Foundations of Physics 1

Thermodynamics

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Lecture 1

See Young & Freedman Chapters 17–20
And of course, all of this will be on DUO

1.1   Learning Aims

➤ Describe definition of 'Temperature'
➤ Define 'Thermal Equilibrium' (**TE**)
➤ State Zeroth Law of Thermodynamics
➤ Importance of gas thermodynamics
➤ Absolute temperature scale (Kelvin)

1.2   Temperature

"Measure of degree of 'hotness' of a system". Measured by temperature-dependent changes in second substance i.e. thermometer. These use **TE** to work:

➤ Liquid-in-tube
➤ Gas in fixed volume
➤ Bi-metallic strip (bends when heated as the two metals have different expansion rates)
➤ IR emissions

Two systems are in **TE** with each other when they have the same temperature

1.3   Zeroth Law

"*For two systems that are each in **TE** with a third system independently, the two are in **TE** with each other*". This will aid with calculations later on. Use 273.15 as converter for $\mathbf{K} \leftrightarrow^\circ C$:

$$\frac{T_2}{T_1} = \frac{p_2}{p_1} \tag{1.1}$$

At 0 K, system energy is minimum.

Lecture 2

2.1 Recap

- ➤ **TE** is same temperature in different systems
- ➤ Zeroth Law of Thermodynamics
- ➤ Thermometers converge at -273.15°C, 0 K

2.2 Learning Aims

- ➤ Nature of heat
- ➤ Define specific heats - mass & molar
- ➤ Role of heat in phase changes
- ➤ Define Latent Heats
- ➤ Phase Changes
- ➤ Colorimetry calculations

Temperature is a property of materials; heat is not – it is a type of energy transfer between bodies at different temperatures i.e. to reach **TE**, Heat must be energy. Hence, units of heat are Joules (J)

2.3 Specific Heat Capacities

How much heat energy, Q, needs to be transmitted to a material to raise temperature by a certain amount?

Experimentally, heat is related to mass, m, & change in time, ΔT:

$$Q = mc\Delta T \quad \text{(K or C, not F).} \tag{2.1}$$

c is mass specific heat capacity – energy required to change temperature of 1 kg of material by 1 K

$$Q = nC\Delta T, \text{ for using moles instead of mass} \tag{2.2}$$

C is molar specific heat capacity

Heat capacities are measured:

- ➤ At constant pressure for solids
- ➤ At constant volume for gases

Dulong & Petit Rule – The molar heat capacity of most metals is approx. 25 J mol^{-1} K^{-1}

2.4 Phase Transition

Addition or removal of heat to/from a system can change its phase

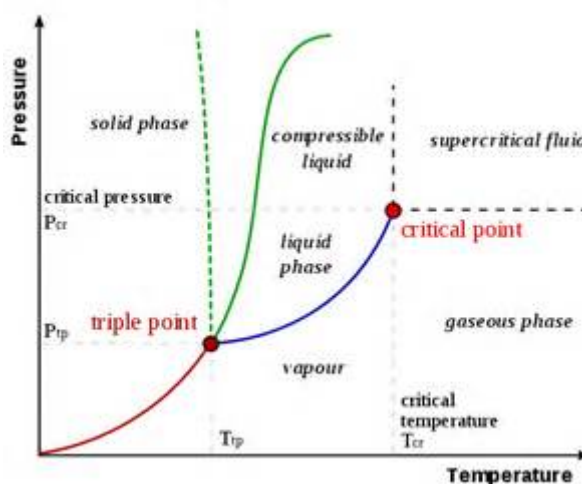The amount of heat energy required to change the phase of 1 kg of material depends on the latent heat, L

$$Q = \pm mL \tag{2.3}$$

2.5 Phases of matter

Solid High pressure, low temperature

Liquid High pressure, high temperature

Vapour/gas Low pressure, high temperature

➤ At the phase boundaries, both states of matter can exist in phase equilibrium.
➤ All three phases co-exist at the triple point.
➤ Beyond the critical point, you cannot define between liquid and gas.
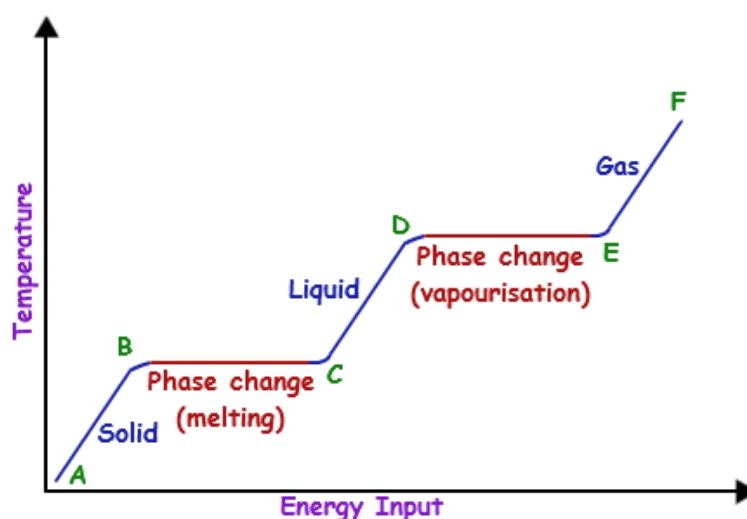➤ Dotted green line is for water.

2.6 Phase Changes

Phase changes occur at a unique temperature for set pressure, and use the latent heat specific to each transition:

Between solid & liquid: latent heat of fusion

Between liquid & gas: latent heat of vaporisation

Between solid & gas: latent heat of sublimation

2.7 Calorimetry

➤ Calculations of energy transferred as heat to change temperature & heat
➤ Heat is conserved for closed systems
➤ Chemical reactions analogous to phase changes e.g. heat of combustion

2.8   Applications of Phase Changes

➤ Steam-heating systems – Victorian era stuff
➤ Temperature control
➤ Perspiration – sweat cooling

Lecture 3

3.1 Recap

➤ Heat: energy transferred between bodies at different temperatures.
➤ Specific heat capacity: J mol^{-1} K^{-1} / J kg^{-1} K^{-1}
➤ Phase changes and calorimetry

3.2 Learning Aims

➤ Thermal Expansion using original dimensions and temp. change of material
➤ Define thermal stress in terms of elastic properties
➤ Characteristics of 3 heat transfer mechanisms
➤ Define heat current in terms of thermal conductivity
➤ Stefan-Boltzmann Law – Black Bodies

3.3 Thermal Expansion

Used in thermometry. Implications for engineering – rigid structures that are heated.

Linear Thermal Expansion:
➤ Original rod length, L_0
➤ Small change in temp, $\Delta T \to$ change in length, ΔL

$$\Delta L = \alpha L_0 \Delta T \tag{3.1}$$

α is the linear expansion co-efficient with units K^{-1}.

Volume Expansion:
For small temperature, ΔT, we have change ΔV in volume:

$$\Delta V = \beta V_0 \Delta T \tag{3.2}$$

β is the co-efficient of volume expansion, K^{-1}.

Relating α and β:
For a cube of dimension, L, with V = L^3. Consider infinitesimal changes dV, dL, & dT:

$$dV = \frac{dV}{dL}dL = 3L^2 \ dL \tag{3.3}$$

For initial cube dimensions, L_0 and V_0, with $V_0 = L_0^3$:

$$dL = \alpha L_0 dT \tag{3.4}$$
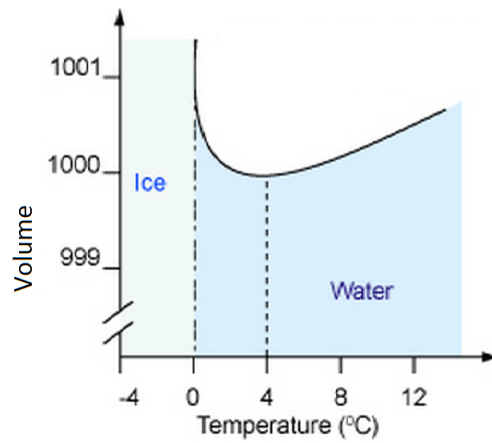$$dV = 3L^2 \alpha L_0 dT = 3\alpha V_0 dT \tag{3.5}$$
$$\Delta V = \beta V_0 \Delta T \tag{3.6}$$
$$\beta = 3\alpha \tag{3.7}$$

3.4 Thermal Expansion of Water

Expansion of water is approximately linear to temperature macroscopically.

Water contracts as it cools down to 4°C, then expands. This explains why ponds freeze from the top which was critical for evolution.

3.5 Thermally-Induced Stress

Consider a material held in position such that the dimensions can't be changed. Now change temperature → stress is created

$$\text{Stress} = \frac{F}{A} \tag{3.8}$$

Young's modulus, Y – Elastic behaviour of material:

$$Y = \frac{F}{A}\frac{L_0}{\Delta L} - \text{ratio of stress/strain} \tag{3.9}$$

For L_0, $(\frac{\Delta L}{L_0})_{thermal} = \alpha\Delta T$. When expansion is prevented: Using Young's modulus

$$\left(\frac{\Delta L}{L_0}\right)_{thermal} = \frac{F}{AY} \implies \left(\frac{\Delta L}{L_0}\right)_{thermal} + \left(\frac{\Delta L}{L_0}\right)_{force} = \alpha\Delta T + \frac{F}{AY} = 0 \implies \frac{F}{A} = -Y\alpha\Delta T. \tag{3.10}$$

3.6 Heat Transfer Process

Three mechanisms of heat transfer:
➤ convection – motion of mass between regions
➤ conduction – vibration through materials
➤ radiation – electromagnetic radiation; no medium

Conduction:
➤ Heat flows from hot to cold.
➤ Energy dQ is transferred in time dt.
➤ Heat current = $H = \frac{dQ}{dt}$; $H \propto A$.
➤ Experimentally, $H = \frac{dQ}{dt} = kA\frac{T_H - T_C}{L}$, where k is the thermal conductivity of the material in $W \ m^{-1} \ K^{-1}$.

The general form for H, for non-uniform dT, is given by:

$$H = \frac{dQ}{dt} = -kA\frac{dT}{dx}, \tag{3.11}$$

where the negative sign indicates heat flows in direction of decreasing temperature. Engineers use thermal resistance, $R = L/k$, in units of $K \ m^2 \ W^{-1}$

Convection:

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➤ Convey heat energy from one location to another by movement of fluid (gas or liquid) with higher temperature.
➤ Two types:
   ➥ Natural Convection e.g. hot air rising
   ➥ Forced Convection e.g. blood circulation
➤ This is from complex fluid dynamics processes and so, there are no simple models.

Radiation:

➤ Through the electromagnetic spectrum so does not require a medium – can go through vacuums.
➤ Radiation depends on body temperature – hotter bodies emit shorter wavelengths of radiation.

$$H = Ae\sigma T^4 \tag{3.12}$$

➤ Rate of heat loss proportional to A, emissivity, e, & temperature.
➤ This is the Stefan-Boltzmann Law, where $\sigma = 5.67 \times 10^{-8} \ W \ m^{-2} \ K^{-4}$.
➤ Net heat current is the sum of the energy out and in from the surroundings at a temperature, T_s, & an emissivity, e_s:

$$H_{net} = Ae\sigma T^4 - Ae_s\sigma T_s^4 \tag{3.13}$$

Lecture 4

4.1 Recap

➤ Black body emissivity, $e = 1$.
➤ $T_{peak} \propto f_{rad}$.
➤ Many astro-bodies are approximately black bodies.

4.2 Learning Aims

➤ Define an ideal gas & understand the equation of state
➤ How a real has differs from an ideal gas
➤ Particle interactions & importance of potential wells
➤ Phase diagrams & importance of the triple & critical points

4.3 Equations of state

The state of a material can be entirely described by a small number of variables. Gases are described by the relationship between p, V, T, & n. All of this is combined into the equation of state.

4.4 Ideal Gases

For total mass, m_{total}, & known molar mass then we get number of moles, n:

$$m_{total} = n \times \text{gfm} \tag{4.1}$$

Holding other variables constant: (For an ideal gas only)

➤ $V \propto n$
➤ $V \propto \frac{1}{p}$ – Boyle's Law
➤ $V \propto T$ – Charles' Law

4.5 Ideal Gas Law

$$pV = nRT \tag{4.2}$$

R is the universal gas constant, $R \approx 8.31 Jmol^{-1}K^{-1}$. Applicability: works well for moderate pressures and temperatures – typically around ambient temperatures and atmospheric pressures. Gas density:

$$n = \frac{m}{\text{gfm}}, \qquad\qquad \rho = \frac{M}{V} \qquad\qquad \implies \rho = \frac{p \times \text{gfm}}{RT} \tag{4.3}$$

If there is constant mass or n, then nR is constant:

$$\frac{pV}{T} = nR \implies \frac{pV}{T} = k \tag{4.4}$$

$$\therefore \quad \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \tag{4.5}$$

| Ideal Gases	Real Gases
Molecules infinitely small	Molecules have volume
Perfectly elastic collisions	Lose kinetic energy upon collisions
Do no interact with each other	Exert forces on each other

4.6   Van der Waal's Equation

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{4.6}$$

This accounts for particle volume and interactions. b $\approx$ volume of one mole of the gas; a $\approx$ quantifies forces attracting molecules, reducing pressure.

4.7   pV diagrams

These are important for thermodynamic processes.
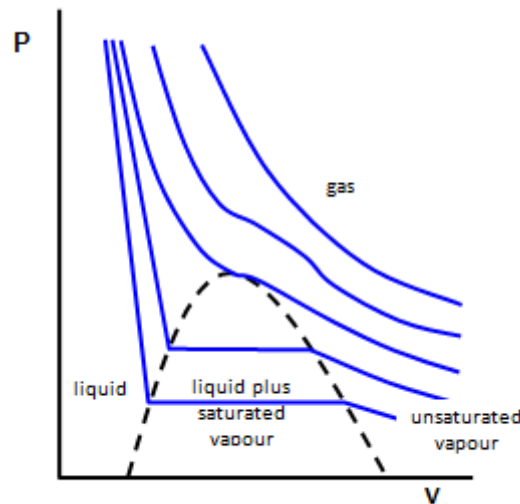
Each line on a pV diagram indicates a fixed temperature – higher temperatures are further from the axes. These lines of fixed temperature are called isotherms. For ideal gas, isotherms represent constant pV. Peak of dotted line shows critical temperature, above which there is no liquid-vapour phase transition. Below the critical temperature, gas condenses to liquid as it is compressed. Equilibrium between liquid and vapour phases inside dotted line region. The gas is never liquid above critical temperature; below critical temperature, gas changes state at constant p in phase equilibrium zone.

4.8   Molecules & Forces

Molecules can vary massively in size. In gases, molecules are free to move; In liquids and solids, they are held together by intermolecular forces. Forces are electrical in origin – attractional/repulsive & $\propto \frac{1}{r^2}$, i.e. $U(r) \propto \int f(r)\, dr$.

4.9   Force & Potential Energy

Molecules are not point charges – they contain +ve & −ve parts. Attractive interactions increase at distance up to r_0 then become repulsive.
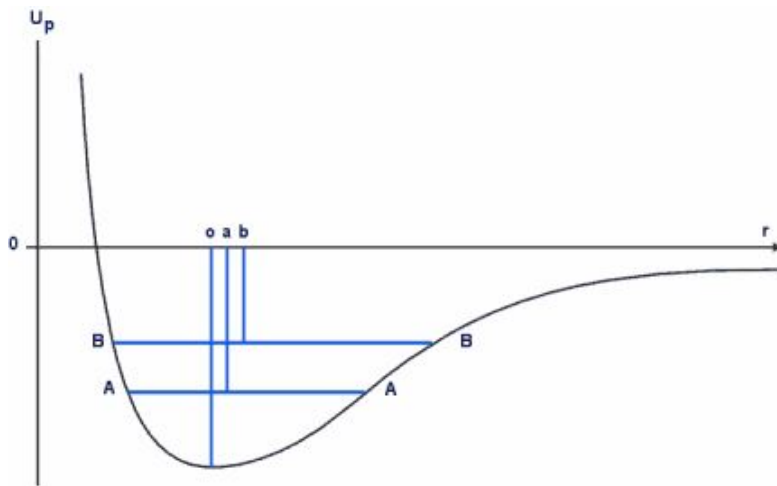
Region near bottom of graph called a potential well – potential U_o at position o.

$$E_k << |U_o| - \text{Solid}; \qquad\qquad E_k < |U_o| - \text{Liquid}; \qquad\qquad E_k > |U_o| - \text{Gas} \qquad (4.7)$$

As temperature increases, the phase changes and importance of kinetic energy increases.

Thermal expansion – molecular view:
As energy ↑, average distance ↑. Adding heat to a solid causes molecules to rise up the potential well. Atomic vibrations increase the radii defined by the sides of the well.

4.10   Phase diagrams

These are plots of p against T. There is only one phase at any specific p & T, apart from phase boundaries where phase equilibrium occurs.

➤ Triple point – there is no liquid phase for materials with a triple point pressure > the given pressure.
➤ Critical point – beyond this, as in latent heat, liquids and gases cannot be distinguished between, and are collectively called fluids.

Lecture 5

➤ Known assumptions of kinetic theory for ideal gases
➤ Demonstrate relation between pressure and molecular properties
➤ Translational kinetic energy
➤ RMS speed
➤ Mean free path

5.1   Kinetic Theory

Model has as large number of molecules in a box. Assumptions made:

➤ Point particles
➤ There is a volume, V, from a large number, N, of molecules with mass, m
➤ Molecules are in constant motion, obeying Newton's law
➤ Perfectly elastic collisions
➤ Walls of box are perfectly rigid and infinitely massive (they do not absorb any energy)

Molecular motion → pressure of system:

$$F = \frac{mv - mu}{t} = \frac{dp}{dt} \tag{5.1}$$

Individual Δp for number, N, of particles. All molecules collide with walls – generate pressure. Assume all have velocity, $v = |v_x|$.

$$m|v_x| - (-m|v_x|) = 2m|v_x| \tag{5.2}$$

$$\text{No. of collisions at A in dt} = \frac{1}{2}\left(\frac{N}{V}\right)\left(A|v_x|dt\right) \tag{5.3}$$

Wall Area, A, and number of molecules per unit volume, N/V. Assume half of these are moving towards the wall:

$$\Delta p_x : dp_x = \frac{1}{2}\left(\frac{N}{V}\right)\left(A|v_x|dt\right) \times 2m|v_x| \implies \frac{NAmv_x^2 dt}{V} \tag{5.4}$$

$$F = \frac{dp_x}{dt} = \frac{NAmv_x^2}{V} \implies p = \frac{F}{A} = \frac{Nmv_x^2}{V} \tag{5.5}$$

$$pV = Nmv_x^2 \implies pV = nRT \tag{5.6}$$

5.2   Average Velocities

Assumed all molecules have v_x. Replace this with $\bar{v}_x$. Must have $v^2 = v_x^2 + v_y^2 + v_z^2$, $\bar{v} = \sum v_{x,y,z}$. Overall, velocities must cancel out:

$$\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 \qquad\qquad \bar{v}_x^2 = \frac{1}{3}\bar{v}^2 \tag{5.7}$$

$$pV = \frac{1}{3}Nm\bar{v}^2 \qquad\qquad \implies pV = \frac{2}{3}N(\frac{1}{2}m\bar{v}^2) \tag{5.8}$$

$$pV = \frac{2}{3}NE_k, \text{ for translational } E_k \tag{5.9}$$

Total translational kinetic energy labelled K_{tr}

$$\bar{K}_{tr} = \frac{1}{2}m\bar{v}^2; \quad \sum N \to \text{total } K_{tr} \tag{5.10}$$

$$pV = \frac{2}{3}K_{tr} = nRT \text{ (whole gas)} \tag{5.11}$$

$$\implies K_{tr} = \frac{3}{2}nRT, \text{ for n moles of gas} \tag{5.12}$$

$$\frac{K_{tr}}{N} = \frac{1}{2}m\bar{v}^2 = \frac{3nRT}{2N} \tag{5.13}$$

$$= \frac{3}{2}\left(\frac{R}{A}\right)T \quad \because \quad \frac{n}{N} = \frac{1}{A} \tag{5.14}$$

$$\bar{K}_{tr} = \frac{1}{2}m\bar{v}^2 = \frac{3}{2}k_BT \quad \because \quad \frac{R}{A} = k_B, \text{ the Boltzmann constant} \tag{5.15}$$

$$pV = Nk_BT \tag{5.16}$$

5.3 RMS Speed

RMS Speed stands for "Root Mean Square" speed:

$$v_{rms} := \sqrt{(\bar{v^2})} \tag{5.17}$$

$$v_{rms} = \sqrt{\frac{3k_BT}{m}}, \text{ for molecules} \tag{5.18}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}, \text{ for the whole gas} \tag{5.19}$$

RMS speed is greater than average speed; RMS speed is greater for molecules with smaller masses.

5.4 Collisions

Consider N spherical molecules of radius, r, with volume, V. Molecules sweep out cylinder of radius 2r as they go – inside this cylinder, collisions will occur. In an interval dt, molecules travel v dt. For dN molecules with cylinder:

$$dN = 4\pi r^2 v dt \left(\frac{N}{V}\right) \tag{5.20}$$

$$\text{Collision Rate: } \frac{dN}{dt} = \frac{4\pi r^2 v N}{V} \tag{5.21}$$

If all particles are moving, a factor of $\sqrt{2}$ is needed:

$$\frac{dN}{dt} = \frac{4\sqrt{2}\pi r^2 v N}{V} \tag{5.22}$$

5.5 Mean free path

We take the reciprocal of above to get time:

$$\frac{dN}{dt} = \frac{4\sqrt{2}\pi r^2 v N}{V} \rightarrow \frac{dt}{dN} = \frac{V}{4\sqrt{2}\pi r^2 v N} \tag{5.23}$$

$$\bar{t} = \frac{V}{4\sqrt{2}\pi r^2 v N} \quad \because \quad dN = 1 \tag{5.24}$$

$$\lambda = v\bar{t} = \frac{V}{4\sqrt{2}\pi r^2 N} \tag{5.25}$$

This can be described macroscopically by using $pV = Nk_BT$:

$$\lambda = \frac{k_BT}{4\sqrt{2}\pi r^2 p} \tag{5.26}$$

Lecture 6

6.1   Learning Aims

➤ Heat capacity of monatomic gas
➤ Equipartition principle
➤ Degrees of freedom & heat capacities of gases
➤ Dulong & Petit rule from equipartition principle
➤ Degrees of freedom reduce at low temperature
➤ Distribution function in terms of molecular speed
➤ Maxwell-Boltzmann distribution

6.2   Heat capacities

Heat is energy in transit; adding heat adds energy. Kinetic energy $\propto$ temperature, for ideal gases. Equipartition theory – energy on average is shared equally across all available Degrees of Freedom (DoFs). For a simple atomic gas – there are 3 axes of translational motion $\therefore$ 3 DoFs. Raising energy raises temperature.

How much heat is needed? *dQ $\to$ dT relates to change in kinetic energy, dK$_{tr}$* Define C_V to be molar heat capacity at constant volume:

$$dQ = dK_{tr} = \frac{3}{2}nRdT \tag{6.1}$$

$$dQ = nC_V dT \tag{6.2}$$

$$C_V = \frac{1}{n}\frac{dQ}{dT} = \frac{1}{n}\frac{dK_{tr}}{dT} \tag{6.3}$$

$$= \frac{1}{n}\frac{3nRdT}{2dT} \tag{6.4}$$

$$C_V = \frac{3}{2}R \tag{6.5}$$

6.3   Degrees of Freedom

There are two additional DoFs in diatomic molecules. Travelling along each dimensional axis, rotating about each axis, and vibrating through bonds all provide a DoF. Monatomic gas – heat only goes into translational DoFs. For other molecules – heat is distributed over all DoFs. Energy, on average, is spread equally between different types of motion. Each molecule carries average energy of $\frac{1}{2}k_B T$ per DoF.

➤ Monatomic – 3 DoFs from each translational dimension $\therefore \frac{3}{2}nRT \to C_V = \frac{3}{2}R$
➤ Diatomic – 5 DoFs from 3 translational and 2 rotational $\therefore \frac{5}{2}nRT \to C_V = \frac{5}{2}R$

There are quantised energy levels in vibrational DoFs.
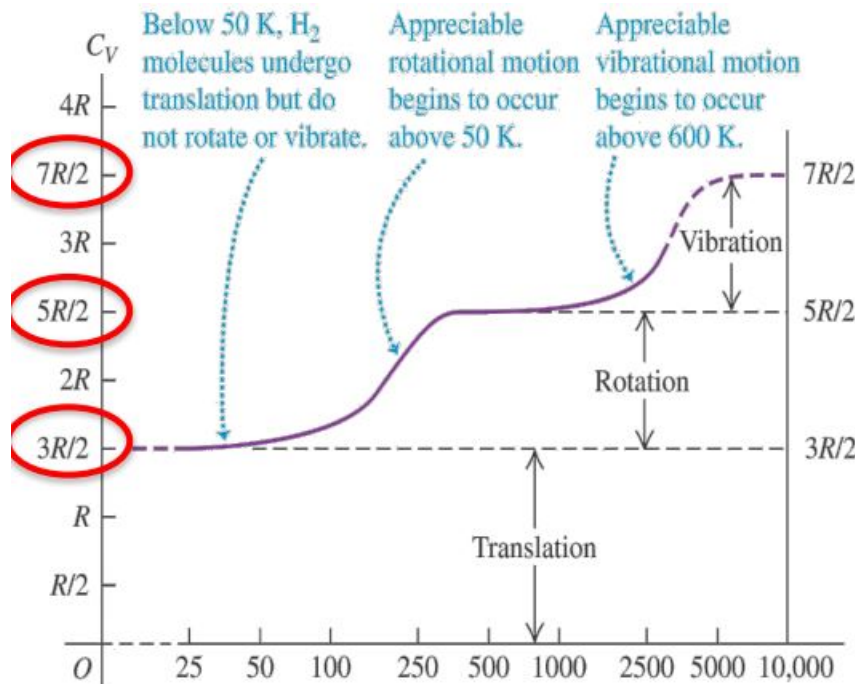
Motions are "frozen out" at lower temperatures; as temperature increases, more DoFs become available.

6.4 Dulong & Petit Rule

Consider the crystalline lattice of a solid. Each bond is under SHM – x,y,z motion. Stretching of bonds stored potential energy in each axis.

Dulong & Petit Rule $\approx 25 J mol^{-1} K^{-1} \approx 3R$ for solids. For a simple spring model: there are 6 DoFs; 3 translational, 3 vibrational potential:
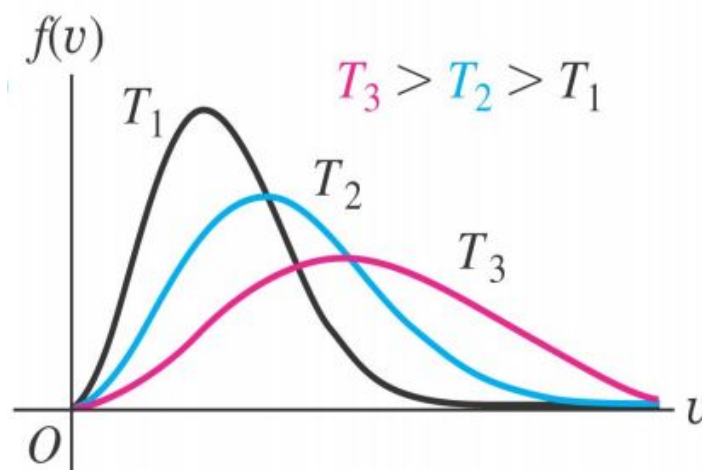
$$\text{Average energy per molecule} = \frac{6}{2} k_B T = 3 k_B T = 3R \tag{6.6}$$

$$\text{Over whole solid: } E_{total} = 3N k_B T = 3nRT \tag{6.7}$$

$$\text{Molar heat capacity, } C_V = 3R \tag{6.8}$$

6.5 Molecular Speeds

Use a speed distribution function to map out molecular speeds: Each plot has the same area.

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$$\text{The number of molecules with set speeds: } dN = N f(v) \, dv \tag{6.9}$$

$$\text{The probability that a molecule has a speed: } f(v) \, dv \tag{6.10}$$

3 key values for molecular speeds:

➤ most probable; v_{mp}, where $\frac{df}{dv} = 0$

➤ average; $v_{av} = \int_0^\infty v f(v) \, dv$

➤ rms; $v_{rms} = \sqrt{(\bar{v^2})} = \sqrt{\int_0^\infty v^2 f(v) \, dv}$

$f(v)$ is described by the Maxwell-Boltzmann distribution:

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{\frac{-mv^2}{2k_B T}} \tag{6.11}$$

Substituting this $f(v)$ into previous speed equations gives:

$$v_{mp} = \sqrt{\frac{2k_B T}{m}}; \qquad \bar{v} = \sqrt{\frac{8k_B T}{\pi m}}; \qquad v_{rms} = \sqrt{\frac{3k_B T}{m}}. \tag{6.12}$$
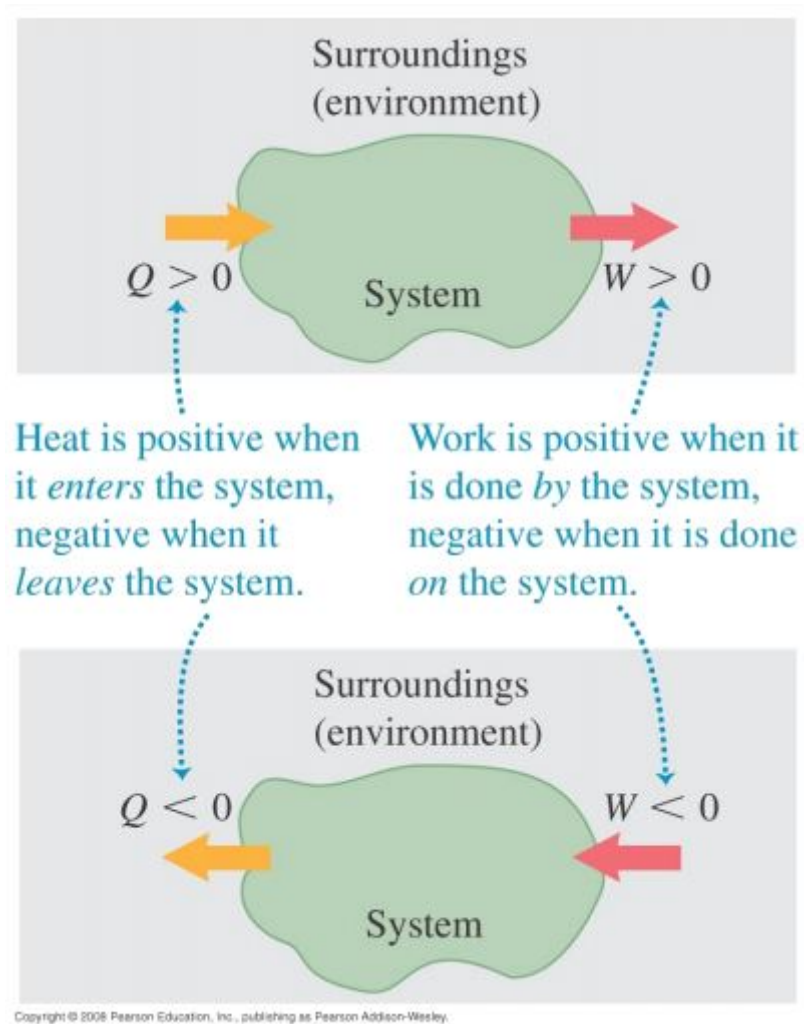
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Lecture 7

7.1 Learning Aims

➤ The First Law of Thermodynamics

7.2 Thermodynamic Systems

Definition: A collection of objects regarded as a single unit → beyond those objects is classified as the surroundings

Heat, Q, can flow *in to* or *out of* a system; Work, W, can be *done by* or *done on* a system.

Heat is positive when it *enters* the system, negative when it *leaves* the system.

Work is positive when it is done *by* the system, negative when it is done *on* the system.

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Consider gas in a piston: Molecules hit piston, transfer energy as piston moves out → lower kinetic energy so lower temperature
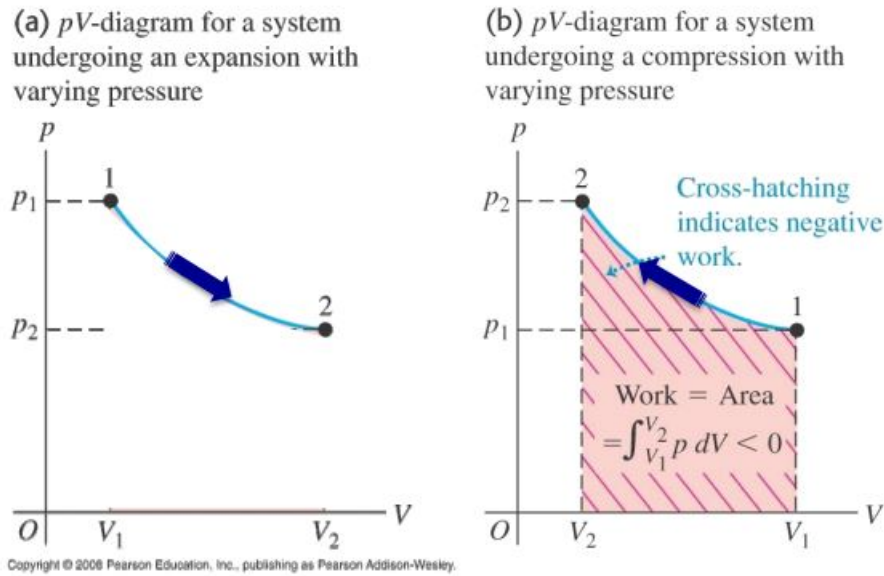
$$\text{Work } dW = F \, dx \tag{7.1}$$

Piston pushes molecules, transfers energy as piston moves in: higher kinetic energy so higher temperature

$$F = pA \rightarrow dW = F \, dx = pA \, dx \tag{7.2}$$

$$A \, dx = dV \rightarrow dW = p \, dV \tag{7.3}$$

$$W = \int_{V_1}^{V_2} p \, dV - [\text{Integrate over volume change}] \tag{7.4}$$

However, pressure depends on volume and temperature.

(a) pV-diagram for a system undergoing an expansion with varying pressure

(b) pV-diagram for a system undergoing a compression with varying pressure

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Work is the area under the curve:

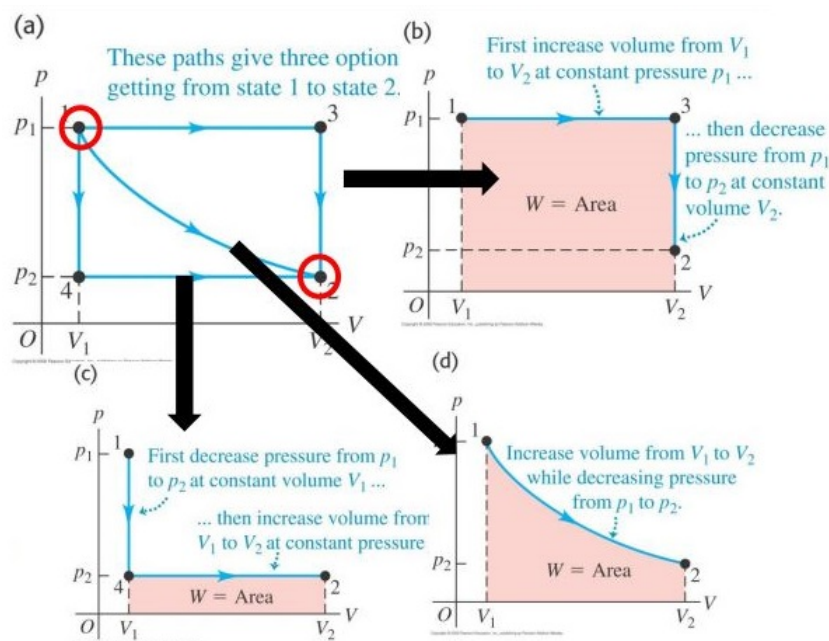$$p_1 V_1 = nRT_H; \; p_2 V_2 = nRT_H \tag{7.5}$$

$$p_2 = 2p_1 \therefore V_2 = \frac{V_1}{2} \tag{7.6}$$

$$W = \int_{V_1}^{V_2} p \, dV = \int_{V_1}^{V_2} \frac{nRT_H}{V} \, dV \tag{7.7}$$

$$= nRT_H [\ln V]_{V_1}^{V_2} = nRT_H \ln \frac{V_2}{V_1} \tag{7.8}$$

$$W = -nRT_H \ln 2 \tag{7.9}$$

Work is path-dependent: different routes from initial to final volumes and pressures will require a different amount of work – due to work being the area under the graph.

(c) takes the least work as it has the smallest area

7.3   First Law of Thermodynamics

Internal energy, U – sum of all E_k and E_p in a system (not gravitational potential though).

$$\Delta U = U_2 - U_1 \tag{7.10}$$
$$+Q, \uparrow U \rightarrow \Delta U = Q \tag{7.11}$$

Work done uses internal energy: $W = -\Delta U$. The first law of thermodynamics is stated as:

$$U_2 - U_1 = \Delta U = Q - W \text{OR:} \tag{7.12}$$
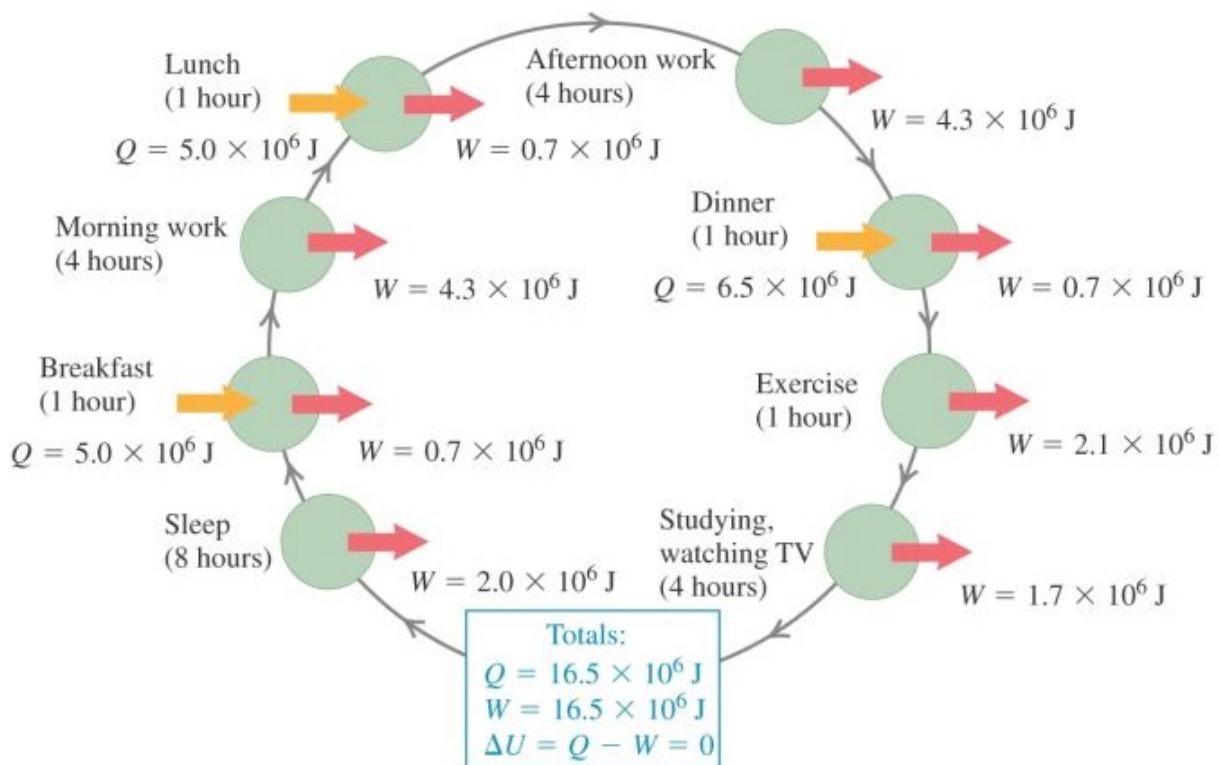$$Q = \Delta U + W; \; dU = dQ - dW \tag{7.13}$$

Absolute U is difficult to measure for a system; ΔU is not. Experimentally: Q & W depend on path taken but $\underline{\Delta U \text{ is independent of path}}$.

7.4   Special Case 1

Isolated system – no work or heat is interchanged with surroundings: $W = Q = 0$. U is constant, only depends on T.

7.5   Special Case 2

Cyclic process – a system that returns to initial state: $U_2 = U_1$ & $Q = W$ $\therefore$ U is constant overall.

Lecture 8

8.1   Recap

➤ For ideal gases: $E_T = K_{tr} = \frac{3}{2}RT$ (per mole?)
➤ For real gases: $E_T = K_{tr} + E_P = \frac{3}{2}RT - \frac{a}{V}$ (per mole?)
➤ Free expansion causes decrease in temperature – reason for extra term in real gases

8.2   Learning Aims

➤ Four thermodynamic process
➤ Ideal gases & different molar heat capacities for constant volume & pressure
➤ Derive relationship between these heat capacities
➤ Derive relationship for adiabatic process

8.3   Thermodynamic Processes
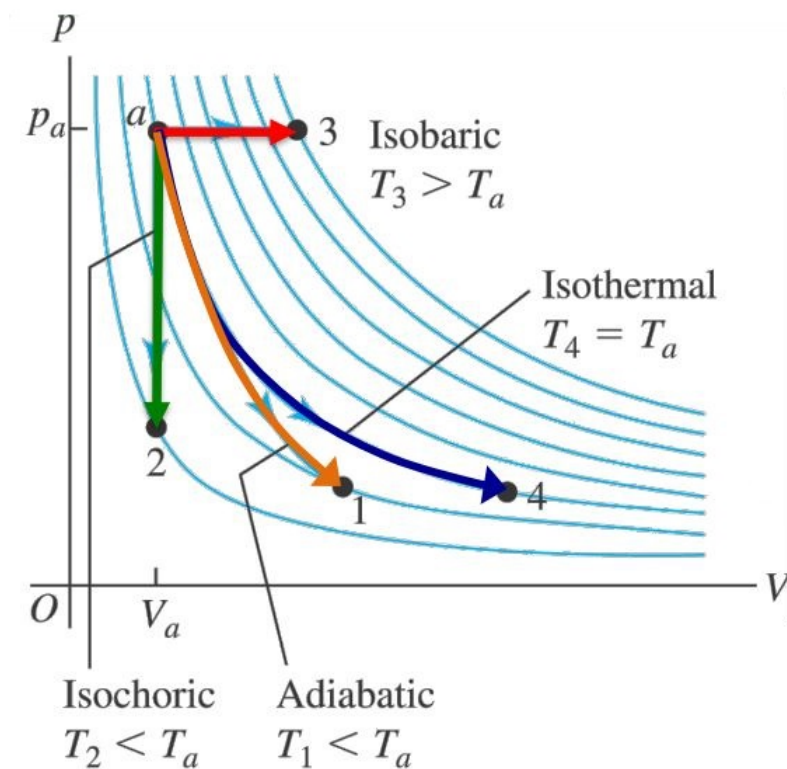
For an ideal gas:
➤ Isobaric process, $\Delta p = 0$
➤ Isochoric process, $\Delta V = 0 \rightarrow W = 0$
➤ Isothermal process, $\Delta T = 0$
➤ Adiabatic process, $Q = 0$

8.4   Isobaric Processes

Constant pressure process:

$$W = p(V_2 - V_1) \tag{8.1}$$

8.5 Isochoric Processes

Constant volume process:

$$\Delta V = 0 \therefore W = 0 \tag{8.2}$$
$$p\,dV = 0 \tag{8.3}$$
$$U_2 - U_1 = \Delta U = Q \tag{8.4}$$

All energy added to the system as heat goes into raising the internal energy.

8.6 Isothermal Processes

Constant temperature process. Heat flow must occur slowly enough for thermal equilibrium to be maintained. Generally – W, Q, & $\Delta U \neq 0$. Ideal gas – $\Delta U = 0$, $Q = W$. i.e. All heat energy taken in is output as work done

8.7 Adiabatic Processes

No heat transfer process:

$$Q = 0 \therefore U_2 - U_1 = \Delta U = -W \tag{8.5}$$

Occurrences:

1. System is well-insulated
2. Process was so quick that heat flow was neglected

For ideal gases in expansion, W is positive so ΔU drops $\rightarrow$ temperature drops.

8.8 Heat Capacity

Two molar heat capacities:

➤ At constant volume, C_V
➤ At constant pressure, C_p

For ideal gases, $C_p > C_V$:
Consider n moles of gas at temperature T in constant volume, V. Add heat, dQ:

$$dQ = nC_V dT \tag{8.6}$$
$$dU = nC_V dT \because W = 0 \tag{8.7}$$
$$dQ = nC_p dT \tag{8.8}$$

Material expands when heated so from ideal gas law:

$$dW = p\,dV = nR\,dT \tag{8.9}$$

Using the first law of thermodynamics:

$$dQ = dU + dW \tag{8.10}$$
$$nC_p dT = nC_V dT + nRdT \tag{8.11}$$
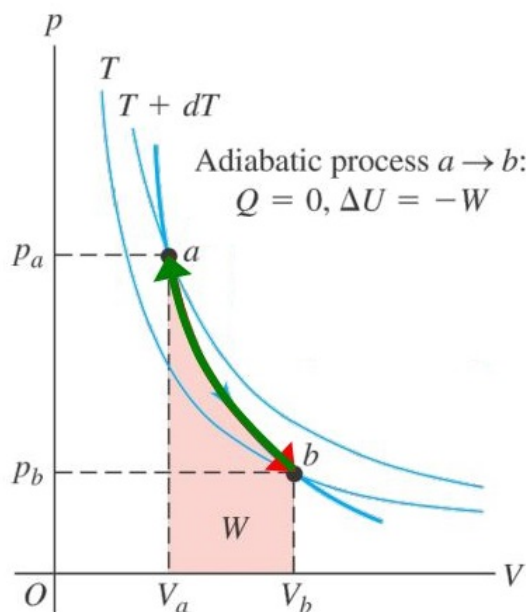$$C_p = C_V + R \because dT \text{ is the same} \tag{8.12}$$

8.9 Ratio of heat capacities

$$\gamma = \frac{C_p}{C_V} \tag{8.13}$$

For a monatomic gas, $\gamma \approx 1.67$; for a diatomic gas, $\gamma = 1.4$.

8.10   The Adiabatic Process

An adiabatic curve at any point is always steeper than the isotherm passing through the same point.

Idealised process so one of two cases:
1. Really fast process – no heat is exchanged
2. Really slow process – Thermal Equilibrium is maintained

For an ideal gas: temperature drops for expansion and rises for compression

8.11   Relating V, T, p, & W

$$dU = -dW \text{ [infinitesimal process]} \tag{8.14}$$

$$nC_V dT = -pdV \ \& \ pV = nRT \tag{8.15}$$

$$nC_V dT = -\frac{nRT}{V} dV \tag{8.16}$$

$$\frac{dT}{T} + \frac{R}{C_V}\frac{dV}{V} = 0. \ \gamma = \frac{C_p}{C_V} \tag{8.17}$$

$$\frac{R}{C_V} = \frac{C_p - C_V}{C_V} = \frac{C_p}{C_V} - 1 = \gamma - 1 \tag{8.18}$$

Now take last equation and integrate:

$$\int \left[\frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0 \right] \tag{8.19}$$

$$\ln T + (\gamma - 1)\ln V = k \tag{8.20}$$

$$\ln T + \ln V^{\gamma-1} = k \tag{8.21}$$

$$\ln TV^{\gamma-1} = k \tag{8.22}$$

$$TV^{\gamma-1} = \kappa \tag{8.23}$$

Hence, for initial and final states, (T_1, V_1) & (T_2, V_2):

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \tag{8.24}$$

$$T = \frac{pV}{nR} \tag{8.25}$$

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \tag{8.26}$$

Now considering work:

$$Q = 0 \quad \therefore \quad W = -\Delta U \tag{8.27}$$

$$\Delta U = nC_V \Delta T \text{ for ideal gases} \tag{8.28}$$

$$W = nC_V(T_1 - T_2) \tag{8.29}$$

$$pV = nRT \rightarrow W = \frac{C_V}{R}(p_1 V_1 - p_2 V_2) \tag{8.30}$$

$$W = \frac{1}{\gamma - 1}(p_1 V_1 - p_2 V_2) \tag{8.31}$$

Lecture 9

9.1 Learning Aims

- ➤ Principles of a heat engine & its thermal efficiency
- ➤ Sketch the Otto cycle, describe each step, & understand its limitations
- ➤ Describe differences between Otto cycle & the diesel engine
- ➤ How a fridge works & derive the coefficient of performance

9.2 Definitions

- ➤ A device that converts heat into mechanical energy of work is known as a heat engine.
- ➤ Matter inside this engine undergoes thermodynamic processes – *the working substance.*
- ➤ The simplest engines are those in which the working substance undergoes a cyclic process.

9.3 A Simple Heat Engine
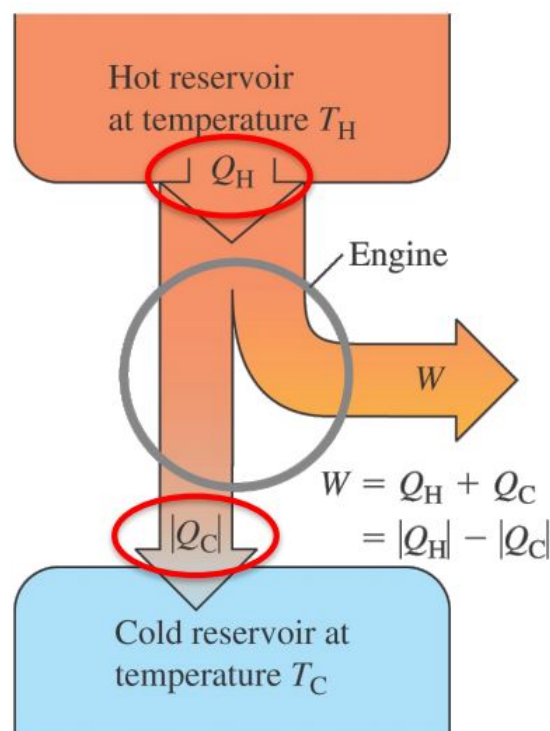
All heat engines absorb heat from the hot reservoir & discard it to the cold reservoir. Energy from the hot reservoir, Q_H, is positive; energy lost to cold reservoir, Q_C, is negative. The energy difference is the work done, W.

9.4 Efficiency

Q_H and Q_C are the heat energies absorbed and rejected in one cycle of the heat engine – the difference is the Work done:
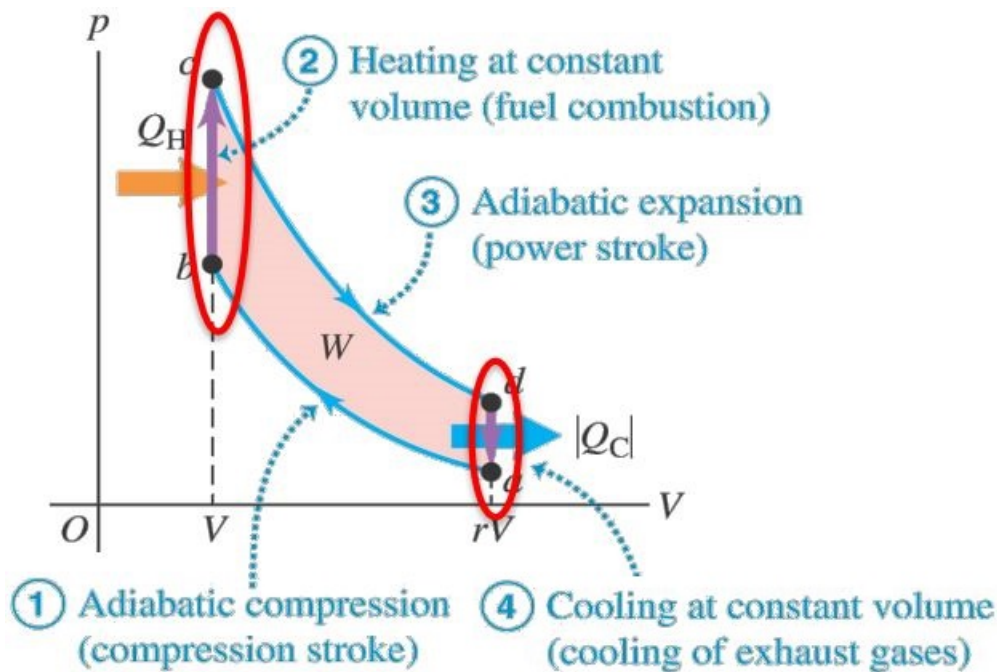
$$W = \Delta Q = Q_H + Q_C = |Q_H| - |Q_C| \tag{9.1}$$

Thermal efficiency, e:

$$e = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \left|\frac{Q_C}{Q_H}\right| \tag{9.2}$$

A heat engine can never be 100% efficient → $e < 1$. If $|Q_C| = 0$, then there can be no heat flow so no work can be undertaken.

9.5   The Otto Cycle

The Otto Cycle is an idealised model for an internal combustion engine.

The maximum volume of the cylinder is a factor, r – the compression ratio, larger than the minimum volume: $V_{max} = rV_{min}$. $Q_H > Q_C$ ∴. Work is done.

bc & da are at constant volume so:

$$Q_H = nC_V(T_c - T_b) > 0 \ \& \ Q_C = nC_V(T_a - T_d) < 0 \tag{9.3}$$

$$e = \frac{Q_H + Q_C}{Q_H} = \frac{T_c - T_b + T_a - T_d}{T_c - T_b} \tag{9.4}$$

For ab and cd:

$$T_a(rV)^{\gamma-1} = T_b V^{\gamma-1} \ \& \ T_d(rV)^{\gamma-1} = T_c V^{\gamma-1} \tag{9.5}$$

$$e = \frac{T_d r^{\gamma-1} - T_a r^{\gamma-1} + T_a - T_d}{T_d r^{\gamma-1} - T_a r^{\gamma-1}} = \frac{(T_d - T_a)(r^{\gamma-1} - 1)}{(T_d - T_a)r^{\gamma-1}} \tag{9.6}$$

$$e = 1 - \frac{1}{r^{\gamma-1}} < 1, \, always \tag{9.7}$$

e.g. for air: $\gamma = 1.4$, $r = 8 \implies e \approx 0.56$. r cannot be increased too much as the temperature of adiabatic compression rises too high & the air/fuel mixture ignites early – 'knocking'.

In reality, the Otto cycle neglects many other sources of energy loss e.g. friction, turbulence, incomplete combustion etc. This leads to further inefficiencies so in example above, $e \approx 0.35$ in reality.
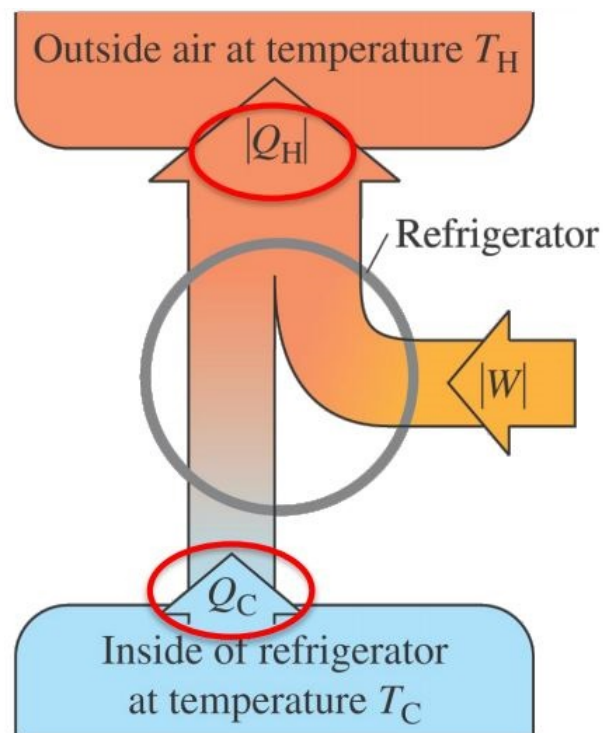
9.6 The Diesel Cycle
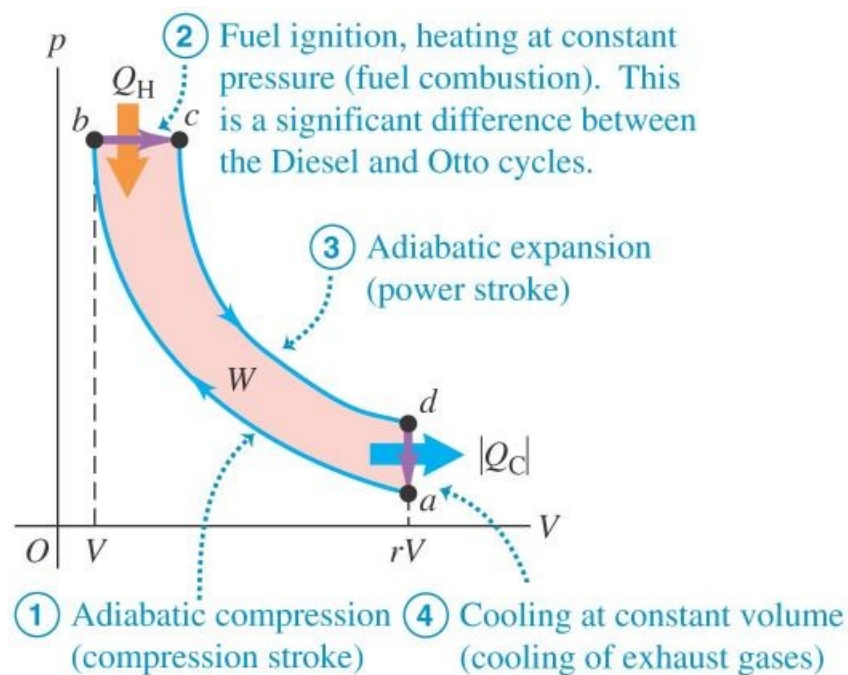
Differences to the Otto Cycle:

➤ No spark plugs – high temperature caused by adiabatic compression is used to ignite fuel at constant pressure
➤ Fuel is injected after compression – no early ignition can occur
➤ Can have bigger r (15-20)
➤ More efficient – $e \approx 0.7$, ideally

9.7 Fridges

Fridges can be considered a heat engine in reverse. Requires net input of work to drive extraction of heat from cold to hot. In this case, Q_C is positive, and Q_H & W are negative (negative work is done on the system).

9.8 Co-efficient of Performance

For a cyclic process, from the first law:

$$Q_H + Q_C - W = 0 \text{ or } -Q_H = Q_C - W \tag{9.8}$$

$$Q_H \text{ \& } W < 0 \implies |Q_H| = Q_C + |W| \tag{9.9}$$

The best fridge removes the most heat for the least work – evaluated by the coefficient of performance, K:

$$K = \frac{Q_C}{W} = \frac{|Q_C|}{|Q_H| - |Q_C|} \tag{9.10}$$

Air conditioners use the same principle: for heat current H, input power P, & time t:

$$K = \frac{|Q_C|}{|W|} = \frac{Ht}{Pt} = \frac{H}{P} \tag{9.11}$$

It is impossible to have a fridge without some input of work. A heat pump functions as an inside-out fridge: it takes heat from cold outside air to heat the inside

Lecture 10

10.1 Learning Aims

➤ Reversible & irreversible processes
➤ Directionality of irreversible processes leads to the second law of thermodynamics and entropy
➤ Processes that form the Carnot Cycle & its efficiency
➤ Importance of the Carnot Cycle as a heat engine & temperature measurement

10.2 Direction of Processes

The key to the second law of thermodynamic processes is the direction of thermodynamic processes. Real-life processes only proceed in one direction: Heat moves from hot to cold and cannot spontaneously reverse. It is possible to have idealised processes that are reversible – these can only occur close to equilibrium (known as *quasi-equilibrium*).
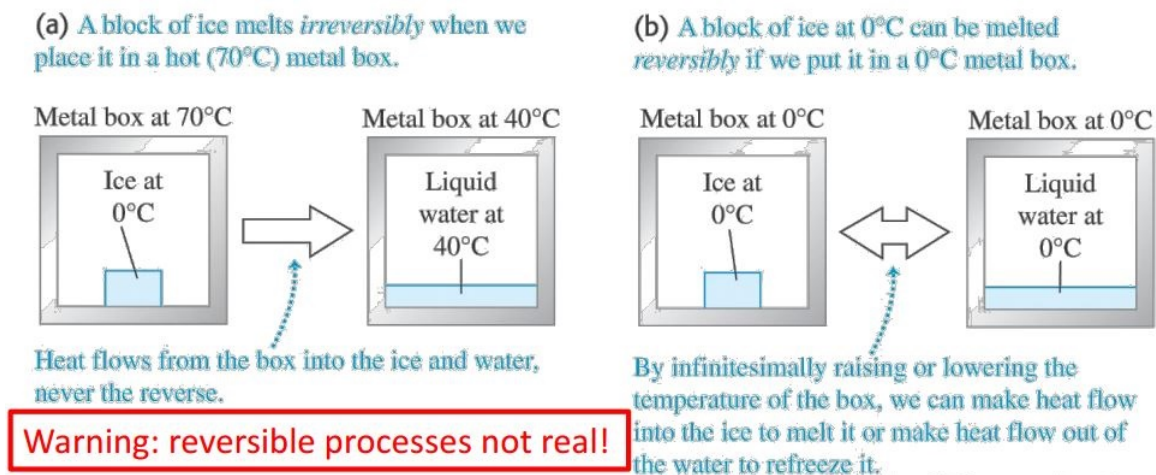
10.3 The Second Law of Thermodynamics
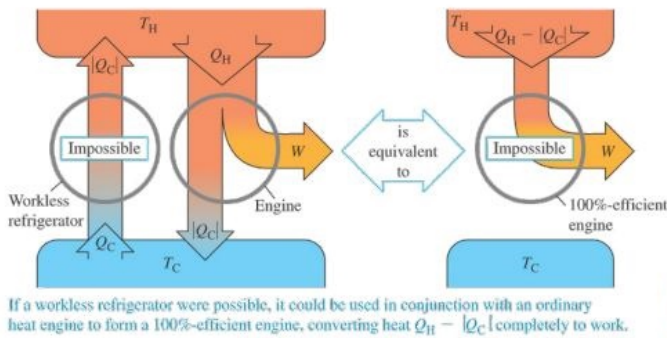
Kelvin-Planck statement on engines:
"It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which is began."

Restating the Second law – the Clausius statement on fridges:
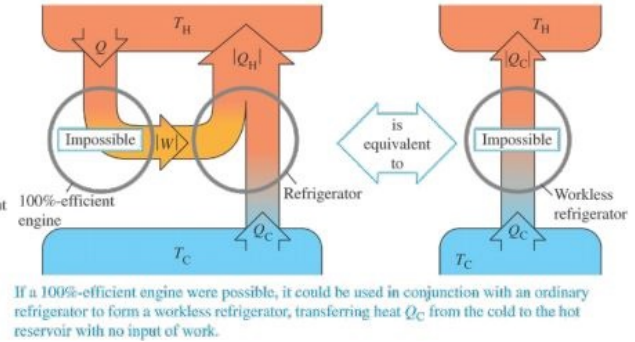*"It is impossible for any process to have as its sole result the transfer of heat from a cooler body to a hotter one."*

If one form of the law is violated, then it can be used to violate the other form as well. There is no observational test for either expression of the law – it is accepted as an axiom.

(a) The "engine" statement of the second law of thermodynamics

If a workless refrigerator were possible, it could be used in conjunction with an ordinary heat engine to form a 100%-efficient engine, converting heat $Q_H - |Q_C|$ completely to work.

(b) The "refrigerator" statement of the second law of thermodynamics

If a 100%-efficient engine were possible, it could be used in conjunction with an ordinary refrigerator to form a workless refrigerator, transferring heat Q_C from the cold to the hot reservoir with no input of work.

Consider a moving body of molecules:

➤ Molecules have random motion; KE & PE linked to internal energy
➤ Superimposed is a coordinated motion – macroscopic motion & KE

Friction converts this macroscopic KE to random molecule motion but cannot fully convert random motion back into ordered macroscopic motion/ The direction of motion is linked to the *degree of disorder*.

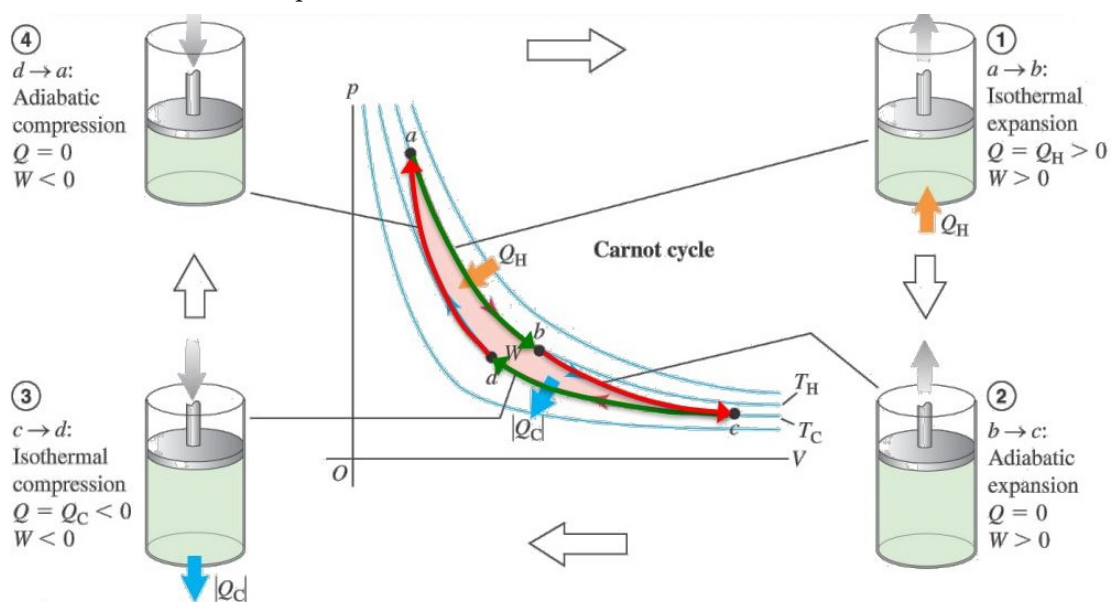## 10.4   The First Law vs The Second Law

Certain processes are allowed by the First Law (energy conservation) but not by the Second Law (direction of processes), e.g. powering a speedboat by extracting heat energy from the sea. The Second Law is a separate law of nature; it is not derived from the First Law.

➤ First Law: Energy cannot be created or destroyed
➤ Second Law: The availability of useful energy is limited

10.5   The Carnot Cycle

A hypothetical, idealised engine with maximum efficiency. This is consistent with the Second Law. Runs entirely on reversible processes:

➤ Isothermal heat transfers – to avoid irreversible heat flow
➤ Adiabatic temperature changes – to avoid irreversible heat transfer
➤ Thermal & mechanical equilibrium must be maintained

④ $d \to a$: Adiabatic compression $Q = 0$ $W < 0$

① $a \to b$: Isothermal expansion $Q = Q_H > 0$ $W > 0$

Carnot cycle

③ $c \to d$: Isothermal compression $Q = Q_C < 0$ $W < 0$

② $b \to c$: Adiabatic expansion $Q = 0$ $W > 0$

10.6   Carnot Efficiency

ab & cd are isothermal so $\Delta U = 0$:

$$Q_H = W_{ab} = nRT_H \ln \frac{V_b}{V_a} \tag{10.1}$$

$$Q_C = -nRT_H \ln \frac{V_c}{V_b} \tag{10.2}$$

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H} \frac{\ln(V_c/V_d)}{\ln(V_b/V_a)} \tag{10.3}$$

bc & da are adiabatic so:

$$T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1} \;\&\; T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1} \tag{10.4}$$

$$\frac{V_b^{\gamma-1}}{V_a^{\gamma-1}} = \frac{V_c^{\gamma-1}}{V_d^{\gamma-1}} \;\;\therefore\; \frac{V_b}{V_a} = \frac{V_c}{V_d} \tag{10.5}$$

This means that the logarithms in the isothermal equation are equal, and therefore cancel:

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H} \implies \frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \tag{10.6}$$

The efficiency of the Carnot engine is therefore given by:

$$e_{Carnot} = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H} \tag{10.7}$$

Therefore, the larger the temperature difference, the more efficient the Carnot engine.

10.7   Carnot Fridge

Since all steps in the Carnot Cycle are reversible, the entire cycle may be run backwards to create a maximally efficient fridge. From the coefficient of performance & the previous Carnot analysis:

$$K = \frac{|Q_C|}{|Q_H| - |Q_C|} = \frac{|Q_C|/|Q_H|}{1 - |Q_C|/|Q_H|} \tag{10.8}$$

$$\frac{|Q_C|}{|Q_H|} = \frac{T_C}{T_H} \tag{10.9}$$

$$K_{Carnot} = \frac{T_C}{T_H - T_C} \tag{10.10}$$

10.8   Carnot Cycle and the Second Law

No engine or fridge is more efficient than the Carnot cycle. All Carnot engines operating between the same two temperatures have the same efficiency, irrespective of the nature of the working substance. The Carnot efficiency sets the upper limit for real engines so T_H is always maximised in practice.

10.9   The Kelvin Scale

As the Carnot Cycle efficiency is independent of the working substance, Kelvin proposed to use this to define his temperature scale as follows:

$$\frac{T_C}{T_H} = \frac{|Q_C|}{|Q_H|} = -\frac{Q_C}{Q_H} \tag{10.11}$$

Uses the triple point of water at 273.16 K to set the scale so identical to ideal has scale. Absolute zero is minimum (not zero) energy of a system – leads to the Third Law of Thermodynamics.

Lecture 11

11.1   Learning Aims

➤ Entropy & entropy change for a reversible process
➤ Understand relationship between changes in entropy & changes between states
➤ State the Second Law in terms of entropy
➤ Difference between macroscopic & microscopic state descriptions
➤ Understand the Second Law in terms of microscopic state probabilities

11.2   Entropy

The Second Law appears unlike other laws:

➤ Series of statements of impossibility
➤ Not a quantitive relationship

However, it can be made quantitive by introducing concept of Entropy: entropy is a measure of disorder.

11.3   Defining entropy

Consider a reversible infinitesimal isothermal expansion of ideal gas:

$$\Delta U = 0 \implies dQ = dW = p\,dV = \frac{nRT}{V}\,dV \implies \frac{dV}{V} = \frac{dQ}{nRT} \tag{11.1}$$

Expansion → molecules into a larger volume – more disordered so $\frac{dV}{V}$ is a measure of increase in disorder. Denote entropy as S and infinitesimal change dS:

$$dS = \frac{dQ}{T} \implies \Delta S = \frac{\Delta Q}{T},\text{ for whole process} \tag{11.2}$$

Generalise any reversible process from state 1 to state 2 as a series of infinitesimal steps at temperature, T:

$$\Delta S = \int_1^2 \frac{dQ}{T} \tag{11.3}$$

Entropy is a function of the state of the system i.e. is independent of the path between the two states. This is similar to internal energy which is also state-, not path-dependent. Also similar to U, it is trivial to calculate changes in entropy ΔS, but not absolute value of entropy, S. For reversible, cyclic processes, $\Delta S = 0$.

11.4   Entropy in Irreversible Processes

Since ΔS is independent of path – can model any change of state as a series of reversible processes so the previous equation can be used to calculate entropy change for irreversible processes too. All irreversible processes lead to an increase in entropy. Unlike energy, entropy is not a conserved quantity. Overall, Reversible cycles have $\Delta S = 0$; Irreversible processes always have positive ΔS. It is possible to calculate ΔS for free expansion by considering the isothermal path:
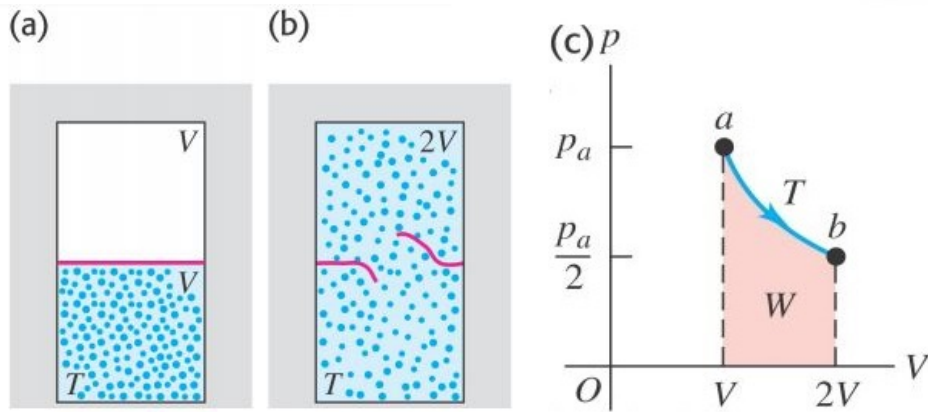
11.5 Entropy and the Second Law

Reversible cycles have a zero net entropy change. Irreversible processes always have a positive entropy change (increase in disorder).

New statement of the Second Law: *"No process is possible in which the total entropy decreases, when all systems taking part in the process are included."*

Irreversible processes lead to a loss of opportunity to utilise energy; in a less ordered state, the energy is less available for us to use. The universe is continually getting more disordered:

➤ Entropy is *the arrow of time*
➤ Ultimate fate of the Universe is heat death

11.6 Microscopic Interpretation of Entropy

Consider N coins:
If all N coins are heads, the system is totally ordered. The most likely macroscopic state is half heads and half tails – there are many possible microscopic states, but little is known about the state of individual coins → the system is maximally disordered, and has the most entropy. The same arguments can be applied to molecules in a has – macroscopic p, V, and T vs microscopic position and velocity.

"For any system, the most probable macroscopic state is the one with the greatest number of corresponding microscopic states, which is also the macroscopic state with the greatest disorder and highest entropy."

11.7 Calculating Entropy From Microscopic States

For a number, w, of possible microscopic states for a given macroscopic state, the entropy is:
$$S = k_B \ln |w| \tag{11.4}$$

Increasing the number of states, w, will increase entropy, S. Entropy is at a minimum for a single microscopic state:
$$w = 1 \implies S = 0, \; S \not< 0 \tag{11.5}$$

It is more common to calculate ΔS:
$$\Delta S = S_2 - S_1 = k_B \ln |w_2| - k_B \ln |w_1| \tag{11.6}$$
$$\Delta S = k_B \ln \left| \frac{w_2}{w_1} \right| \tag{11.7}$$

11.8 Microscopic States & the Second Law

The entropy of a system can never decrease – i.e. the number of possible microscopic states can never spontaneously decrease. E.g. free compression –

➤ All air particles would move randomly to one side of the room
➤ Not impossible, just very unlikely
➤ Probability $\approx \left(\frac{1}{2}\right)^{40000000000000000000000000000000}$

This has almost certainly never occurred anywhere. For all practical purposes, the Second Law has never been violated.