Thermodynamics lecture 1

W.A.L.T. (we are learning today)

Basic concepts and terminology

Summary:

1. Some introductory remarks and motivation
2. Terminology and concepts
3. The laws of thermodynamics

Quantum mechanics,
General relativity,

Details of structure:
particles, forces, fields

Thermodynamics

Things are made of “stuff”;
we reason in terms of
energy and entropy

Many thermodynamic concepts (e.g. energy) are strictly accurate at any scale, but some (e.g. temperature) become precise only in the **thermodynamic limit**, which is the limit of large systems (more precisely, those with a large number of internal degrees of freedom such as particle- or field- positions and momenta).

Some example questions

- Is it true that if you leave a tray of water out overnight, the water may freeze even though the air temperature and ground temperature never fell below zero?

- It is possible to boil water and burn paper by focussing sunlight with a lens. How about moonlight? Would a big enough lens work?

Yes / No / Don’t know / Don’t know and don’t care

Solving the world's energy needs (?)

Oceans: (total volume 1 billion cubic kilometres, mass 10^{21} kg)

coastal waters: 1 million km^3, mass 10^{18} kg

total Daily Energy Consumption of world: DEC = 10^{18} joules

water: 4000 joules of energy per kg per degree-Celcius change

So if we extract DEC from the coastal water, its temperature falls by just 1/4000 = 0.00025 °C .

Is this a good method?

Direction of physical processes

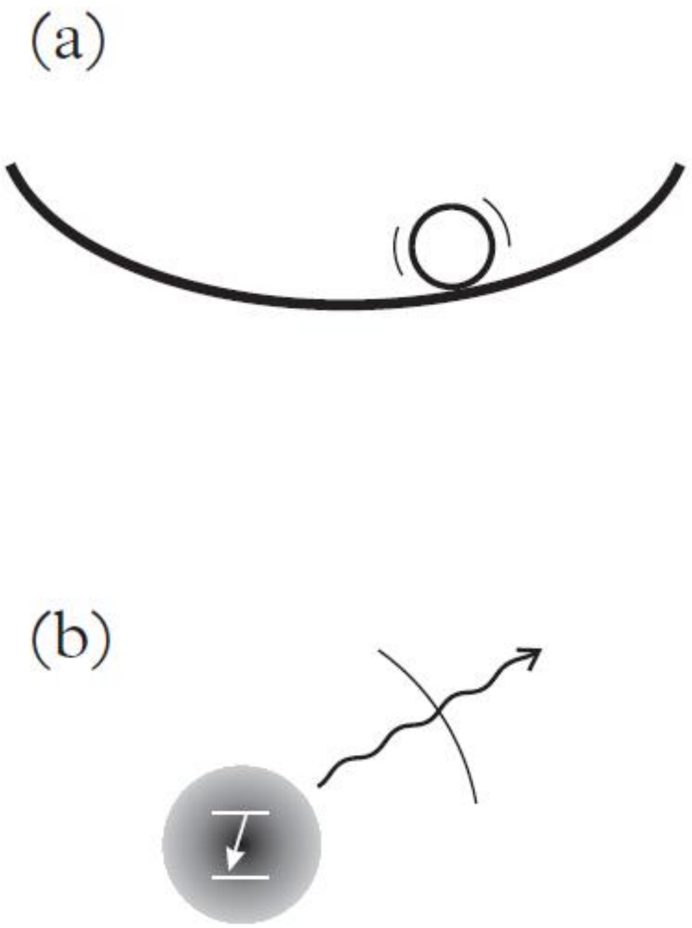


Fig. 3.1 *(a) A ball rolls in a curved bowl; (b) an atom emits a photon.*

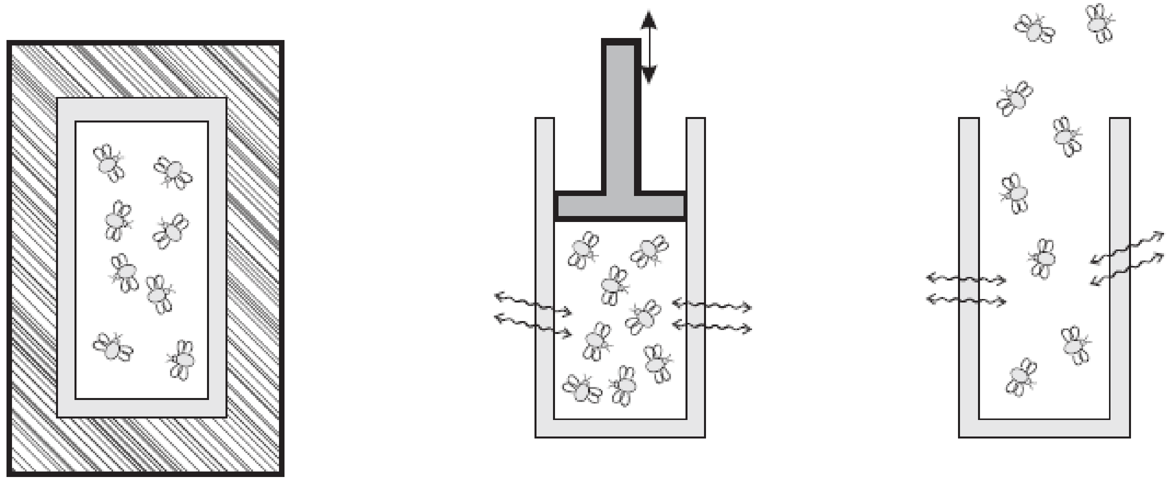
Why does the ball settle at the bottom of the bowl?
[Hint: it is not just about energy because there is strict energy conservation.]

We say the atom "spontaneously" emits and goes to the ground state.

OK, but the total energy (in atom plus field) has not changed. Why doesn't the atom also spontaneously absorb and go back to the excited state?

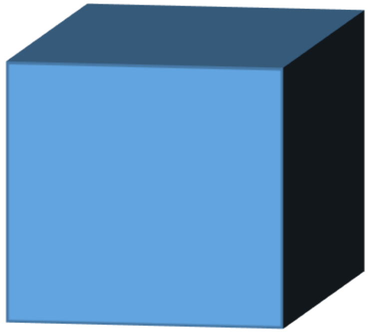
2. Terminology and concepts

Isolated **Closed** **Open**

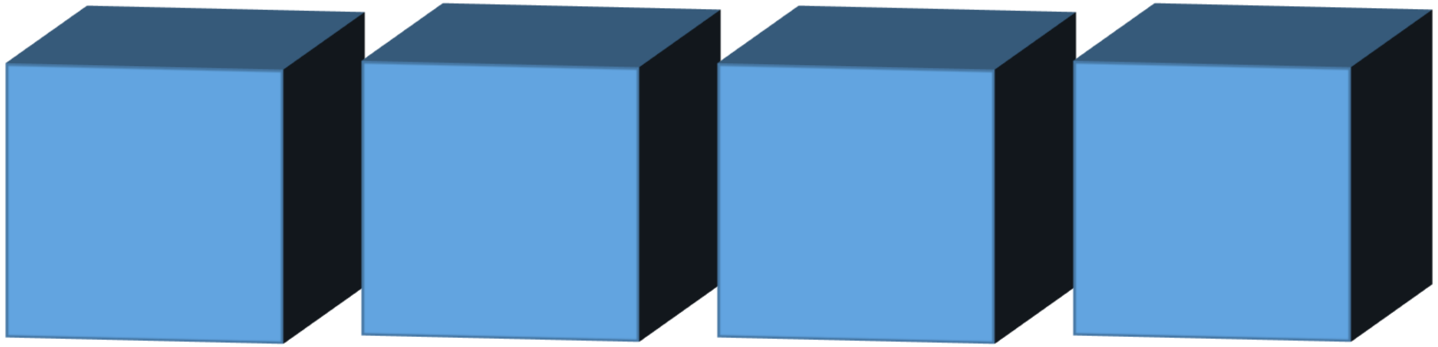


Thermodynamic system Type	Definition and examples		Conserved quantities
Isolated	Not influenced at all by other things		U, N, V
	e.g.	a gas in a rigid, insulated chamber	
		a swarm of bees in such a chamber	
Closed	Cannot exchange matter with surroundings		N = number of particles
	e.g.	a gas in a cylinder with movable piston	
		a swarm of bees in a thin flexible bag	
Open	Can exchange matter with surroundings		–
	e.g.	a pool of water in the open air	
		a swarm of bees flying freely	

Extensive, intensive



A system with given properties



Make N copies and join them together.

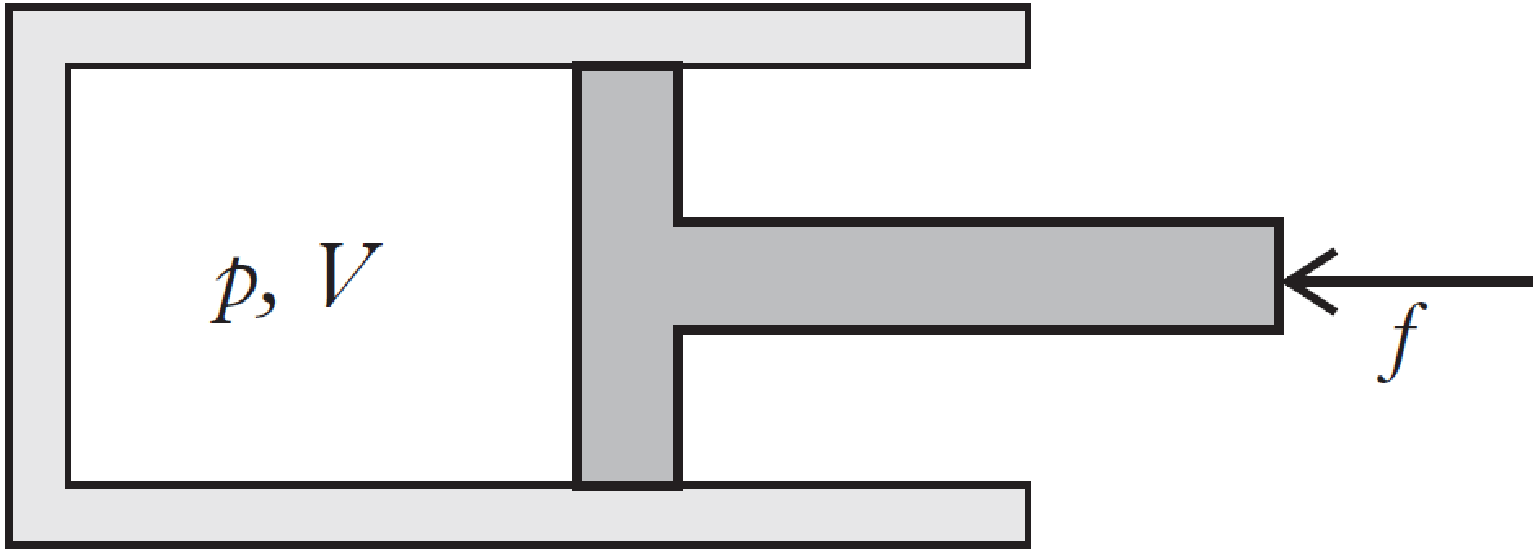
Property unchanged (e.g. pressure, temperature) → **intensive**

Increased by factor N (e.g. total energy, volume, mass) → **extensive**

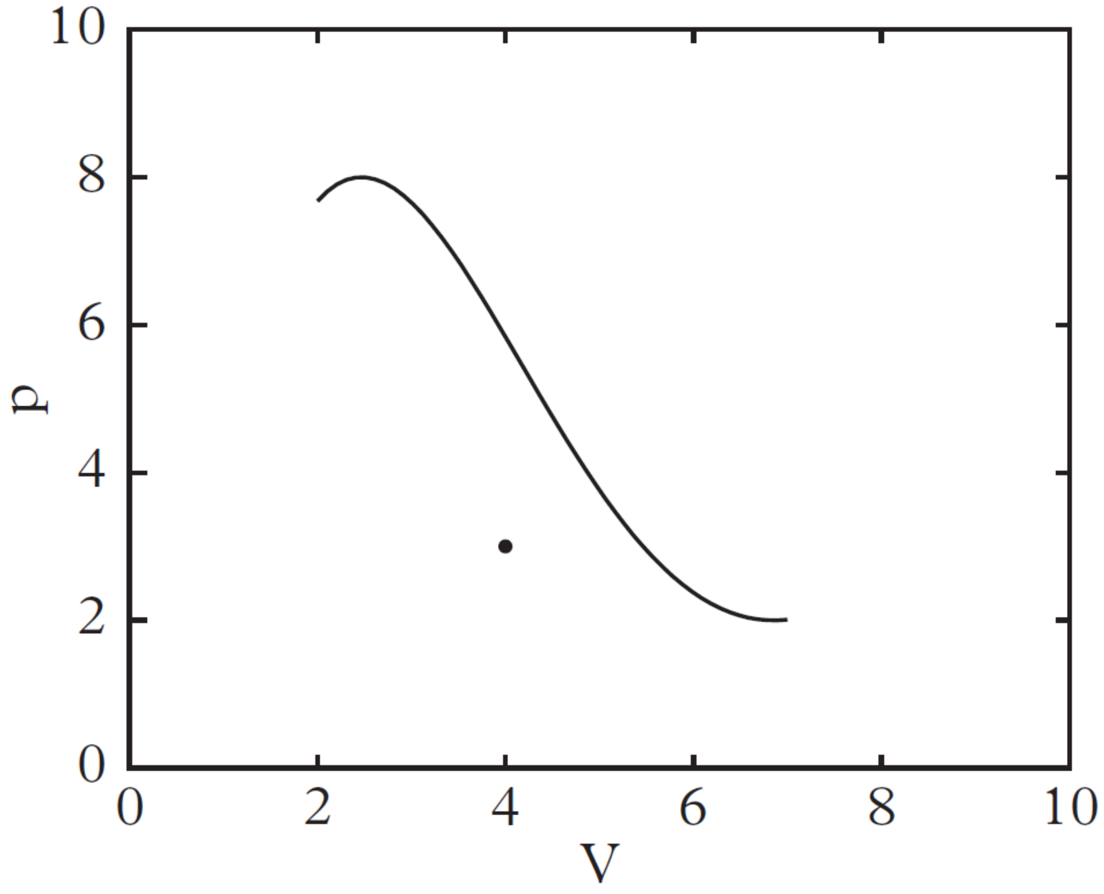
Changed by some other factor → neither intensive nor extensive

Simple compressible system:

- It can be compressed
- Just two quantities (e.g. pressure, volume) are sufficient to define the state



Indicator diagram



A point indicates one state of the system.

A line indicates a set of states of the system, e.g. the states which the system passed through during some change.

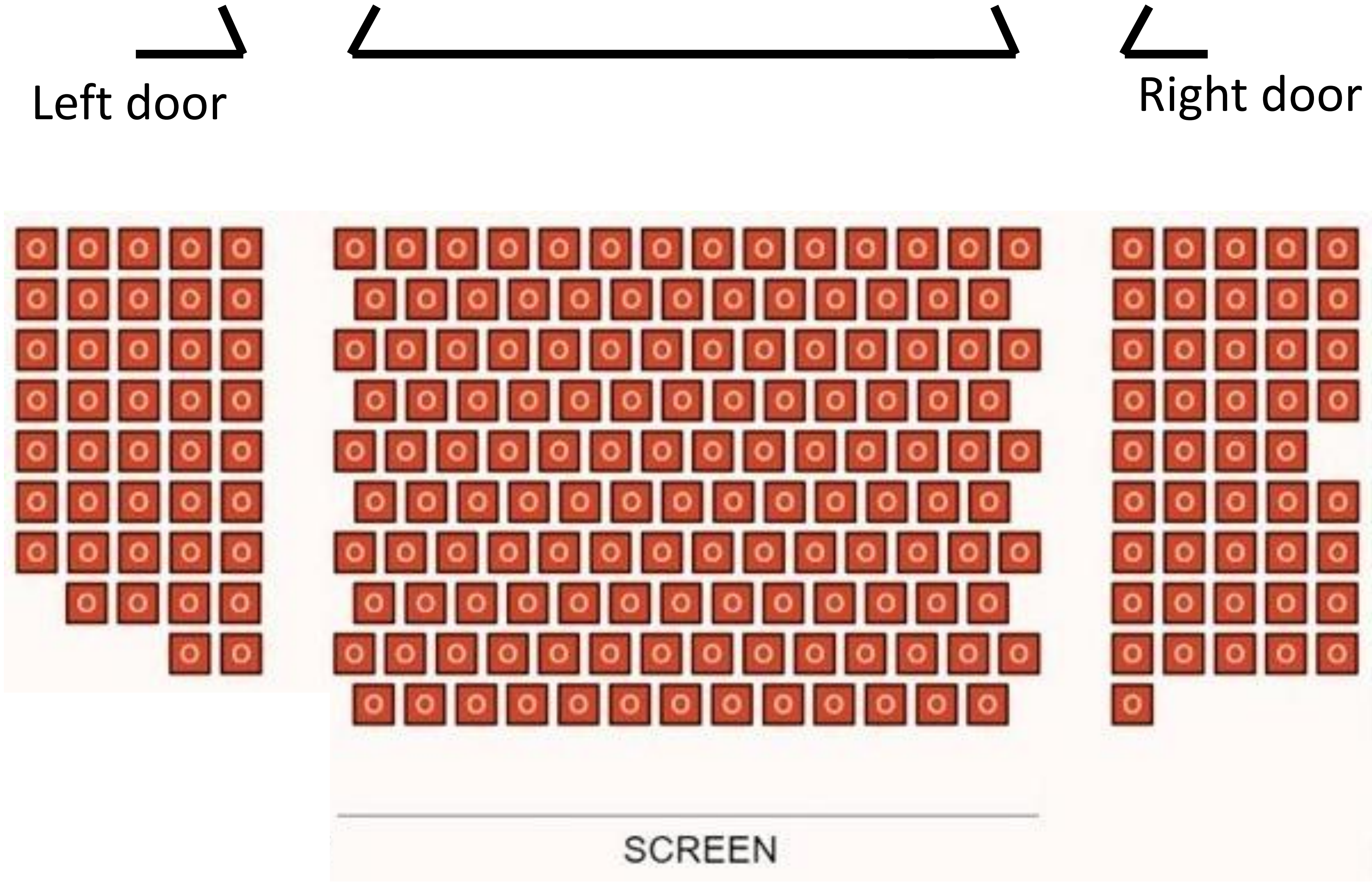
Function of state

A quantity F is a function of state if and only if the change ΔF, when a system passes between any given pair of states, depends only on the initial and final states, not on the path.

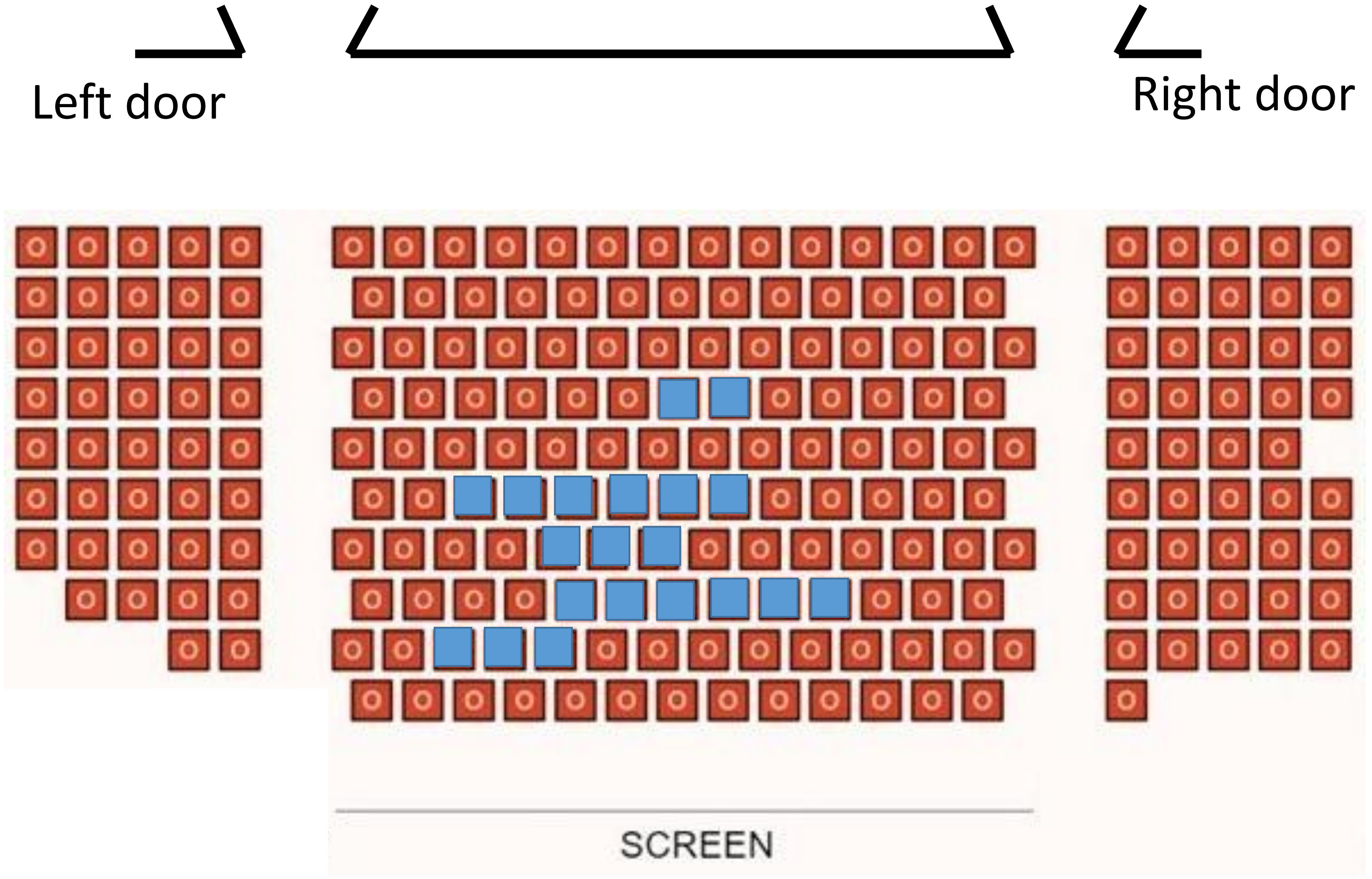
e.g. volume, pressure, temperature, heat capacity, compressibility, …

But not

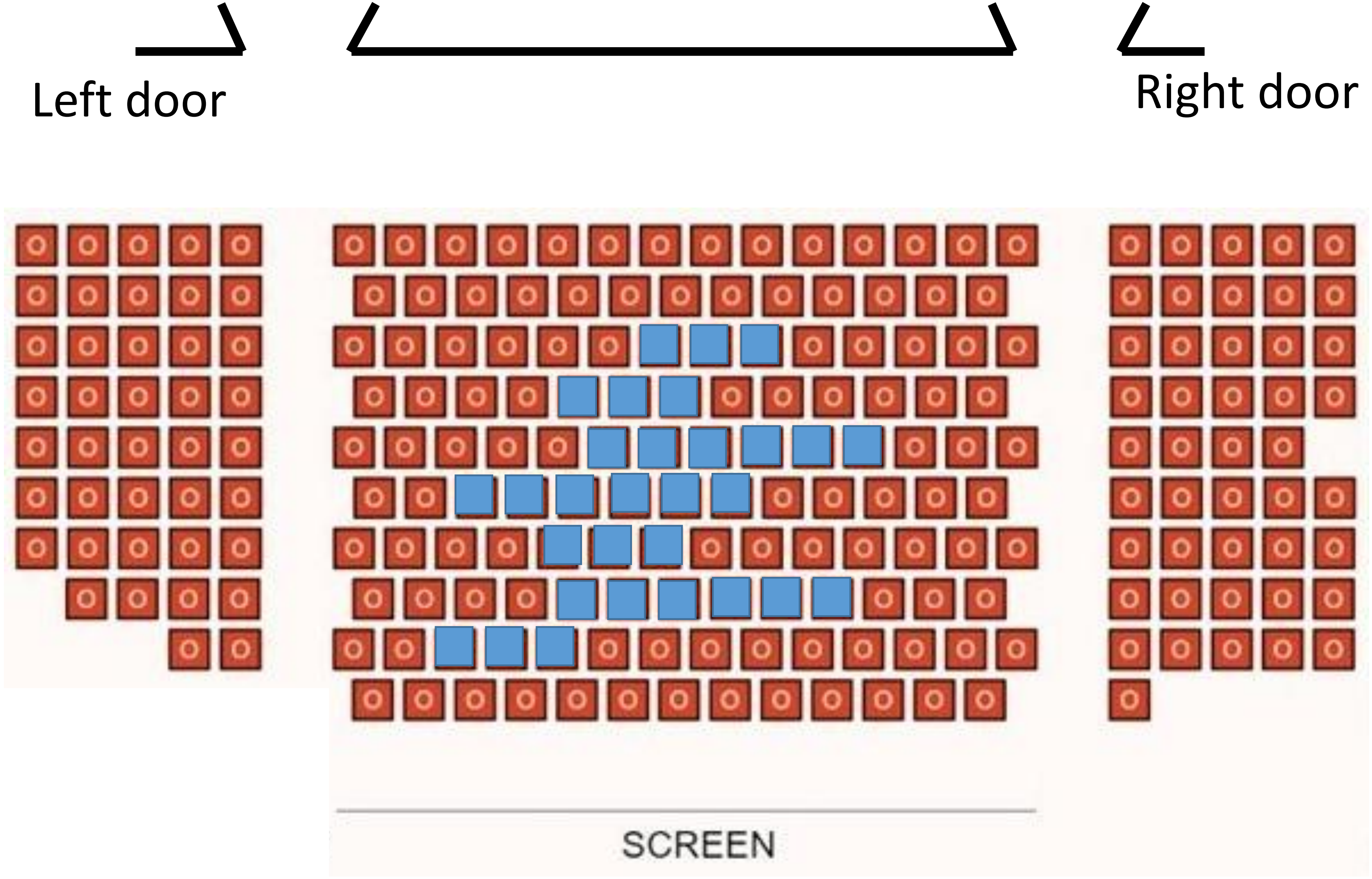
heat delivered, work done, time taken to perform a change, …



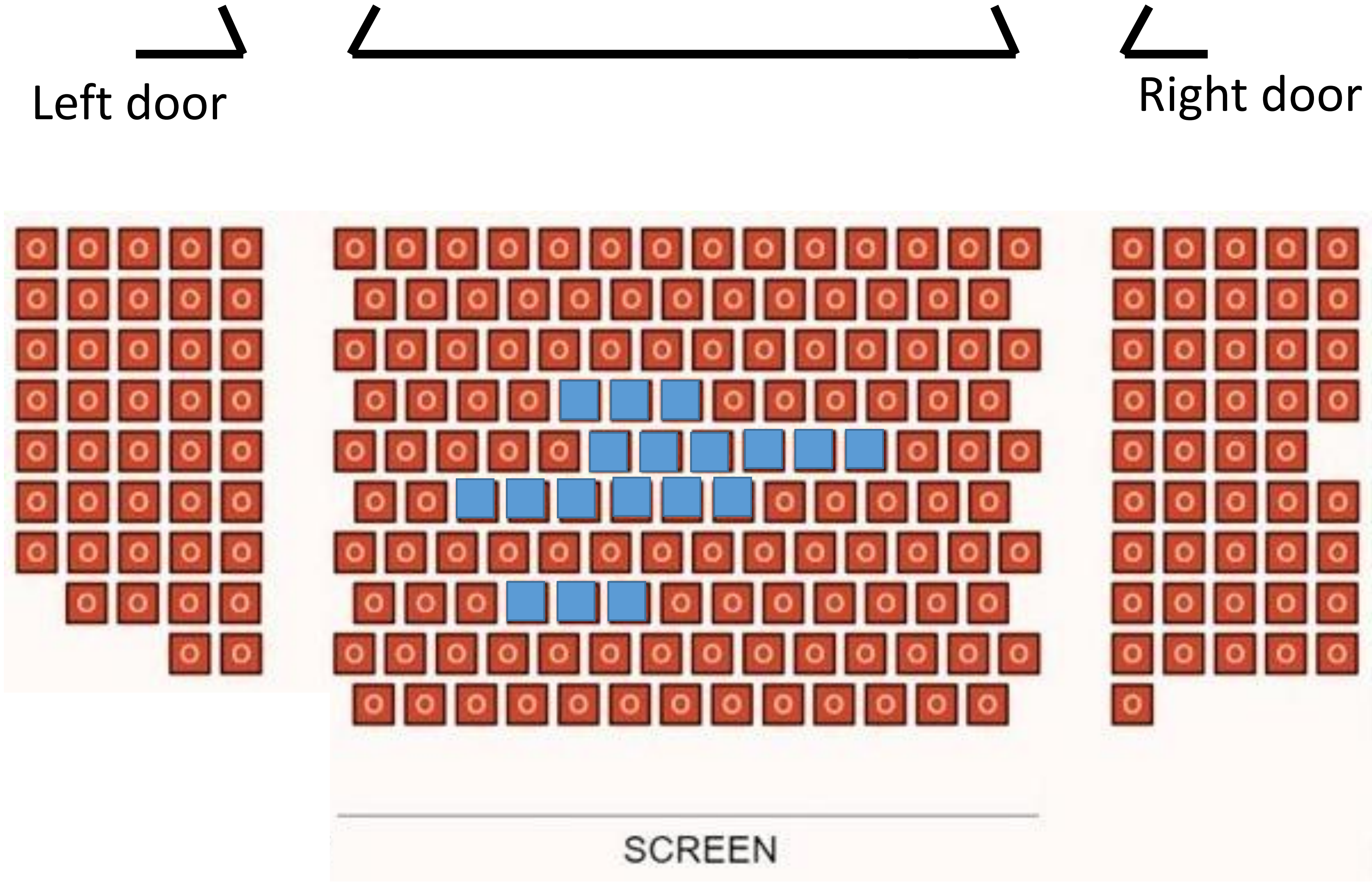
0 People in the cinema



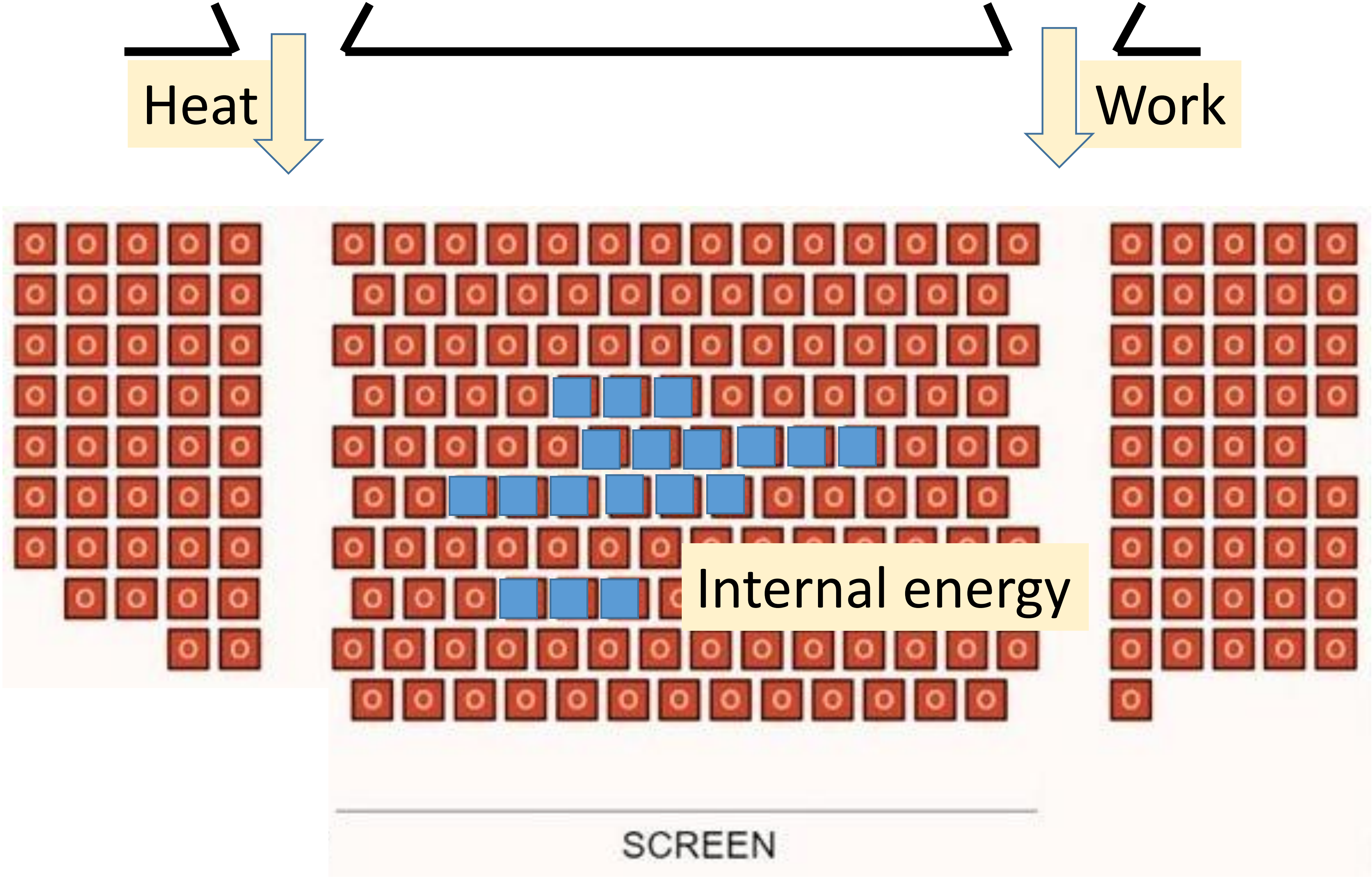
20 People in the cinema



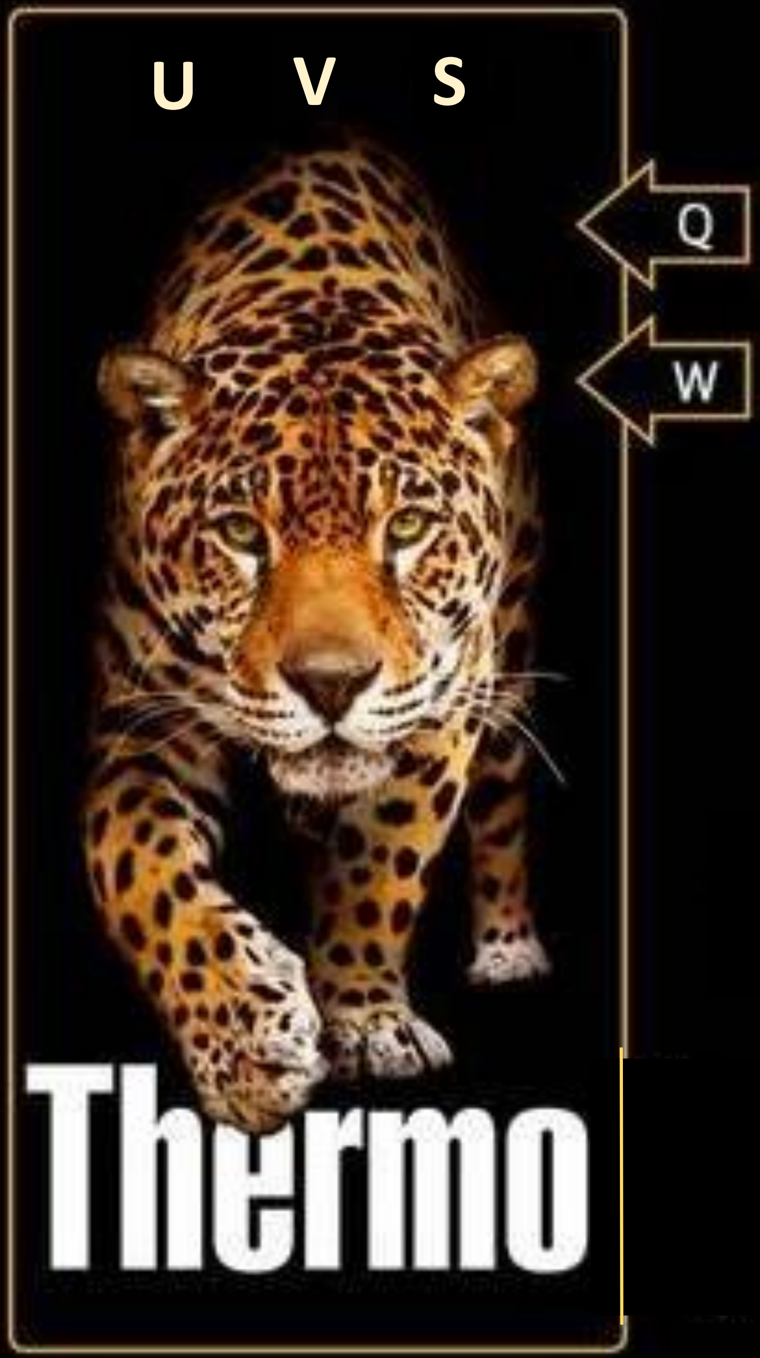
30 People in the cinema



18 People in the cinema



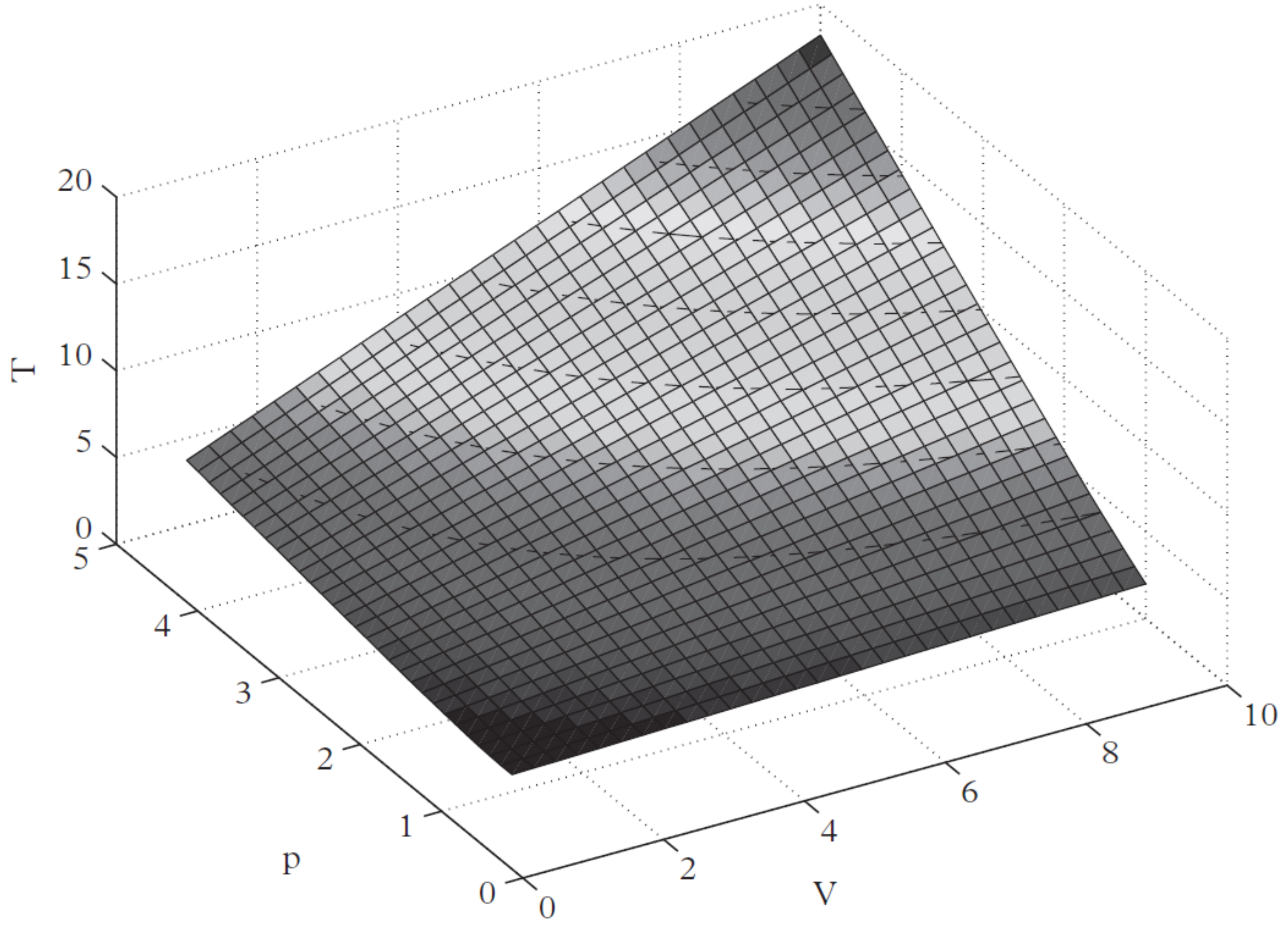
 People in the cinema


U
V
S
Q
W
Thermo

Function of state

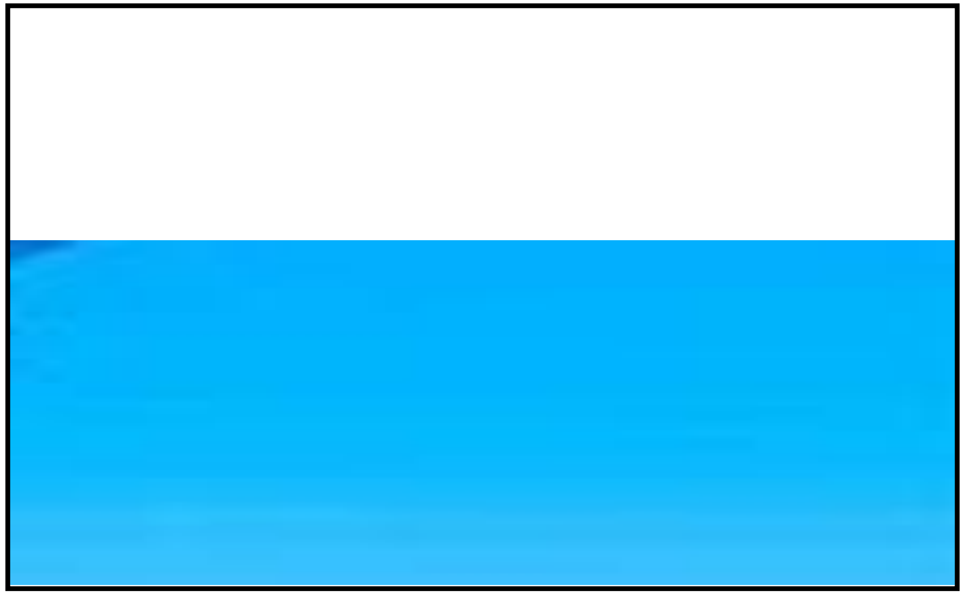
$$\text{state of system} \xrightarrow{\text{uniquely fixes}} \text{value of function of state}$$

Temperature is a function of state



Thermodynamic equilibrium:

the state which an undisturbed system tends to over time.

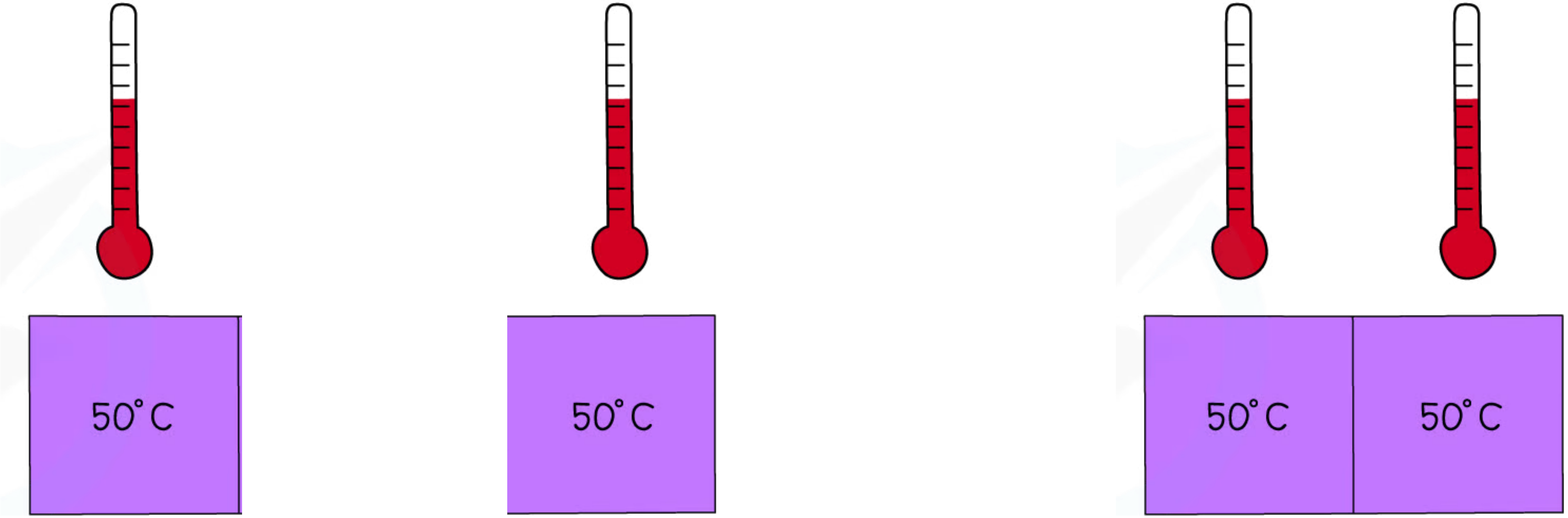


Thermal equilibrium: no heat flow

Mechanical equilibrium: no unbalanced forces

Chemical equilibrium: no movement of material between places or types

Thermal equilibrium and temperature



Temperature is defined as the property which indicates whether one body will be in thermal equilibrium with another. Two bodies which, if they were to be placed in thermal contact, would be found to be in thermal equilibrium with one another without any changes taking place, have, by definition, the same temperature.

Quasistatic process

A process which can be considered, to sufficient approximation, as a sequence of equilibrium states.

Reversible process (in the thermodynamic sense)

The direction of the process can be reversed by an infinitesimal change in the conditions (= there is no hysteresis);

Alternative definition (equivalent to the first):

The system can be returned to its initial state with no net change in the surroundings.

All reversible processes are quasistatic.

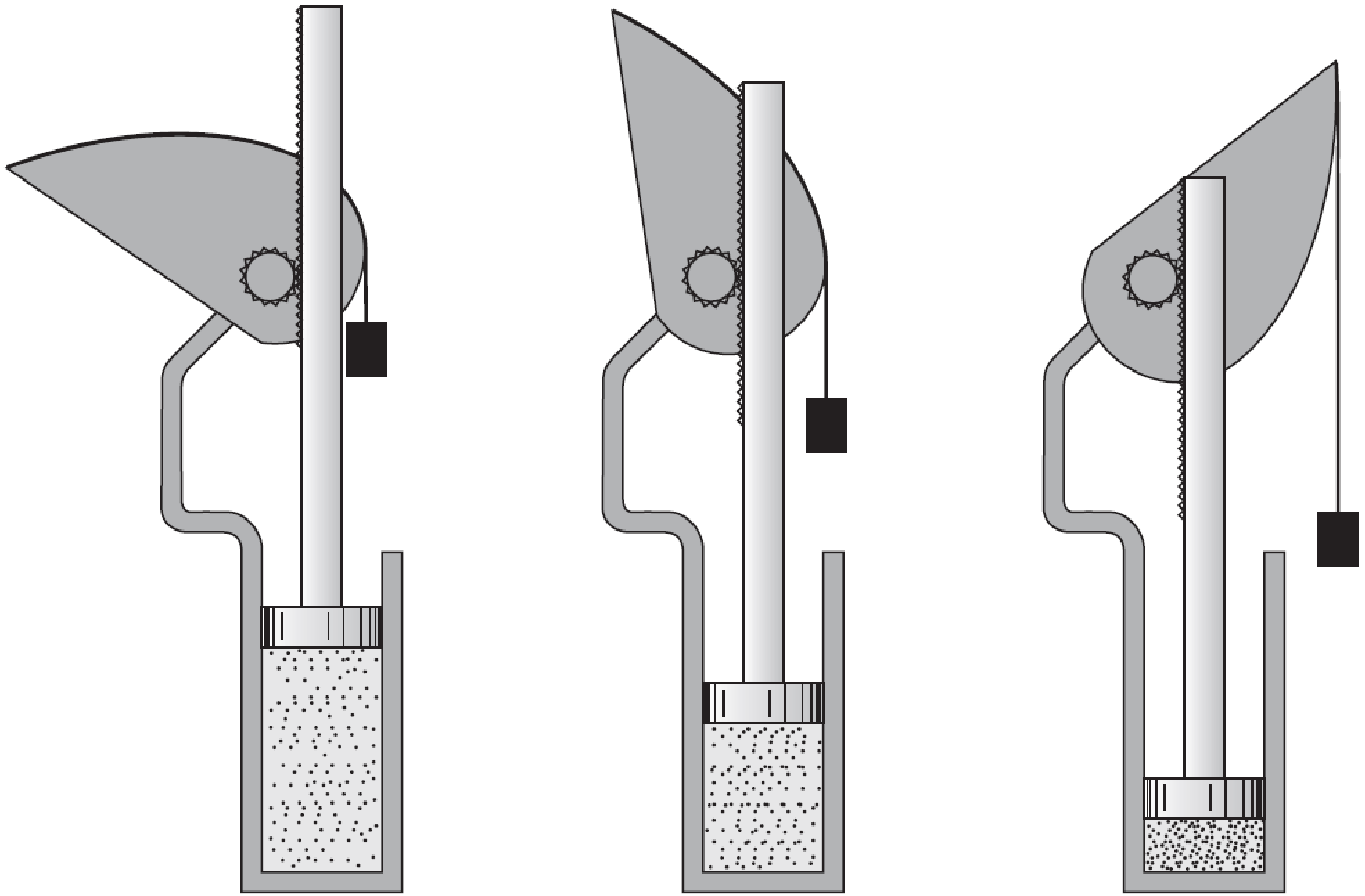
But not all quasistatic processes are reversible (e.g. toothpaste)

Example reversible process (assuming friction is negligible): slowly compressing or expanding a gas

This is **not** like a pendulum!

The system is in equilibrium at each stage, apart from a tiny imbalance which makes the process go in one direction or the other.

Note also: there CAN in principle be heat flow in or out of the system (this will depend on the conditions).



- Isothermal = at constant temperature
  (and, N.B., there is usually heat flow)
- Adiathermal = without heat flow
- Isentropic = reversible and adiathermal
- Adiabatic used to mean adiathermal; is now often taken to mean isentropic; that is how we will use it

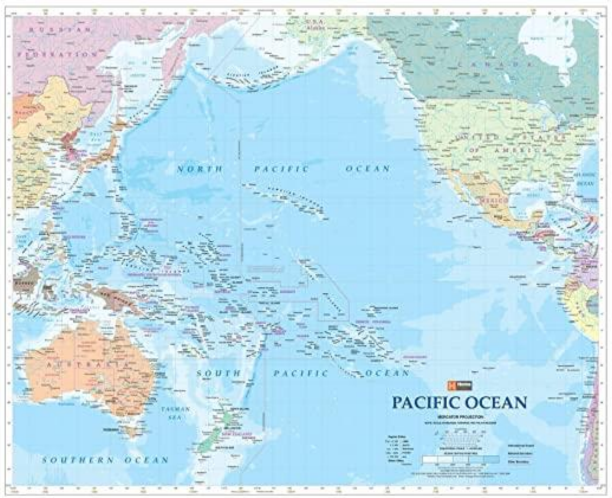
Name	Definition	Value for ideal gas
Isothermal compressibility	$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right\|_T$	$\frac{1}{p}$
Adiabatic compressibility	$\kappa_S = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right\|_S$	$\frac{1}{\gamma p}$
Isobaric expansivity	$\alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right\|_p$	$\frac{1}{T}$
Heat capacity at constant volume	$C_V = \frac{đQ_V}{dT}$	typically in the range 1.5–$3Nk_B$
Heat capacity at constant pressure	$C_p = \frac{đQ_p}{dT}$	$C_V + Nk_B$
Isothermal bulk modulus	$B_T \equiv 1/\kappa_T$	p
Adiabatic bulk modulus	$B_S \equiv 1/\kappa_S$	γp

Thermal reservoir
(a.k.a. "heat bath"):

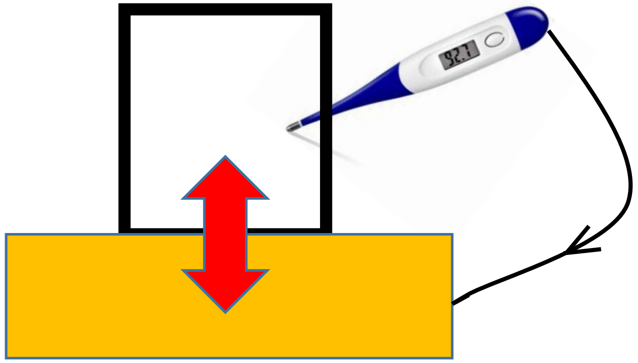
a body in/out of which arbitrary amounts of heat can be transferred without affecting the temperature.

e.g.

1. The Pacific Ocean (approximately)

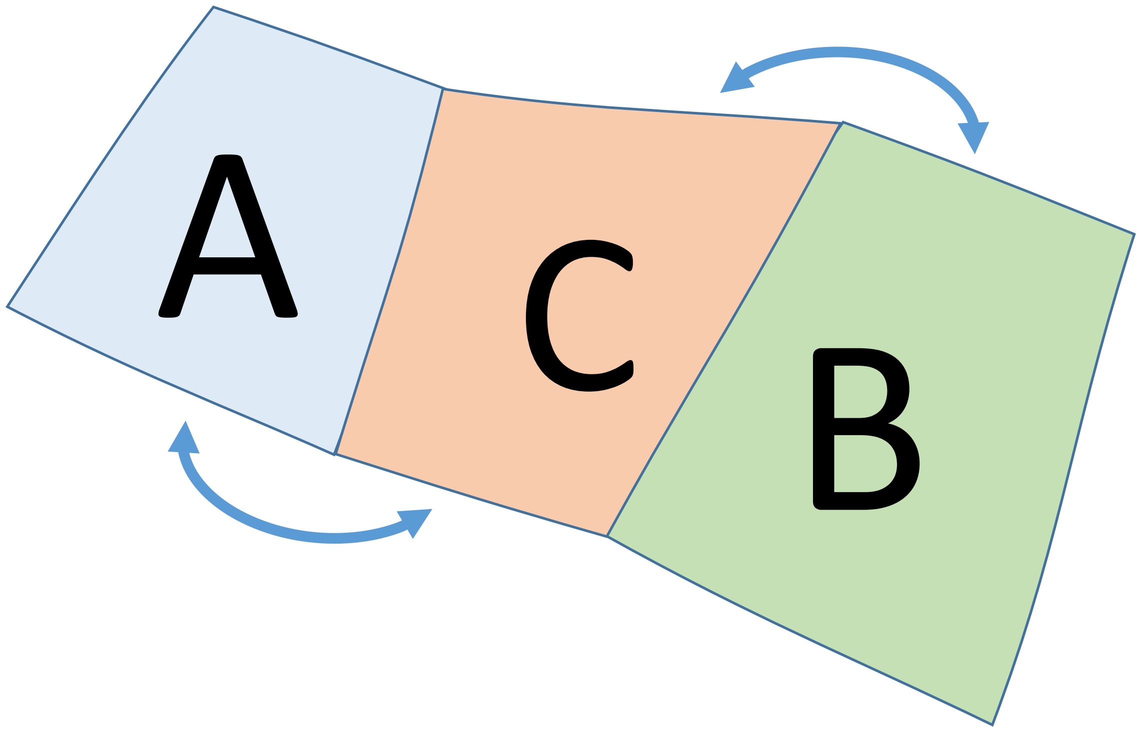


2. An apparatus with a thermostat (i.e. temperature sensor and heater/cooler in a feedback loop)



3. Introduction to three Laws of Thermodynamics

Zeroth law



If two bodies A and B are separately in a condition of thermal equilibrium with a third, then they must be in thermal equilibrium with one another.

First law

Energy is conserved.

The alternative statement is

The amount of work required to change the state of a thermally isolated system depends solely on the initial and final states.

The second law of thermodynamics

Clausius statement: No process is possible whose sole effect is the transfer of heat from a colder to a hotter body.

Kelvin statement: No process is possible whose sole effect is to extract heat from a single reservoir and convert it into an equivalent amount of work.

Carathéodory statement: In the neighbourhood of any state K of a thermally isolated system, there are states K' which are inaccessible from K.

Entropy statement: There exists an additive function of state known as the *equilibrium entropy* S, which can never decrease in a thermally isolated system.

Where we are heading

$$\begin{array}{lcl} \text{Zeroth law} & \rightarrow & T \text{ (temperature)} \\ \text{First law} & \rightarrow & U \text{ (energy)} \\ \text{Second law} & \rightarrow & S \text{ (entropy)} \end{array}$$

Ratio of heats for a reversible engine:
(this is how a temperature scale is defined)

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

The fundamental relation:

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N$$