \times \text{distance} = \text{Work} \quad \checkmark$$

Examples ! Assume reversible / quasi-equilibrium !

How much work is done by a gas expanding against a piston from 46 L to 65 L at a constant external pressure of 101,325 Pa (1 atmosphere)?

$$1 \text{ Pa} = 1 \frac{\text{J}}{\text{m}^3} \quad (W = P \cdot \Delta V \rightarrow P = W / \Delta V [=] \frac{\text{J}}{\text{m}^3})$$

$$1 \text{ L} = (10 \text{ cm})^3 = 1000 \times 10^{-6} \text{ m}^3 = 1 \times 10^{-3} \text{ m}^3.$$

$$W = P \cdot \Delta V = 101,325 \frac{\text{J}}{\text{m}^3} \times (65 - 46) \times 10^{-3} \text{ m}^3 \approx 1925 \text{ J} \text{ (tive) by}$$

Consider a gas in a cylinder at room temperature ($T = 293 \text{ K}$), with a volume of 0.065 m^3 . The gas is confined by a piston with a weight of 100 N and an area of 0.65 m^2 . The pressure above the piston is atmospheric pressure. What is the pressure of the gas?

$$\begin{aligned} P_{\text{atm}} & \\ \text{Force bal: } & \begin{array}{c} \downarrow P_{\text{atm}} \times A \\ \downarrow \text{Weight} \\ \uparrow P_{\text{gas}} \times A \end{array} \} \quad P_{\text{atm}} \times A + mg = P_{\text{gas}} \times A \\ & \Rightarrow P_{\text{gas}} = P_{\text{atm}} + \frac{mg}{A} \\ & = 101,325 + \frac{100}{0.65} \\ & \approx 101,500 \text{ Pa} \end{aligned}$$

The gas is heated, expanding it and moving the piston up. If the volume occupied by the gas doubles, how much work has the gas done?

$$\begin{aligned} & V = 0.065 \text{ m}^3 \\ & \Delta V = V = 0.065 \text{ m}^3 \\ & \circ \text{ assume constant pressure process} \\ & P = 101,500 \text{ Pa} \\ W = P \cdot \Delta V & \end{aligned}$$

$$= 101,500 \times 0.065$$

$$\frac{\text{J}}{\text{m}^3} \times \text{m}^3$$

$$\approx 6600 \text{ J} \quad (\text{tive work done by system})$$

Process types & PV diagrams

- Isobaric: constant (iso) pressure (baric)
- Isochoric: constant (iso) volume (choric)
- Isothermal: constant (iso) temperature
- adiabatic: no heat transfer

For ideal gas, PV systems

$$SW = PdV \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{along quasi-equil. path.}$$

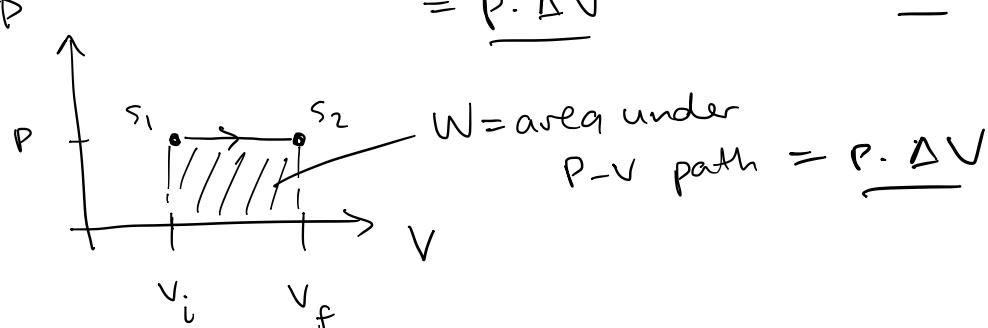
or $W = \int_{\text{path}} PdV$

i.e. Work is area under P-V path

d: change in state var
δ: change in small amount of process var.

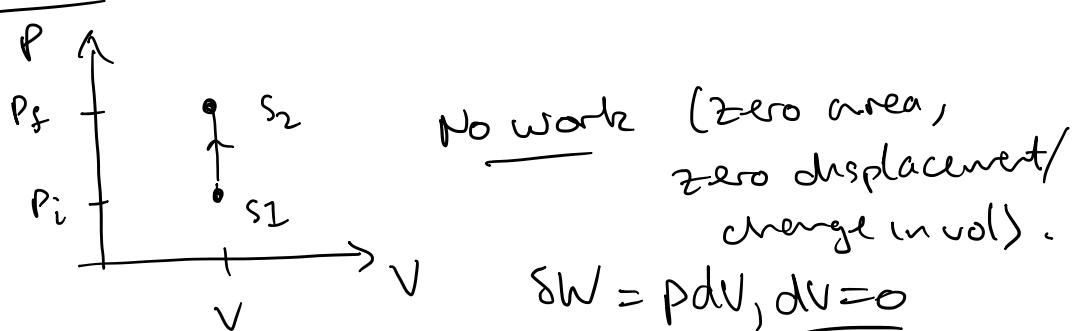
constant pressure: $W = \int pdV = p \int dV$

$$= p \cdot \Delta V \quad (\text{isobaric})$$



constant volume

(isochoric)



Isothermal process

the work by system

e.g. constant temperature expansion

⇒ note, requires heat transfer to keep constant temp!

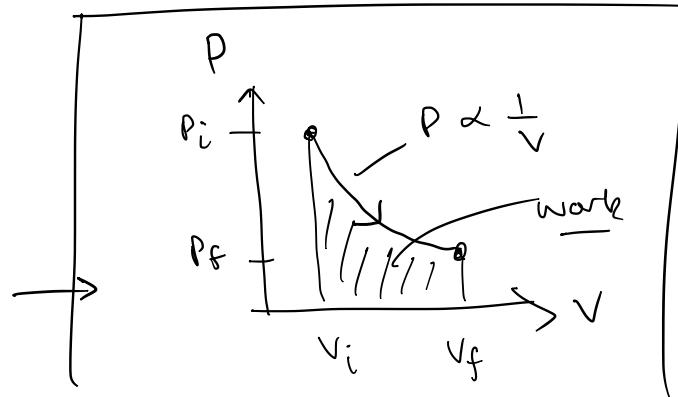
$$W = \int_{V_i}^{V_f} P dV \quad \& \quad P = \frac{nRT}{V}$$

$$\Rightarrow W = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{1}{V} dV = nRT \ln \left[\frac{V_f}{V_i} \right] = nRT \ln \left[\frac{V_f}{V_i} - 1 \right]$$

Upshot:

Isothermal:

$$\Rightarrow W = nRT \ln \left(\frac{V_f}{V_i} \right)$$



Adiabatic process

- No heat transfer
- May change temperature!
- Can show $PV^\gamma = \text{constant} = K$
for adiabatic processes, γ is specific heat ratio: $\frac{C_p}{C_v}$ eq 1-4
for air.

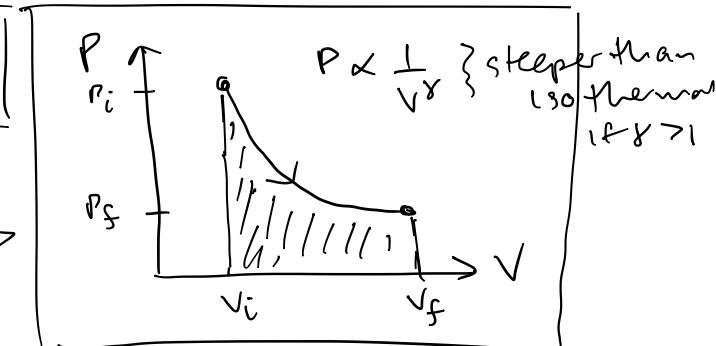
$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{K}{V^\gamma} dV = K \cdot \frac{(V_f^{1-\gamma} - V_i^{1-\gamma})}{1-\gamma} = \frac{P_f V_f^{\gamma} - P_i V_i^{\gamma}}{1-\gamma}$$

Upshot

$$\Rightarrow W = \frac{P_i V_i - P_f V_f}{\gamma - 1}$$

for adiabatic

careful of
(i-f
& γ-1 etc)

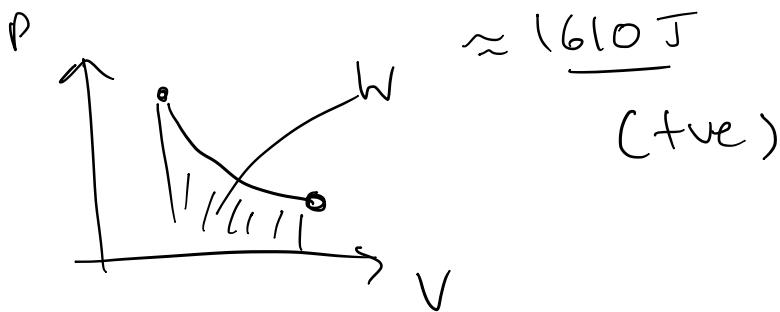


Examples

How much work is done by 1.88 mols of a gas expanding isothermally at 298 K against a piston from 46 L (at 1.013×10^5 Pa) to 65 L?

$$\boxed{W = nRT \ln \frac{V_f}{V_i}} = 1.88 \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \times \ln \left(\frac{65}{46} \right)$$

ratio, so units
don't matter
as long as
same



How much work is done by 1.88 mols of gas expanding adiabatically against a piston from 46 L at 1.013×10^5 Pa to 65 L and 6.24×10^4 Pa?

usually
given

$$\boxed{W = \frac{P_i V_i - P_f V_f}{\gamma - 1}}$$

($\gamma = 1.4$ for air)

$$W = \frac{1.013 \times 10^5 \times 46 \times 10^{-3} - 6.24 \times 10^4 \times 65 \times 10^{-3}}{1.4 - 1}$$



$$\boxed{\begin{aligned} P_i &= 1.013 \times 10^5 \text{ Pa} \\ &\sim \text{J/m}^3 \\ V_i &= 46 \times 10^{-3} \text{ m}^3 \\ P_f &= 6.24 \times 10^4 \text{ J/m}^3 \\ V_f &= 65 \times 10^{-3} \text{ m}^3 \\ (1 \text{ L} &= (10 \text{ cm})^3 \\ &= 1000 \times 10^{-6} \text{ m}^3 \\ &= 10^{-3} \text{ m}^3) \end{aligned}}$$

Lecture 09

Topics

Heat engines & efficiency limits } origin of
2nd law: general form } 2nd law
Spontaneous processes }
2nd law & limits on eff. }

6.5 & 6.6

what you
should be
able to
do

understand heat engines &
do basic eff. calc.

understand & state
second law

know which processes are
spontaneous for isolated systems

understand connection between
general 2nd law form & limit
on work extraction &
def'n of 'reversible' process

Example Qs

Worksheet

2. A reversible heat engine operates between a hot reservoir at 900K and a cold reservoir at 500K.
- Calculate the efficiency of the engine.
 - The temperature of one of the heat reservoirs can be changed by 100 degrees kelvin up or down. What is the highest efficiency that can be achieved by making this temperature change?

Thor's slides

A new startup company claims to have designed a new heat engine that has 42% efficiency, using a heat source of 500K and a cold sink at 300K. Are they telling the truth?

Heat engines & efficiency

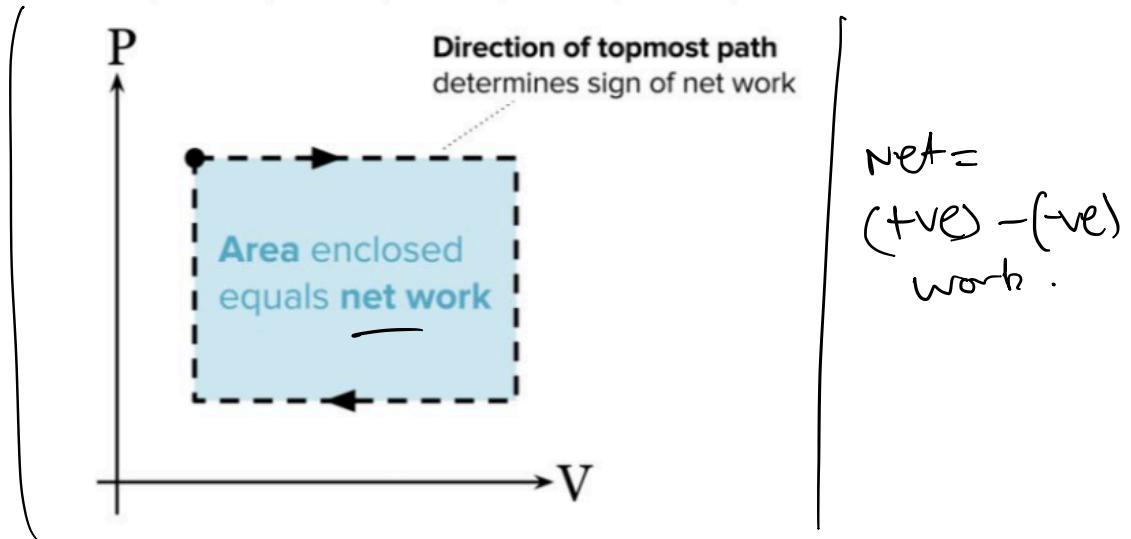
Origin of second law (19th century)

- "How much useful work can we get from thermal energy?"

Heat engines

- convert heat / thermal energy to useful work
 - usually carry out a cycle (or series of cycles)
 - Efficiency & work usually analysed on per cycle basis
- return system
to initial
state; ready for
another

Net work during cycle: (PV system)

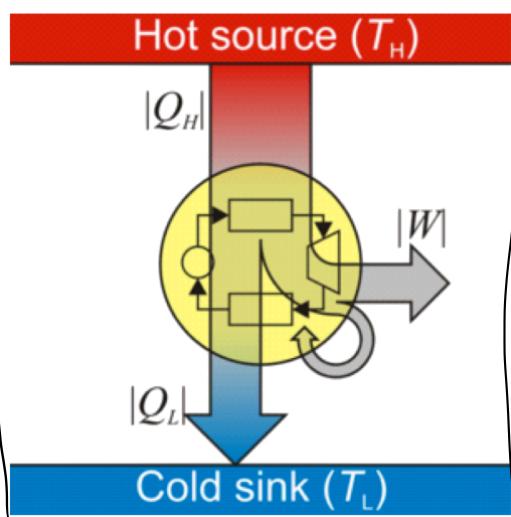


Heat engine

Basic idea

- take heat Q generated by burning fuel
- convert part of this to work
- expel the rest as 'waste' to the environment so that system returns to initial state & hence performs a cycle.

Heat Engine



Analysis:

- since returns to initial state,
 $\Delta U = 0$

- By first law & $\Delta U = 0$,

$$W^{\text{done}} = Q^{\text{net}} = Q^{\text{in}} - Q^{\text{out}}$$

so : work done = heat added - waste heat

Max work from heat engine in cycle :

$$\left| \begin{array}{l} W^{\text{max}} = Q^{\text{in}} \\ \& Q^{\text{out}} = 0 \end{array} \right| \xrightarrow{\text{minimize waste heat}}$$

Carnot efficiency:

$$\left| \begin{array}{l} \eta = \frac{W^{\text{done}}}{Q^{\text{in}}} = \frac{Q^{\text{in}} - Q^{\text{out}}}{Q^{\text{in}}} \leq \frac{T^{\text{in}} - T^{\text{out}}}{T^{\text{in}}} = \eta_{\text{max}} \\ \text{work per heat added} \end{array} \right| \xrightarrow{\text{gives maximum eff. of a heat engine for given } T_s}$$

Higher temp \Rightarrow more eff.

$$\Rightarrow \left| \begin{array}{l} \eta \leq \eta_{\text{max}} \leq 1 \\ \text{actual} \quad \text{reversible} \end{array} \right| \quad \left\{ \begin{array}{l} \text{2nd law} \\ \text{heat engine version.} \end{array} \right.$$

Examples

Worksheet $\rightarrow \eta = \eta_{\max}$

2. A **reversible** heat engine operates between a hot reservoir at 900K and a cold reservoir at 500K.
- Calculate the efficiency of the engine.
 - The temperature of one of the heat reservoirs can be changed by 100 degrees kelvin up or down. What is the highest efficiency that can be achieved by making this temperature change?

$$a) \eta = \frac{900 - 500}{900} \approx 0.44 \text{ ie } \sim 44\%$$

$$b) \eta = 1 - \frac{T_2}{T_1} \quad \left. \begin{array}{l} \rightarrow 1 - \frac{400}{900} \approx 0.56 \\ \rightarrow 1 - \frac{500}{1000} \approx 0.5 \end{array} \right\} \begin{array}{l} \text{minimise} \\ \text{waste heat /} \\ \text{waste temp.} \\ \text{to increase} \\ \text{eff.} \end{array}$$

Thor's slides

A new startup company claims to have designed a new heat engine that has 42% efficiency, using a heat source of 500K and a cold sink at 300K. Are they telling the truth?

$$\eta_{\max} = \frac{T_1 - T_2}{T_1} = \frac{500 - 300}{500} = 0.4$$

$$\begin{aligned} & \uparrow \\ & \left. \begin{array}{l} \text{max} \\ \text{eff. given} \\ \text{fixed temps.} \end{array} \right\} \Rightarrow \eta_{\max} = 0.4 \\ & (\text{real system} \quad \text{---} \quad \eta_{\text{claimed}} = 0.42 > \eta_{\max} \\ & \text{always worse}) \end{aligned}$$

No!

The second law

Turns out to be a fundamental physical principle

→ not just about steam engines!

→ relates to order/disorder, probability, arrow of time etc etc

→ subtle!

Simple to state verbally however:

The entropy of an isolated system is non-decreasing (change is ≥ 0)

Change (in an isolated system) is zero only for reversible processes → definition of reversible

& Mathematically too:

$$| \delta Q \leq T dS | \}$$

δQ small amount of added heat
 T absolute temp
 dS small change in entropy (is a state var)

$$| \delta Q_{rev} = T dS |$$

← reversible only.

Definition of reversible:

→ no entropy production

so $| \delta Q = T dS \text{ & } \delta S = 0 |$

Entropy?

o entropy is a state variable

→ a property of a system at equilibrium

→ loosely, a macroscopic measure of 'disorder' or lack of detailed

→ a 'statistical' property info about system of a system & knowledge of.

Interpretations of second law

"disorder increases in an isolated system"

"useful macroscopic energy/work tends to be 'lost' to less useful microscopic energy/work (thermal energy/heat)"

"energy quantity is conserved but energy quality degrades"

Using 2nd law

$$\textcircled{2} \quad \boxed{\delta Q \leq T dS} \quad (\underbrace{\text{external work}}_{\text{internal thermal}} \leq \underbrace{\text{internal thermal}}_{\text{work}})$$

define

$$\Rightarrow \boxed{T \delta^i s = T dS - \delta Q \geq 0} \quad \left. \begin{array}{l} \text{entropy production} \\ \delta^i s \geq 0 \end{array} \right\}$$

Irreversible internal work total internal thermal work heat supply (external)

ie total, internal thermal work = external heat supplied + work due to internal entropy production

For reversible: $T \delta^i s = 0$

$$\Rightarrow \boxed{T dS = \delta Q}$$

reversible heat supply

entropy production means more internal thermal work than just heat added externally

Isolated: $\delta Q = 0 \Rightarrow T dS = T \delta^i s \geq 0$

⇒ all entropy change is irreversible production in isolated system.

Spontaneous/possible for isolated system: $\Delta S > 0$

Much? Efficiency & Work

More internal thermal work \Rightarrow less mechanical work extracted

$$\rightarrow \text{1st law} \quad dU = SW + SQ \quad \left. \right\} \text{here } SW = SW^{\text{on}} = -SW^{\text{by}}$$

$$\rightarrow \text{Internal state change} \quad dU = pdV + Tds \quad \text{for } U(V, S) \text{ system}$$

$$\rightarrow \text{2nd Law} \quad Tds = SQ + TS^{\text{is}}, \quad S^{\text{is}} \geq 0$$

$$\Rightarrow \underbrace{pdV + Tds}_{\text{internal state change}} = \underbrace{SW + SQ}_{\text{external supply}} \quad \left. \right\} \text{'always' true: overall eqn.}$$

o ideal, reversible only:

$$pdV = SW \quad \left. \right\} \text{parts of equation}$$

$$\& Tds = SQ$$

o non-ideal:

$$Tds \geq SQ$$

$$\Rightarrow SW - pdV = Tds - SQ \quad \left. \right\} > 0$$

non-ideal: slippage

$$pdV + Tds = SW + SQ$$

\Rightarrow Work supplied externally exceeds internal mechanical work for 'real' systems
"slippage" in work transfer

\Rightarrow or work extracted from system is less than the ideal internal work available

\Rightarrow "slippage" in work extraction

Takeaways:

- entropy of an isolated system increases
 - spontaneous (real) processes require $\Delta S \geq 0$ in isolated systems
 - related to lack of detailed knowledge & to efficiency limits due to this 'macroscopic' description
 - reversible processes are ideal case where entropy production = 0.
-

Next : non-isolated systems
& entropy ?