

Thermodynamics versus Kinetics

- ❑ Thermodynamics deals with stability of systems. It tells us ‘*what should happen?*’. ‘*Will it actually happen(?)*’ is not the domain of thermodynamics and falls under the realm of kinetics.
- ❑ At -5°C at 1 atm pressure, ice is more stable than water. Suppose we cool water to -5°C . “Will this water freeze?” (& “how long will it take for it to freeze?”) is (are) not questions addressed by thermodynamics.
- ❑ Systems can remain in metastable state for a ‘long-time’.
 - Window pane glass is metastable— but it may take geological time scales for it to crystallize!
 - At room temperature and atmospheric pressure, graphite is more stable than diamond— but we may not lose the glitter of diamond practically forever!

* The term *metastable* is defined in the [chapter on equilibrium](#).

Thermodynamics (TD): *perhaps the most basic science*

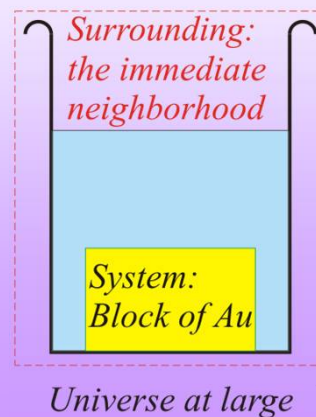
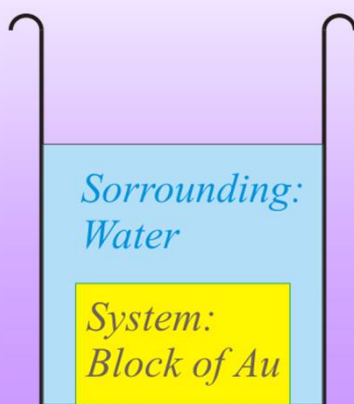
- ❑ One branch of knowledge that all engineers and scientists must have a grasp of (*to some extent or the other!*) is thermodynamics.
- ❑ In some sense thermodynamics is perhaps the ‘most abstract subject’ and a student can often find it very confusing if not ‘motivated’ strongly enough.
- ❑ Thermodynamics can be considered as a ‘**system level**’ science- i.e. it deals with descriptions of the whole system and *not with interactions (say) at the level of individual particles*.
 - I.e. it deals with quantities (like T,P) averaged over a large collection of entities (like molecules, atoms)*.
 - This implies that questions like: “What is the temperature or entropy of an atom?”; do not make sense in the context of thermodynamics (*at lease in the usual way!*).
- ❑ TD puts before us some fundamental laws which are universal** in nature (and hence applicable to fields across disciplines).

* *Thermodynamics deals with spatio-temporally averaged quantities.*

** *They apply to the universe a whole as well! (Though the proof is lacking!).*

The language of TD

- ❑ To understand the laws of thermodynamics and how they work, first we need to get the terminology right. Some of the terms may look familiar (as they are used in everyday language as well)- but their meanings are *more 'technical' and 'precise'*, when used in TD and hence we should **not** use them 'casually'.
- ❑ **System** is region where we focus our attention (*Au block in figure*).
- ❑ **Surrounding** is the rest of the universe (*the water bath at constant 'temperature'*).
- ❑ **Universe = System + Surrounding** (the part that is within the dotted line box in the figure below)
- ❑ More practically, we can consider the 'Surrounding' as the immediate neighbourhood of the system (the part of the universe at large, with which the system 'effectively' interacts). In this scheme of things we can visualize: a system, the surrounding and the universe at large.
- ❑ Things that matter for the surrounding: (i) T, (ii) P, (iii) ability to: do work, transfer heat, transfer matter, etc. Parameters for the system: (i) Internal energy, (ii) Enthalpy, (iii) T, (iv) P, (v) mass, etc.

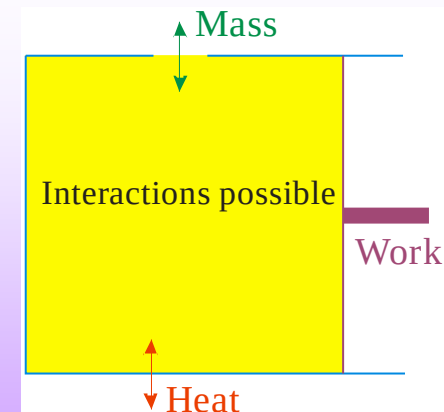


In TD we usually do not worry about the universe at large!

Open, closed and isolated systems

- ❑ To a thermodynamic system two ‘things’ may be added/removed:
 - **energy** (in the form of heat &/or work) ➤ **matter**.
- ❑ An **open system** is one to which you can add/remove matter (e.g. a open beaker to which we can add water). When you add matter- you also end up adding heat (which is contained in that matter).
- ❑ A system to which you cannot add matter is called **closed**.
Though you cannot add/remove matter to a closed system, *you can still add/remove heat* (you can cool a closed water bottle in fridge).
- ❑ A system to which *neither matter nor heat* can be added/removed is called **isolated**.
A closed vacuum ‘thermos’ flask can be considered as isolated.

Type of boundary	Interactions
Open	All interactions possible (Mass, Work, Heat)
Closed	Matter cannot enter or leave
Semi-permeable	Only certain species can enter or leave
Insulated	Heat cannot enter or leave
Rigid	Mechanical work cannot be done*
Isolated	No interactions are possible**



* By or on the system

** Mass, Heat or Work

- ❑ **Matter** is easy to understand and includes **atoms, ions, electrons**, etc.
- ❑ Energy may be transferred ('added') to the system as heat, electromagnetic radiation etc.
- ❑ In TD the **two modes of transfer** of energy to the system considered are **Heat** and **Work**.
 - 😊➤ ***Heat and work are modes of transfer of energy and not 'energy' itself.***
 - 😊➤ *Once inside the system, the part which came via work and the part which came via heat, cannot be distinguished*. More sooner on this!*
 - 😊➤ *Before the start of the process and after the process is completed, the terms heat and work are not relevant.*
- ❑ From the above it is clear that, *bodies contain internal energy and not heat (nor work!)*.
- ❑ Matter when added to a system brings along with it some energy. The 'energy density' (energy per unit mass or energy per unit volume) in the incoming matter may be higher or lower than the matter already present in the system.

* The analogy usually given is that of depositing a cheque versus a draft in a bank. Once credited to an account, cheque and draft have no meaning. (Also reiterated later).

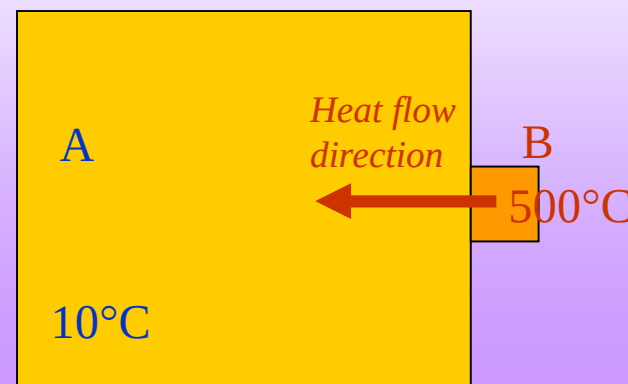
Processes in TD

We will deal with some of them in detail later on

- ❑ Here is a brief listing of a few kinds of processes, which we will encounter in TD:
- **Isothermal process** → the process takes place at constant temperature
(e.g. freezing of water to ice at $-10\text{ }^{\circ}\text{C}$)
- **Isobaric** → constant pressure
(e.g. heating of water in open air → under atmospheric pressure)
- **Isochoric** → constant volume
(e.g. heating of gas in a sealed metal container)
- **Reversible process** → the system is close to equilibrium at all times (and *infinitesimal* alteration of the conditions can restore the universe (system + surrounding) to the original state. (Hence, there are no truly reversible processes in nature).
- **Cyclic process** → the final and initial state are the same. However, **q** and **w** need not be zero.
- **Adiabatic process** → dq is zero during the process (no heat is added/removed to/from the system)
- ❑ A combination of the above are also possible: e.g. 'reversible adiabatic process'.

Temperature

- ❑ Though we all have a feel for temperature ('like when we are feeling hot'); in the context of TD temperature is technical term with 'deep meaning'.
- ❑ As we know *(from a commons sense perspective)* that temperature is a measure of the 'intensity of heat'. 'Heat flows' *(energy is transferred as heat)* from a body at higher temperature to one at lower temperature. (Like pressure is a measure of the intensity of 'force applied by matter' → matter *(for now a fluid)* flows from region of higher pressure to lower pressure).
- ❑ That implies *(to reiterate the obvious!)* if I connect two bodies– (A)-one weighing 100kg at 10°C and the other (B) weighing 1 kg at 500°C, then the 'heat will flow' from the hotter body to the colder body *(i.e. the weight or volume of the body does not matter)*.
- ❑ But, temperature comes in two important 'technical' contexts in TD:
 - 1➤ it is a measure of the average **kinetic energy** (or velocity) of the constituent entities *(say molecules)*
 - 2➤ it is **the** parameter which determines the distribution of species *(say molecules)* across various energy states available.



Temperature as a parameter determining the distribution of species across energy levels

- Let us consider various energy levels available for molecules in a system to be promoted to.
- At low temperatures the lower energy levels are expected to be populated more, as compared to higher energy levels. As we heat the system, more and more molecules will be promoted to higher energy levels.
- The distribution of molecules across these energy levels is given by:

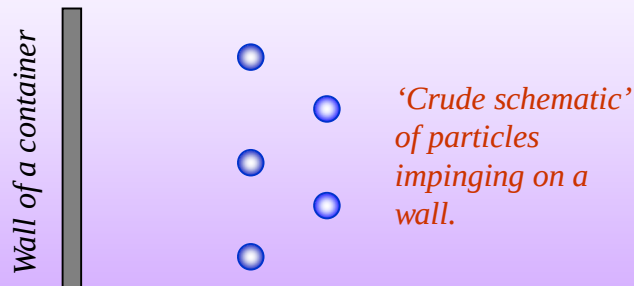


Few points about temperature scales and their properties

- Celsius (Fahrenheit, etc.) are relative scales of temperature and zero of these scales do not have a fundamental significance. **Kelvin scale is an absolute scale.**
Zero Kelvin and temperatures below that are not obtainable in the classical sense.
- Classically, at 0K a perfect crystalline system has zero entropy (i.e. system attains its minimum entropy state). However, in some cases there could be some *residual entropy* due to degeneracy of states (*this requires a statistical view point of entropy*).
- At 0K the kinetic energy of the system is not zero. There exists some **zero point energy**.

Pressure

- ❑ Pressure* is force per unit area (*usually exerted by a fluid on a wall***).
- ❑ It is the **momentum transferred** (*say on a flat wall by molecules of a gas*) **per unit area, per unit time**. (*In the case of gas molecules it is the average momentum transferred per unit area per unit time on to the flat wall*).
 - $P = \text{momentum transferred/area/time}$.
- ❑ Pressure is related to **momentum**, while **temperature** is related to **kinetic energy**.



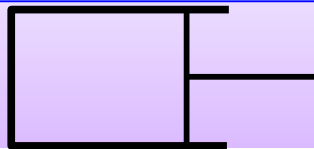
* 'Normal' pressure is also referred to as hydrostatic pressure.

** Other agents causing pressure could be radiation, macroscopic objects impinging on a wall, etc.

Heat and Work

- ❑ Work (W) in mechanics is displacement (d) against a resisting force (F). $W = F \times d$
- ❑ Work has units of energy (Joule, J).
- ❑ Work can be **expansion work** ($P\Delta V$), electrical work, magnetic work etc. (*many sets of stimuli and their responses*).
- ❑ **Heat** as used in TD is a tricky term (*yes, it is a very technical term as used in TD*).
 - The transfer of energy as a result of a temperature difference is called heat.
 - “In TD heat is NOT an entity or even a form of energy; heat is a mode of transfer of energy” [1].
 - “Heat is the transfer of energy by virtue of a temperature difference” [1].
 - “Heat is the name of a process, not the name of an entity” [1].
 - “Bodies contain internal energy (U) and not heat” [2].
- ❑ The ‘flow’ of energy down a temperature gradient can be treated mathematically by considering heat as a mass-less fluid [1] → this does not make heat a fluid!

Expansion work



To give an example (inspired by [1]):

assume that you start a rumour that there is ‘lot of’ gold under the class room floor. This rumour ‘may’ spread when persons talk to each other. The ‘spread of rumor’ with time may be treated mathematically by equations, which have a form similar to the diffusion equations (or heat transfer equations). *This does not make ‘rumour’ a fluid!*

☐ **Work** is coordinated flow of matter.

- Lowering of a weight can do work
- Motion of piston can do work
- Flow of electrons in conductor can do work.

☐ **Heat** involves random motion of matter (or the constituent entities of matter).

- Like gas molecules in a gas cylinder
- Water molecules in a cup of water
- Atoms vibrating in a block of Cu.

☐ Energy may enter the system as heat or work.

☐ Once inside the system:

- it does not matter how the energy entered the system* (i.e. work and heat are terms associated with the surrounding and once inside the system there is no ‘memory’ of how the input was received and
- the energy is stored as potential energy (PE) and kinetic energy (KE).

☐ This energy can be withdrawn as work or heat from the system.

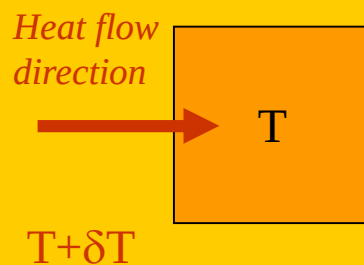
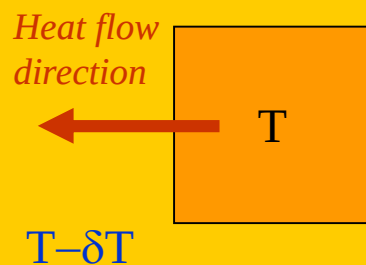
* As Aktins put it: “money may enter a bank as cheque or cash— but once inside the bank there is no difference”.

Reversible process

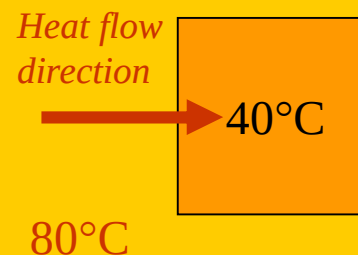
'Reversible' is a technical term (like many others) in the context of TD.

- ❑ A reversible process is one where an infinitesimal change in the conditions of the surroundings leads to a 'reversal' of the process. (The system is very close to equilibrium and infinitesimal changes can restore the system and surroundings to the original state).
- ❑ If a block of material (at T) is in contact with surrounding at $(T-\delta T)$, then 'heat will flow' into the surrounding. Now if the temperature of the surrounding is increased to $(T+\delta T)$, then the direction of heat flow will be reversed.
- ❑ If a block of material (at 40°C) is contact with surrounding at 80°C then the 'heat transfer' which takes place is not reversible.
- ❑ Though the above example uses temperature differences to illustrate the point, the situation with other stimuli like pressure (differences) is also identical.
- ❑ Consider a piston with gas in it at pressure ' P '. If the external pressure is $(P+\delta P)$, then the gas (in the piston) will be compressed (slightly). The reverse process will occur if the external (surrounding pressure is slightly lower).
- ❑ Maximum work will be done if the compression (or expansion) is carried out in a reversible manner.

Reversible process

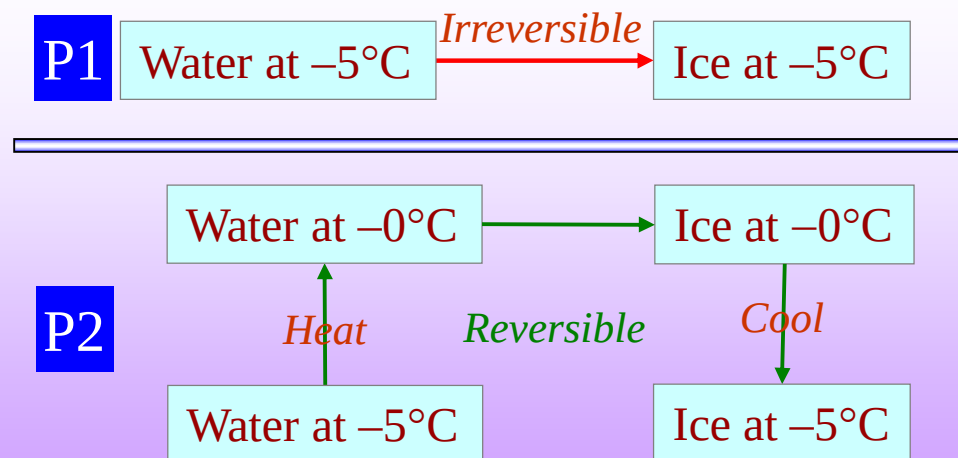


NOT a Reversible process



How to visualize a 'reversible' equivalent to a 'irreversible' processes?

- ❑ Let us keep one example in mind as to how we can (sometimes) construct a 'reversible' equivalent to a 'irreversible' processes.
- ❑ Let us consider the example of the freezing of 'undercooled water'* at -5°C (at 1 atm pressure). This freezing of undercooled water is irreversible (P1 below).
- ❑ We can visualize this process as taking place in three reversible steps ➤ hence making the entire process reversible (P2 below).



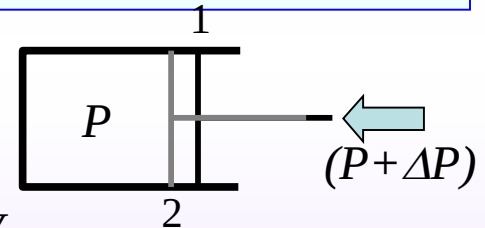
* 'Undercooled' implies that the water is held in the liquid state below the bulk freezing point! How is this possible?→ read chapter on phase transformations

Reversible P-V work on a closed system

- ❑ In a **closed system** (piston in the example figure below), if infinitesimal pressure increase causes the volume to decrease by ΔV , then the work done on the system is:
- ❑ The system is close to equilibrium during the whole process thus making the process **reversible**.

$$dw_{\text{reversible}} = -PdV$$
- ❑ As ΔV is negative, while the work done is positive (*work done on the system is positive, work done by the system is negative*).
If the piston moves outward under influence of P (i.e. ' P ' and ΔV are in opposite directions, then work done is negative.

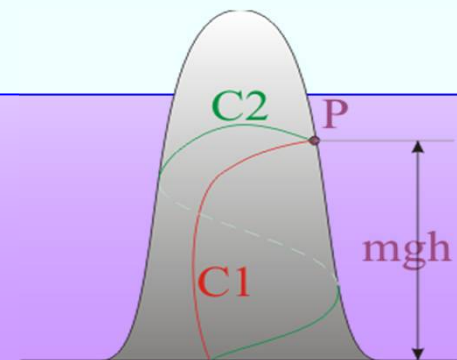
Note that the ' P ' is the pressure inside the container. For the work to be done reversibly the pressure outside has to be $P + \Delta P$ ($\sim P$ for now). Since the piston is moving in a direction opposite to the action of P , the work done by the surrounding is $P\Delta V$ (or the work done by the system is $-P\Delta V$, i.e. negative work is done by the system).



- ❑ '**Ultimately**', all forms of energy will be converted to heat!!
- ❑ One nice example given by Atkins: consider a current through a heating wire of a resistor. There is a net flow of electrons down the wire (in the direction of the potential gradient) → i.e. work is being done.
Now the electron collisions with various scattering centres leading to heating of the wire → i.e. work has been converted into heat.

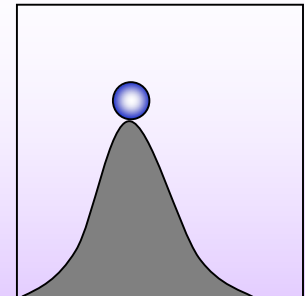
State functions in TD

- ❑ A property which depends only on the current state of the system (as defined by T, P, V etc.) is called a state function. This does not depend on the path used to reach a particular state.
 - Analogy: one is climbing a hill- the potential energy of the person is measured by the height of his CG from 'say' the ground level. If the person is at a height of 'h' (at point P), then his potential energy will be mgh , irrespective of the path used by the person to reach the height (paths C1 & C2 will give the same increase in potential energy of mgh - in figure below).
- ❑ In TD this state function is the internal energy (U or E). (Every state of the system can be ascribed to a unique U).
- ❑ Hence, the work needed to move a system from a state of lower internal energy ($=U_L$) to a state of higher internal energy (U_H) is $(U_H) - (U_L)$. $W = (U_H) - (U_L)$
- ❑ The internal energy of an isolated system (which exchanges neither heat nor mass) is constant → this is one formulation of the *first law of TD*.
- ❑ A process for which the final and initial states are same is called a **cyclic process**. For a cyclic process change in a state function is zero.
E.g. $\Delta U_{(\text{cyclic process})} = 0$.



Spontaneous and Driven processes

- ❑ A spontaneous process is one which occurs ‘naturally’, ‘down-hill’ in energy*. I.e. the process does not require input of work in any form to take place.
 - Melting of ice at 50°C is a spontaneous process.
- ❑ A driven process is one which wherein an external agent takes the system uphill in energy (usually by doing work on the system).
 - Freezing of water at 50°C is a driven process (you need a refrigerator, wherein electric current does work on the system).
- ❑ Later on we will note that the entropy of the universe will increase during a spontaneous change. (*I.e. entropy can be used as a single parameter for characterizing spontaneity*).



Spontaneous process
(Click to see)

* The kind of ‘energy’ we are talking about depends on the conditions. As in the topic on [Equilibrium](#), at constant temperature and pressure the relevant TD energy is Gibbs free energy.

Heat Capacity

- ❑ Heat capacity is the **amount of heat** (measured in Joules or Calories) needed to raise an **unit amount of substance** (measured in grams or moles) by an **unit in temperature** (measured in °C or K). As mentioned before bodies (systems) contain internal energy and not heat.
- ❑ This ‘heating’ (addition of energy) can be carried out at *constant volume* or *constant pressure*. At constant pressure, some of the heat supplied goes into doing work of expansion and less is available with the system (to raise its temperature).
- ❑ **Heat capacity at constant Volume (C_V):**
It is the slope of the plot of internal energy with temperature.

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$
- ❑ **Heat capacity at constant Pressure (C_P):**
It is the slope of the plot of enthalpy with temperature.

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$
- ❑ Units: **Joules/Kelvin/mole**, J/K/mole, J/°C/mole, J/°C/g.
- ❑ Heat capacity is an extensive property (depends on ‘amount of matter’)
- ❑ If a substance has higher heat capacity, then more heat has to be added to raise its temperature. Water with a high heat capacity (of $C_P = 4186 \text{ J/K/mole} = 1 \text{ Cal/°C/Kg}$) heats up slowly as compared to air (with a heat capacity, $C_P = 29.07 \text{ J/K/mole}$) $\Rightarrow$ this implies that oceans will heat up slowly as compared to the atmosphere.
- ❑ As $T \rightarrow 0\text{K}$, the heat capacity tends to zero. I.e. near 0 Kelvin very little heat is required to raise the temperature of a sample. (This automatically implies that very little heat has to be added to raise the temperature of a material close to 0K.
This is of course bad news for cooling to very low temperatures— small leakages of heat will lead to drastic increase in temperature).

The Laws of Thermodynamics

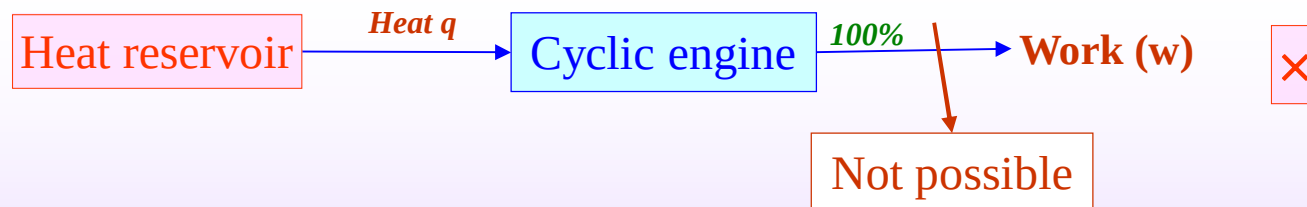
The First Law

- ❑ The internal energy of an isolated system is constant.
- ❑ A closed system may exchange energy as heat or work. Let us consider a close system at rest without external fields.
- ❑ There exists a state function **U** such that for any process in a closed system:
$$\Delta U = q + w \quad [1]$$
 - **q** → heat flow in to the system
 - **w** → work done **on** the system (*work done by the system is negative of above- this is just 'one' sign convention*)**q** & **w** are **not** state functions → i.e. they depend on the path of a process.
- ❑ U is the internal energy. Being a state function for a process ΔU depends only of the final and initial state of the system. $\Delta U = U_{\text{final}} - U_{\text{initial}}$. In contrast to U, **q** & **w** are **NOT** state functions (i.e. depend on the path followed).
- ❑ For an infinitesimal process eq. [1] can be written as: $dU = dq + dw$
- ❑ The change in U of the surrounding will be opposite in sign, such that:
$$\Delta U_{\text{system}} + \Delta U_{\text{surrounding}} = 0$$
- ❑ Actually, it should be ΔE above and not ΔU {however, in many cases K and V are zero (e.g. a system at rest considered above) and the above is valid- as discussed elsewhere}.
- ❑ It is to be noted that in '**w**' work done by one part of the system on another part is not included.

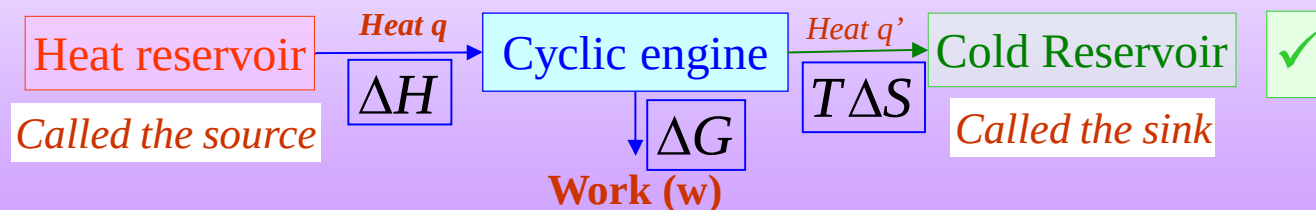
The Second Law

The second law comes in many equivalent forms

- ❑ It is impossible to build a cyclic machine* that converts heat into work with 100% efficiency → Kelvin's statement of the second law.
- ❑ Another way of viewing the same:
it is impossible to construct a cyclic machine** that completely (with 100% efficiency) converts **heat**, which is energy of *random molecular motion*, to mechanical **work**, which is *ordered motion*.
- ❑ The unavailable work is due to the role of **Entropy** in the process.



Kelvin's statement of the second law



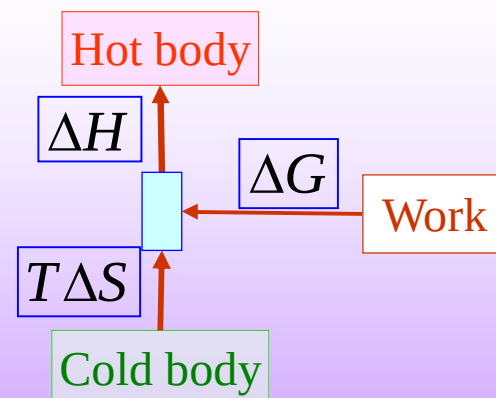
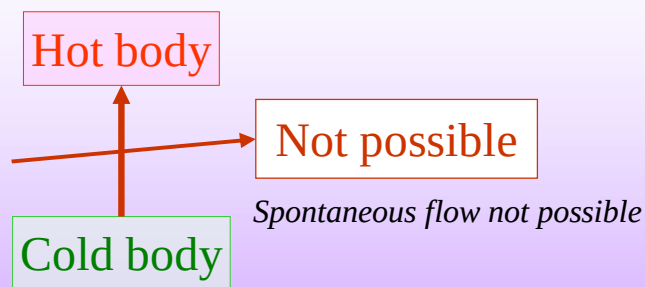
Possible

* For now we are 'building' 'conceptual machines' !

** These 'engines' which use heat and try to produce work are called heat engines.

Another statement of the second law → the Clausius statement

- ❑ Heat does not ‘flow*’ from a colder body to a hotter body, without an concomitant change outside of the two bodies → Clausius’s statement of the second law.^(a)
- ❑ This automatically implies that the spontaneous direction of the ‘flow of heat*’ is from a hotter body to a colder body.^(b)
- ❑ The Kelvin’s and Clausius’s statements of the second law are equivalent. I.e. if we violate Kelvin’s statement, then we will automatically violate the Clausius’s statement of the second law (and vice-versa).



* Used here in the ‘common usage sense’.

(b) is obvious, but not (a) → though they represent the same fact.

A combined (Kelvin + Clausius) statement of the II Law

- ❑ The entropy* of a closed system will increase during any spontaneous change/process.
*If we consider the Universe to be a closed system (without proof!!)**, then*
- ❑ The entropy of the universe will increase during any spontaneous change (process).

You may want to jump to chapter on equilibrium to know about Entropy first

Entropy sets the direction for the arrow of time !

** Soon we will get down to this mysterious quantity.*

*** For all we know the Universe could be 'leaky' with wormholes to other parallel Universes!*

The efficiency of a heat engine

- ❑ The efficiency of a heat engine is the amount of work output divided by the amount of heat input.
 - ❑ This efficiency depends only on the ratio of the temperature of the sink to the temperature of the source. The maximum efficiency achievable is given by the formula below.
 - ❑ This is surprising as:
 - there is no mention of the medium of the system (or its properties),
 - the formula has only temperatures and
 - the temperature of the sink seems to play a major role (as the presence of the sink is usually not intentional or obvious→ in a steam engine sink is the air around the engine and source is the hot steam).
- Important message** ➤ Sink (*characterized by its temperature*) is as important as the source.
- ❑ To increase the maximum possible efficiency of a heat engine, either the temperature of the source has to be increased or the temperature of the sink has to be decreased.

$$\eta_{\text{heat engine}} = \frac{W_{\text{output}}}{Q_{\text{input}}}$$

$$\eta_{\text{heat engine}}^{\text{max}} = 1 - \left(\frac{T_{\text{sink}}}{T_{\text{source}}} \right)$$

*“Reflections on the Motive Power of Fire”,
Chapman & Hall ltd, London, 1897.*

Nicolas Léonard Sadi Carnot in 1824.

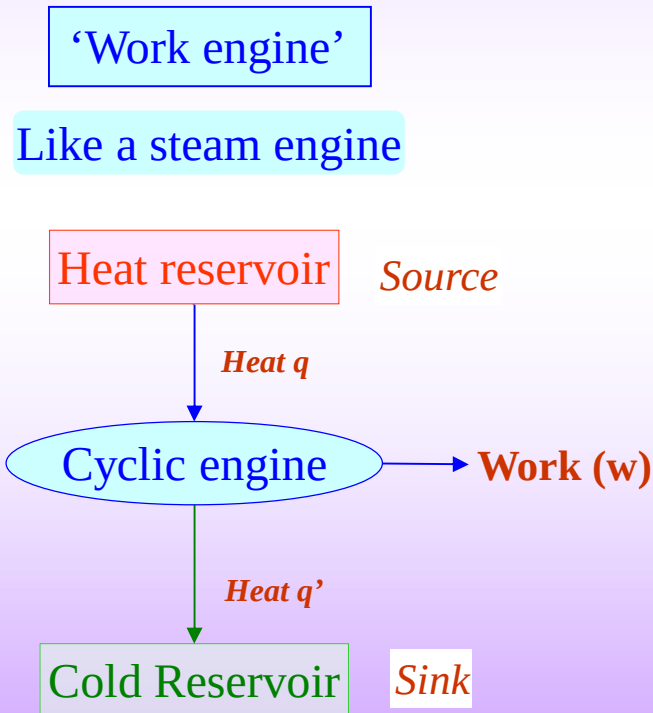
Clausius statement of the second law

- ☐ Heat cannot spontaneously flow from a cold (low temperature) body to a hot body.
- ☐ To make heat flow from a cold body to a hot body, there must be accompanying change elsewhere (work has to be done to achieve this).

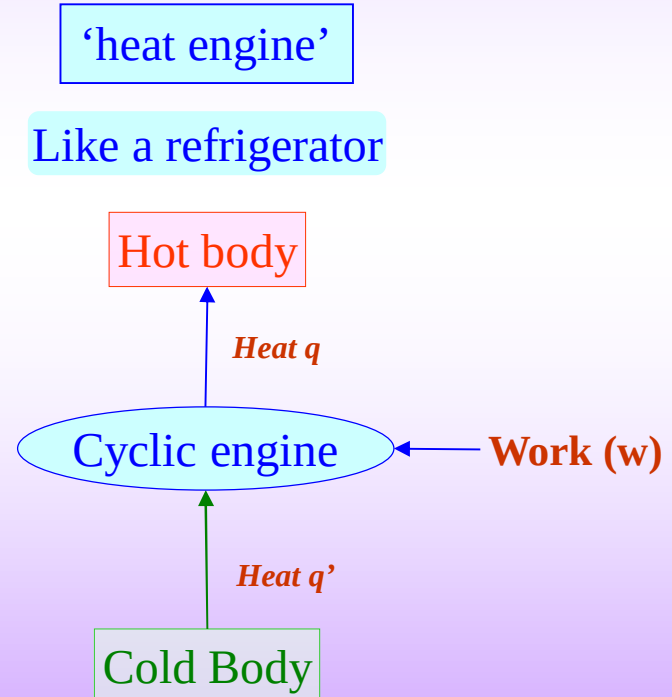
Q & A

What is the difference between 'heat engine' and 'work engine'?

- ❑ Actually both the engines we are going to describe here are usually known as heat engines.
- ❑ We are differentiating two types of engines to see which one produces work and which one actually transfers heat.
- ❑ In the heat engine as the temperature of the cold body tends to zero Kelvin, more and more work has to be done to transfer the heat from the cold body to the hot body.



The main objective here is to produce work



The main objective here is to transfer heat from a cold body to a hot body