Thermodynamics

builds on *Kinetic theory and the behaviour of gases*

Learning outcomes

- relate the Zeroth law of thermodynamics to real thermometers
- explain the relationship between the internal energy of an isolated system, energy transferred as work, and heat transferred (the 1st law of thermodynamics)
- use the 2nd law of thermodynamics to explain heat engines, heat pumps and refrigerators
- state the basic assumptions of the kinetic theory of gases
- derive and use the kinetic theory equation $pV = \frac{1}{3} Nm < v^2 >$
- recall the ideal gas equations $pV = NkT$ and $pV = nRT$, using them to solve quantitative problems
- recall the mean E_k of a gas molecule, $E = \frac{3}{2} kT$
- use dimensional analysis to create and check equations

Teaching challenges

- It is easy to lose sight of the nature of thermodynamics as a ‘big picture’ view of energy, by getting bogged down in detail.
- Understanding kinetic theory assumptions at molecular level can pose difficulties.
- Chemistry students are happy with $pV = nRT$ but need help with relevance of $pV = NkT$

Thermodynamics

Originally developed as a 19thC theory of steam engines, thermo (heat) dynamics (power or capacity) i.e. power created by heat. Sadi Carnot (1824) *Reflections on the Motive Power of Fire.*

Scope of thermodynamics is now ‘almost everything’:

- heat engines, heat pumps and refrigerators (cyclic processes)
- the arrow of time
- chemistry, incl biochemistry: photosynthesis, haemoglobin, ATP
- hurricanes, plate tectonics, magnetisation & demagnetisation
- life processes e.g. ecosystems

Heat engine

device which extracts work as thermal energy flows from a hot reservoir to a cold reservoir.

Categories include

- external combustion engines

  (e.g. steam or Stirling engine)

- internal combustion engine

  (e.g. petrol or diesel engine, jet engine)

Four laws

Zeroth: [an afterthought]: temperature of a system

First: the conservation of energy - internal energy of a system.

Second: why things happen as they do - entropy of a system

Third: Absolute Zero is unattainable, negative temperatures

Key terms

system - part of the universe under study (open or closed)

boundary - what separates a system from its environment (surroundings) e.g. piston head in an engine

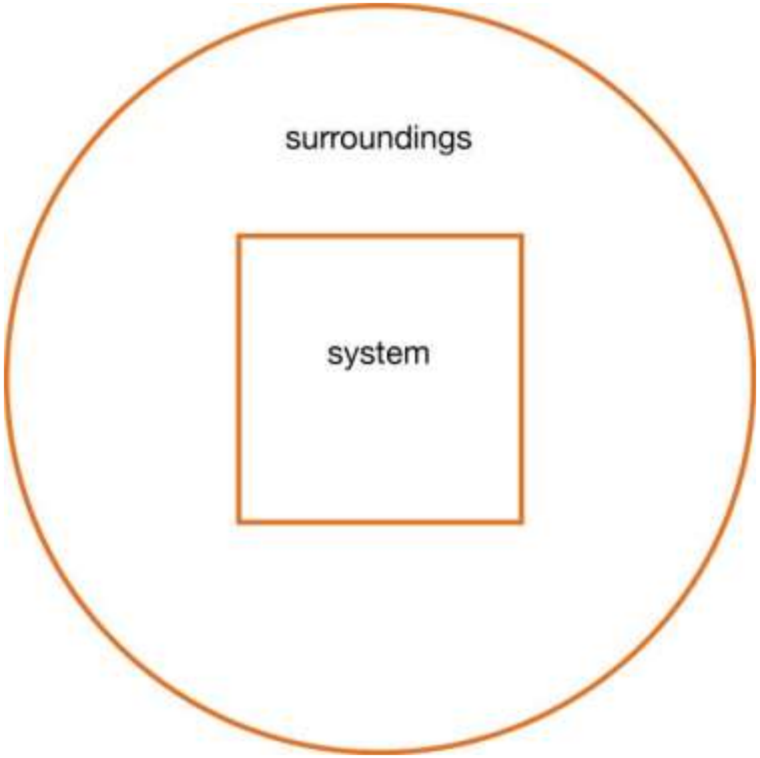
states & state variables

- fluid (pressure, volume, temperature)
- surface (tension, area)
- black-body radiation (energy density, radiation pressure)
- electrical contact (potential, current)

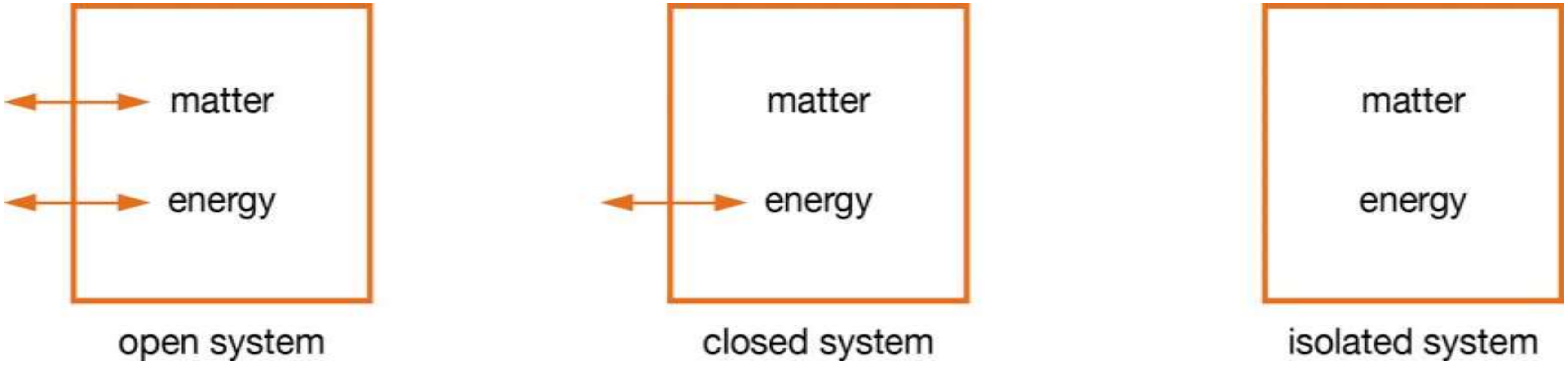
equilibrium, non-equilibrium

work, heat, adiabatic & isothermal changes

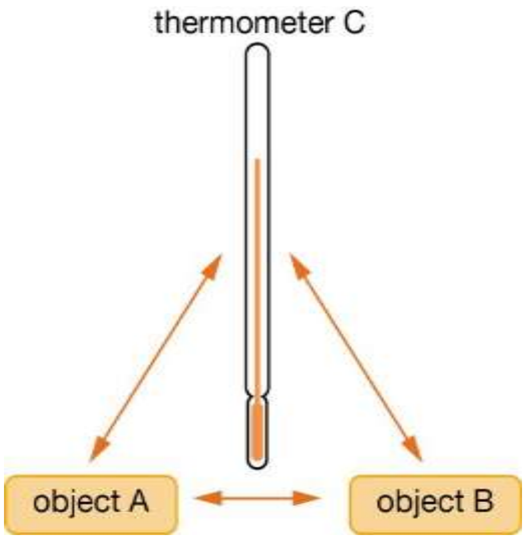
System and surroundings



Different types of system



Zeroth law



If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C will be in thermal equilibrium with A.

In other words, all three systems have the same 'temperature'.

Rigid walls that permit a system to change its state (by thermal transfer) are called 'diathermic'.
Saucepans are diathermic vessels.

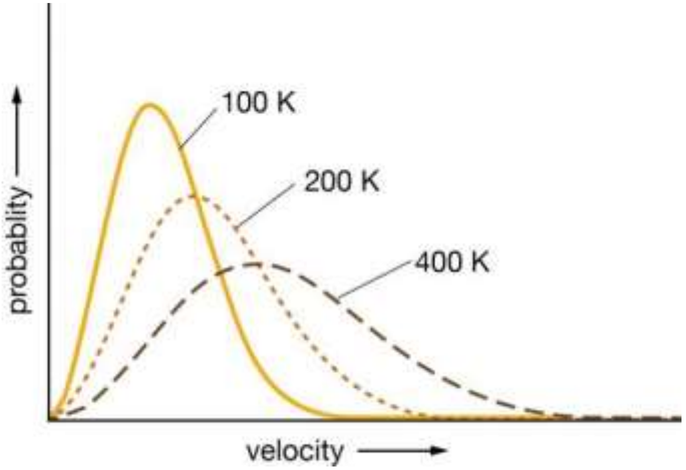
Walls that do NOT permit such changes (by thermal transfer) are called 'adiabatic'.
A vacuum flask is adiabatic.

Temperature scales: Fahrenheit, Celsius, Kelvin.

Zeroth law - particle level

Statistical thermodynamics, developed by Ludwig Boltzmann (1844-1906), describes what happens at atomic or molecular level.

Molecules in a gas have quantised energy levels. In equilibrium, molecules are distributed over a range of allowed states.



Average E_k of a molecule $= \frac{3}{2}kT$

Boltzmann constant,

$k = 1.38\times10^{-23}\,\mathrm{JK}^{-1}$

smaller mass => v larger

Work

Work involves motion against an opposing force, *F*.

$$W = F \cdot s = Fs\cos\theta$$

Any system has an ability to do work. The capacity to do work is called energy.

e.g. churn the contents of a vacuum flask (closed system) with paddles driven by a falling weight.

The same amount of work, however it is performed, always brings about the same change of state of the system.

It is therefore possible to define the internal energy, *U*, for each state of a system. Work required = *U* (final) – *U* (initial)

First law

If the contents of the flask had been churned in a un-insulated vessel, the amount of work necessary to raise its temperature would have been greater.

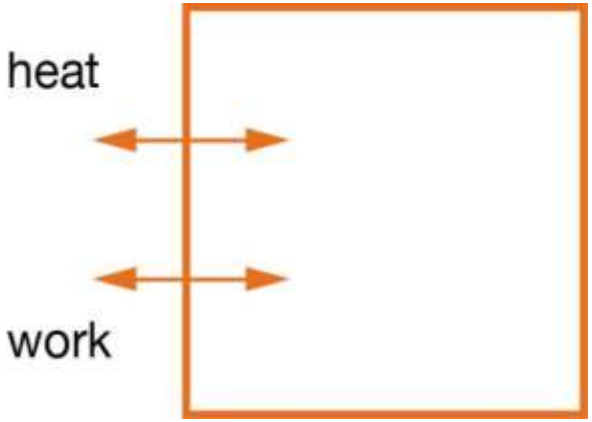
The transfer of energy from a system to its surroundings, as a result of a temperature difference, is called **heat** (thermal transfer).

The change in internal energy, ΔU, of a system is the sum of the work done **on** the system, ΔW, and heat, ΔQ, transferred **to** it. $\Delta U = \Delta W + \Delta Q$

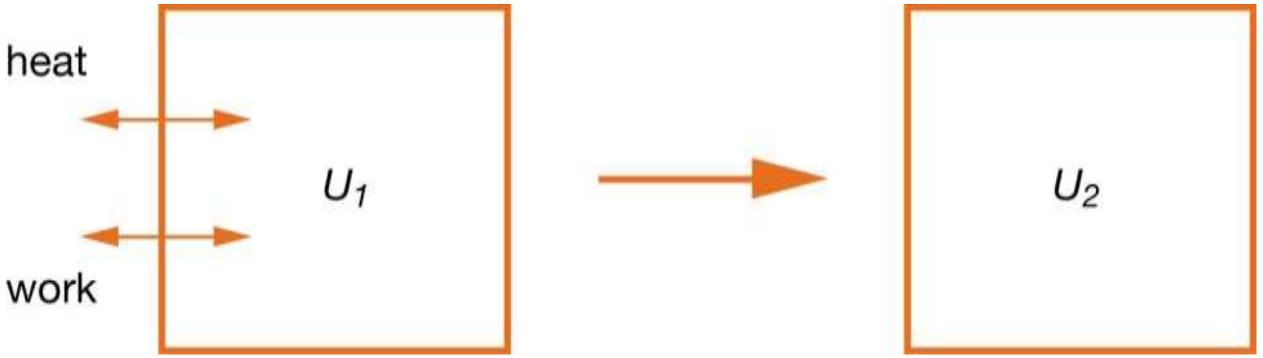
Adiabatic change: $\Delta U = \Delta W$

Heat and work

The two ways in which energy can be transferred into or out of a system – heat and work



Heat and work



The total energy of a system is called its internal energy (*U*) – it changes when energy is transferred into or out of the system.

ΔW, ΔQ, ΔU at molecular level

Work: transfer of energy that makes use of the uniform motion of atoms in the surroundings.

Heat: transfer of energy that makes use of random motion of atoms in the surroundings.

Internal energy: kinetic energy + potential energy of the system’s constituent atoms.

Two related terms

Enthalpy, *H,* heat generated in combustion

$\Delta H = \Delta U + pV$

where p is the pressure of the system, V its volume, pV work done by the product gases.

With fuel in an an open container, no work is done by the product gases, so $\Delta H = \Delta U$. Unit kJ mol^{-1}

Heat capacity. Plot internal energy v temperature: slope gives heat capacity (amount of energy per unit temperature rise).

$\Delta E = mc\Delta T$

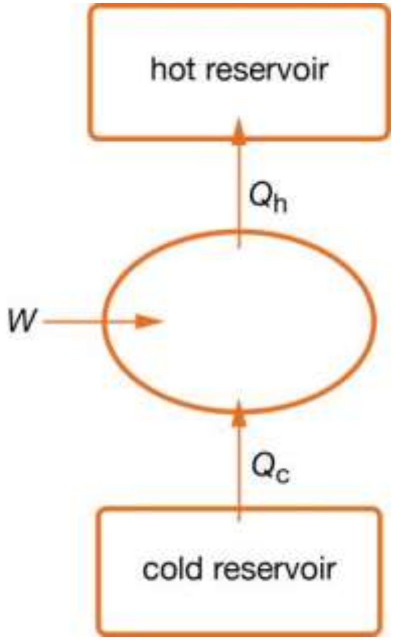
For gases, specify c_V (constant volume) or c_P (constant pressure). At constant pressure, a system does work in expanding.

Second law

Can be stated various ways:

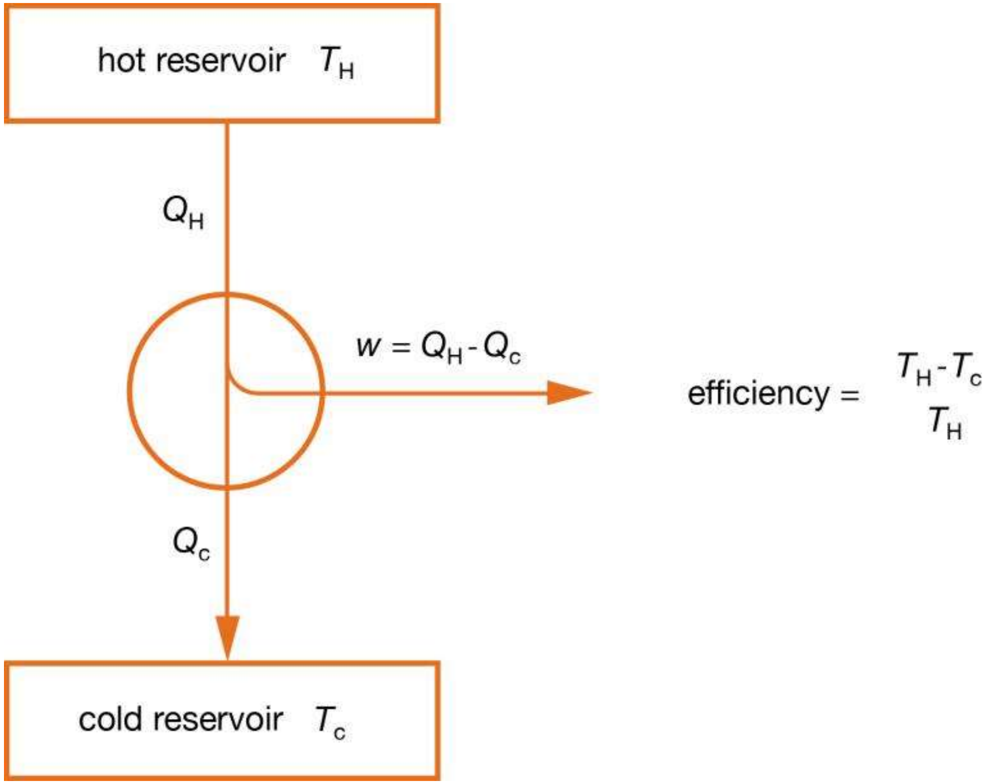
(Kelvin): ‘No cyclic process is possible in which heat is taken from a hot source and converted completely into work.’ (e.g. engine)

(Clausius): ‘Heat cannot pass from a body at low temperature to one at higher temperature without work being done.’ (e.g. refrigerator)



Efficiency

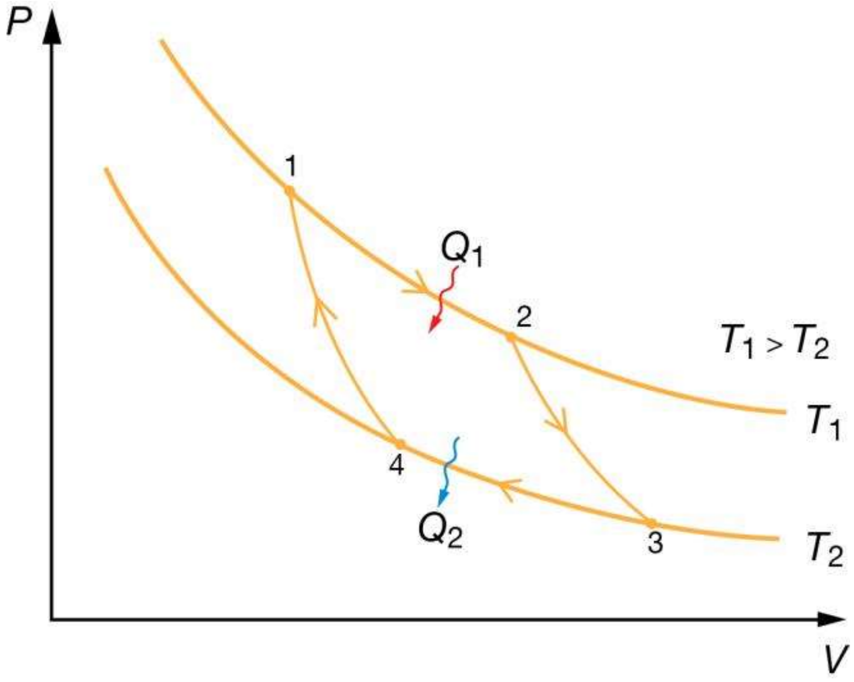
The efficiency of a
Heat engine
depends
on the
temperatures
of the hot and cold
reservoirs (Carnot)



Carnot cycle

proposed by Carnot in 1824.

- the most efficient cycle for an engine, converting a given amount of thermal energy into work
- the most efficient cycle for a refrigerator, creating a temperature difference by doing a given amount of work.



Thermodynamic *T* scale

Kelvin realised that efficiency of a heat engine, ε, could be used to define a temperature scale.

$$\varepsilon = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} = 1 - \frac{T_{cold}}{T_{\text{hot}}}$$

$$T_{\text{cold}} = (1 - \varepsilon) T_{\text{hot}}$$

Needs one fixed point (triple point of water 273.16 K), and measurement of mechanical work done (gives ε).

Entropy of a system, *S*

S is a measure of the disorder of its matter and energy.

A gas has high entropy, crystal has low entropy.

$$\Delta S = \frac{\Delta Q}{T}$$

Second law (again): ‘The entropy of the universe increases during any spontaneous change.’

Entropy increases in the cold sink of a heat engine (waste heat).

Time is irreversible (thermodynamic ‘arrow of time’).

Schrodinger (1943) *What is life?*

‘Life’s ability to maintain itself, expand, and reproduce in a world subject to the second law is a paradox explained by the fact that live beings, open to and dependent upon energy via light or chemical reactions, release heat and other thermodynamic wastes into their environment. … Their high organisation and low entropy is made up for by pollution, heat, and entropic export to their surroundings.’ E Schneider & D Sagan (2005)

Into the Cool: Energy flow, thermodynamics and life

‘Metabolism’ [*Greek*: meta, after + bole, change]

Maintaining life

‘Gradients can be of pressure, chemical concentration, temperature or any work-related potential. As gradients move systems away from equilibrium, the systems shift states so as to oppose the applied gradients. In general, as systems move away from equilibrium, increasingly more energy is needed to keep them there.’

E Schneider & D Sagan (2005)

Into the Cool: Energy flow, thermodynamics and life

Free energy

in a chemical reaction can be described as

EITHER

$-T\Delta S$, where T is the thermodynamic temperature and ΔS is the total entropy change.

OR

the maximum amount of work that can be extracted from the reaction.

The basis of life on Earth is the free energy of captured photons from the Sun. ‘Fuels’ are sources of free energy, which of course can be used up.

Industry

‘… because of industrial nitrogen fixation to make fertilisers, a contemporary person living in Europe or the United States can expect about 40% of the atoms in her body to have seen the inside of factories at some point; in China the figure is closer to 70%.’

E Schneider & D Sagan (2005)

Into the Cool: Energy flow, thermodynamics and life

An ideal gas (kinetic theory)

- huge number of point molecules (occupy negligible volume) in continual random motion (and so ‘kinetic’)
- colliding elastically with each other and with container walls
- no forces between the molecules, except in collision
- time in collisions very small compared to time between collisions
- distance travelled between collisions (‘mean free path’) depends on gas density
- average speed of molecules depends on gas temperature
- in a gas composed of different molecules, the average molecular E_k is the same for all, so those with larger mass have smaller speed

Ideal gas equations

refer to AP OHTs

Thinking about collisions

How kinetic theory fits together

Boltzmann constant and gas molecules

The kinetic energy of a single particle

Practice questions

- TAP *Student questions including efficiency*

- AP *Thermal changes*

- AP *The ideal gas equation*