1 *Atoms*

ALL MATTER CONSISTS OF ATOMS (from Greek word "atomos" = indestructible or indivisible). An atom of an element is characterized by its *atomic number*, Z, which is the number of protons in its nucleus. The *nucleon number* (commonly called the *mass number*), A, is the number of protons and neutrons in the nucleous - collectively known as *nucleons*. Atoms with the same atomic number but different nucleon number are called *isotopes* of the element.

An **extensive property** of bulk mater is a property that depends on the *amount* of substance (e.g volume), whilst an **intensive property** is independent of the amount of substance (eg density, ρ). The state of bulk matter is defined by specifying the values of various measurable or calculable properties. Among them are:

The **mass**, m, a measure of the quantity of matter present (unit Kilogram, kg).

The **volume**, V, a measure of the quantity of space the sample occupies (unit: cubic meter, m^3).

The **amount of substance**, N, a measure of the number of specified entities (usually atoms or molecules) present. Specifically, N_m is the number of moles present (unit: mole, mol).

A **mole** is defined as *the number of carbon atoms in exactly 12g of carbon-12*. A mole of a gas at RTP occupies 24 litres. The number of entities per mole is known as *Avogadro's constant*, N_A, and the currently accepted value is $6.022 \times 10^{23}\ mol^{-1}$. The *molar mass* of a substance, M, (units kilograms per mole, $kg\ mol^{-1}$) is the mass per mole of its atoms or molecules. Thus, the amount of substance can be readily calculated from its mass by noting that

N_A is a constant with units

$N_m = m/M$

Even up to ≈ 100 years ago, many scientists did not accept atomic theory (even though it had been used to explain properties of gases). Einstein (and Smoluchowski) explained that atomic theory could explain brownian motion - the incessant motion of small particles (whether animate or not) suspended in water. Brownian particles would not have a constant velocity but the displacement $\propto \sqrt{(time)}$ due to a *random walk* as a result of collisions with atoms. Perrin's measurements (1908) were conclusive proof of the existence of the *invisible* atoms. This also allowed direct measurement of N_A for the first time, and thus could allow a determination of the size of an atom:

e.g. let's calculate size of gold atom given that its' density, $\rho = 19320\ \mathrm{kg\ m}^{-3}$.

1 mole of gold weighs 197 g, ($A_{Au} = 197$)

$\therefore$ mass of gold atom, $m_{Au} = 197 \times 10^{-3}$ / $6.022 \times 10^{23} = 3.27 \times 10^{-25}$ kg

so $N = \rho / m_{Au} = 19.32 \times 10^3$ / $3.27 \times 10^{-25} = 5.91 \times 10^{28}$ atoms m^{-3}

Volume occupied by each atom $V = 1/N$, assuming $V = r_0^3$, (r_0 is the interatomic spacing)

so $r_0 = N^{-1/3} = 2.6 \times 10^{-10}$ m = 0.26 nm = 2.6 Å

N_A was subsequently calculated (i) by Rutherford who counted a number of α decays and saw how many moles of He gas it produced (ii) by Millikan who measured the charge on an electron, then N_A was the number of electrons in one mole of charge, which would produce one mole of electrolyte. Finally atom size was measured directly by crystallography.

Atoms can be *observed* directly, using scanning tunnelling microscopy.

1.1 *Different states of matter*

WHEN CONSIDERING THE PROPERTIES OF DIFFERENT STATES OF MATTER, it is useful to draw comparisons in terms of **compressibility**, **rigidity**, and **viscosity**. If a given pressure acting on a substance, produces a large change in volume, that substance is deemed highly compressible. Rigidity is the ability to resist a force directed at changing the shape with *no change in volume*. Viscosity is a measure of the ability of a fluid to resist a change of shape when it is *moving at finite speeds*. Viscosity describes a fluid's internal resistance to flow and can be thought of as a measure of *fluid friction*. Put simply, the less viscous the fluid, the greater its ease of movement (fluidity). Liquids and solids can be viewed as **condensed states** of matter, whilst liquids and gases are examples of **fluid forms** of matter.

In terms of bulk behaviour of the three common states of matter:

Solids have high density and low compressibility. They are also rigid, and adopt a shape that is *independent* of the container it occupies.

Liquids have similar densities and compressibility as solids but are not rigid and therefore take the shape of their container (under gravity, the lower part). Viscosity of liquids increase with increasing liquid thickness.

Gases have low density and are highly compressible over wide ranges of volume. They also have no rigidity and low viscosity.

At an atomic level:

In solids, matter is fairly ordered, atoms generally sit in a regular lattice, though with some (mainly vibrational) motion. Liquids are mostly ordered locally in the sense that one molecule is connected

to a small number of other molecules, but the pattern as a whole is a disordered one. Particles are sufficiently free to move through the substance. Movement is in the form of partly rapid vibrations and partly translation. Gases are completely disordered, molecules move around freely and are usually large distances apart (compared to their diameter) colliding occasionally.
There is a **binding energy**, ϵ, between the particles.

Different states can then be characterised by the kinetic energy of the particles.

For solids, k.e. $\ll$ binding energy ϵ (looks like SHM)

For liquids, single bond energy $<$ k.e. $\ll$ total binding energy

For gases, k.e. $\gg$ total binding energy
Two other states of matter are known to exist and both will be covered in more detail in the final lecture. A **Plasma** is an ionised gas where sufficient energy has been provided to free electrons from their atoms and molecules, creating a *cloud* of protons, neutrons, and electrons. Plasmas account for > 99 percent of our universe. A **Bose-Einstein condensate** is a gaseous fluid that occurs at temperatures near to absolute zero. Under such conditions, a large fraction of the atoms collapse into the lowest quantum state, producing a superfluid. This state of matter was first predicted by Satyendra Nath Bose and Albert Einstein in 1925, and the first such condensate was produced by Eric Cornell and Carl Wieman 70 years later in 1995 at the University of Colorado at Boulder, using a gas of rubidium atoms cooled to 170 nanokelvins (nK).

1.2 *Interatomic Potential*

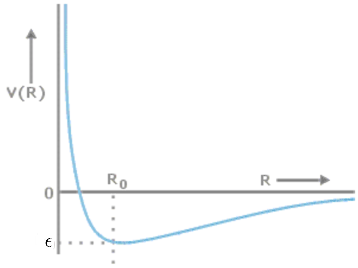

Figure 1: interatomic potential V(R) as a function of separation distance, R

ATOMS HAVE BOTH KINETIC AND POTENTIAL ENERGY. The potential energy arises through interactions between the atoms and is illustrated in fig. 1. At large separation (R) the potential becomes vanishingly small. Very close to the atom there is a strong repulsive force but its range is short and overcome by an attractive 'van-der'Waals' force at moderate proximity. This leads to a minimum in the interatomic potential at R_0 of magnitude ϵ.

To estimate ϵ, it is necessary to consider the interaction between the atom and its neighbours. The most tightly bound solid structure has each atom with 12 neighbours (face-centred cubic), but since a bond is shared between two atoms, there are ≈ 6 bonds per atom. When the temperature is raised, the substance will eventually undergo a *phase transition* as bonds begin to break to form a liquid. A further rise in temperature will cause the liquid to vaporise to form a gas.

For a material that melts and vaporises at similar temperatures, then for one mole of molecules the total energy of bonds = $6 \times N_A \times \epsilon \approx L_{vap} + L_{fus}$, the sum of the molar latent heats of vaporisation and fusion.

e.g. for H_2, the melting point (14.0K) and boiling point (20.3K) are similar, so $6 \times N_A \times \epsilon \approx L_{vap} + L_{fus} = (0.117 + 0.904) \times 10^3$ J

$\epsilon = 2.8 \times 10^{-22}$ J

Assume to a first approximation that K.E. $\propto T = \kappa T$

But H_2 boils at $T_b = 20.3$ K, which implies

$\kappa = \epsilon / T = 2.8 \times 10^{-22} / 20.3 \quad = \quad k_B$

2 Ideal Gas

2.1 State Variables

GASES CAN BE DEFINED BY A COMBINATION OF PARAMETERS such as, volume V, temperature T, pressure P, and number of moles N_m. These are called STATE VARIABLES.

- V is the volume occupied by the gas.
- P is the force per unit area exerted on a wall, due to the gas.
- N_m is a measure of quantity.
- T (absolute temperature) can be defined by the properties of an ideal gas. For a fixed amount of an ideal gas, any process (compress, expand, heat, cool) that leaves it at the same final P, V, results in the same $T \rightarrow$ Hence the properties of an ideal gas can be used as a temperature scale.

1 mole of gas (empirical unit) occupies 22.4 litres (1 litre $= 10^{-3}$ m^3) at Standard Temperature & Pressure (STP 0° C and 100kPa $\approx$ atmosphere) and contains an *Avogadro's number*, $N_A = 6.02 \times 10^{23}$ of particles.

For sufficiently dilute gases i.e. intermolecular distances are large, gases are usually close to ideal (at STP mean separation $\approx$ 33 Å). The **equation of state** is an equation that links the state variables to describe the properties of matter.

2.2 Properties of Ideal Gases

AN IDEAL GAS IS A THEORETICAL GAS COMPOSED OF A SET OF RANDOMLY MOVING, NON-INTERACTING POINT PARTICLES. The ideal gas concept is useful because it obeys a simplified equation of state - the ideal gas law - and is amenable to analysis under *statistical mechanics* (though this aspect will generally not be covered in this course). The ideal gas law works best at high temperatures and low pressures i.e. when gas molecules are far apart and in rapid motion. Through mainly empirical means, a number of conclusions can be drawn concerning the behaviour of gases:

1. $P \propto 1/V$ for a fixed amount of gas at fixed temperature, usually written:

$$PV = constant \qquad \text{(Boyle's law)}$$

2. Volume increases linearly with temperature T (for fixed pressure)

$$V \propto T \qquad \text{(Charles'Law)}$$

3. Volume is proportional to the number of moles of a gas

$$V \propto N_m \qquad \text{(Avogadro's Law)}$$

4. Pressure increases linearly with temperature (for fixed volume of gas)

$$P \propto T \qquad \text{(Gay-Lussac Law)}$$

5. For a homogenous mixture of different gases, pressure increases linearly with overall amount of material (for fixed temperature and volume)

$$P \propto (P_{m1} + P_{m2}) \qquad \text{(Dalton's Law of partial pressures)}$$

By combining $1, 2, \&3$ we obtain the **Ideal Gas Equation of State**:

$$\boxed{PV = N_m RT} \tag{1}$$

where R is a proportionality constant. You might expect this value to be different for different gases but it turns out that at high enough temperature and low enough pressure, R has the same value for *all* gases. It is called the **gas constant** and has a numerical value of $R = 8.31\,\mathrm{JK}^{-1} \cdot \mathrm{mol}^{-1}$. Thus for 1 mole $PV = RT$.

The mass density ρ can also be obtained from the ideal gas equation and expressed in terms of pressure and temperature to give: $\rho = \frac{m}{V} = \frac{MP}{RT}$.

2.3 *Kinetic Theory*

KINETIC THEORY CAN BE USED TO DESCRIBE THE PROPERTIES OF AN IDEAL GAS in terms of moving particles of number density n. It is applicable when n is such that the distance between the particles is very large in comparison to their size. One hallmark of kinetic theory is its ability to describe the pressure of an ideal gas. In the previous section, derivation of the ideal gas law relied on experimental data in order to establish the relationship between the gas variables; the kinetic theory description of pressure relies on classical mechanics and a microscopic description of the system. We start by making some key assumptions, primarily that the particles:

- are point particles (and for now monoatomic),
- don't interact (low number density → particles are far apart and experience no interatomic potential),
- have elastic collisions with walls and each other.

Pressure arises from the collisions of gas particles with the walls of the container; therefore to describe pressure using gas kinetic theory we must consider what occurs during a collision between a gas particle and the wall. Due to conservation of momentum, any change in particle linear momentum must result in an equal and opposite change of momentum of the container wall. A single collision is depicted in figure 2 below:

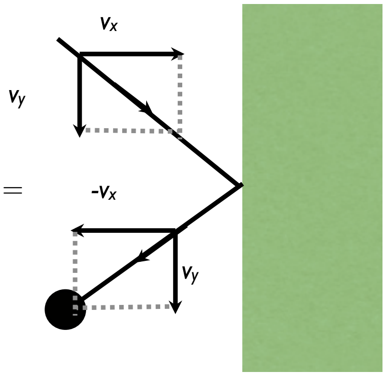

Figure 2: v_x reverses sign, v_y and v_z unchanged

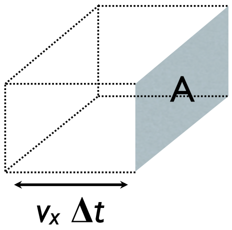

Figure 3: particles travelling toward wall

$\Delta p = |\text{momentum}|$ to wall at each collision $= |\text{mom. change of particle}| = 2m|v_x|$

Let N_{coll} be the number of particles hitting the wall in time Δt. Only particles within distance $|v_x|\Delta t$ reach wall during this time Δt. We also note that:

1. volume of particles capable of reaching the wall $= A|v_x|\Delta t$,
2. number density $n = N/V$ (= number of particles/volume occupied), and
3. On average, only half the particles are travelling towards the wall (other half will be travelling away!)

So $N_{coll} = A|v_x|\Delta t * n * \frac{1}{2}$

$\therefore$ $F = N\Delta p/\Delta t = N_{coll} * 2m|v_x|/\Delta t = A|v_x|\Delta t * n * \frac{1}{2} * 2m|v_x|/\Delta t = A * n * m|v_x|^2$

and pressure $P = F/A = nm|v_x|^2$

However, a typical gas will have a range of v_x, and so we need to replace $|v_x|^2$, with the MEAN SQUARE value $< v_x^2 >$. We also need to average the contribution for each particle so the **Kinetic theory pressure is given by**

$$\boxed{P = \frac{Nm}{V} < v_x^2 >} \qquad (2)$$

2.4 *Internal Energy*

Internal energy can be considered as the energy associated with the random, disordered motion of molecules. It is separated in scale from the *macroscopic* ordered energy associated with the bulk movement of objects. As such:

Internal energy = total energy of particles $= U = N < \epsilon >$, where $< \epsilon >$ is the **mean energy per particle**. For most cases in thermodynamics it usually not necessary to consider all energies belonging to the total intrinsic energy of a sample system, such as the energy given by the equivalence of mass - mainly because thermodynamics is chiefly concerned only with *changes* in the internal energy.

For non-interacting particles P. E. = 0, so,

$$\begin{aligned} <\epsilon> = <\tfrac{1}{2}mv^2> &= (1/N)\sum \tfrac{1}{2}mv^2 \qquad \text{(sum over all particles)} \\ &= (1/N)\tfrac{1}{2}m\sum(v_x^2+v_y^2+v_z^2) \\ &= \tfrac{1}{2}m(<v_x^2>+<v_y^2>+<v_z^2>) \end{aligned}$$

N.B. $(<v_x^2>=\sum v_x^2/N \ etc.)$
but by symmetry → $<v_x^2> = <v_y^2> = <v_z^2>$, so

$$<\epsilon> = \tfrac{3}{2}m<v_x^2>$$

$$U = \tfrac{3}{2}Nm<v_x^2> = \tfrac{3}{2}PV$$

Alternate equation of state

$$\boxed{PV = \tfrac{2}{3}\,U} \qquad (3)$$

This implies for an ideal gas, the internal energy can be written as a function of temperature alone, using $PV = \mathcal{N}_m RT$:

Internal energy monoatomic gas

$$\boxed{U(T) = \tfrac{3}{2}\mathcal{N}_m RT} \qquad (4)$$

2.5 *Equipartition of Energy*

WE EXPECT THAT ON AVERAGE, ENERGY WILL BE PARTITIONED BETWEEN ATOMS EQUALLY. If the total internal energy is given by $U = N<\epsilon>$, then this implies that the average energy of the gas molecule is,

$$<\epsilon> = U/N = \tfrac{3}{2}\mathcal{N}_m RT/N$$

Since one mole of a substance contains an Avogadro's Number N_A of particles, then $\mathcal{N}_m/N = 1/N_A$. So

$$<\epsilon> = U/N = \tfrac{3}{2}(R/N_A)T$$

But $R/N_A = 8.314/(6.02\times10^{23}) = 1.381\times10^{-23}\ \mathrm{JK^{-1}} = k_B$ Boltzmann's constant

$$<\epsilon> = \tfrac{3}{2}k_BT$$

Since each translational degree of freedom (x, y and z) contributes equally, the average energy per particle associated with each degree of freedom is $\frac{1}{2}k_BT$ – (i.e. energy is equally partitioned).

The situation is more complicated for non-monoatomic gases; in that case if there are n_d degrees of freedom, then

Equipartition of energy

$$\boxed{< \epsilon >= \frac{1}{2} n_d k_B T}$$

For a monotonic ideal gas (that has just three translational degrees of freedom), the internal energy can thus be written $U = \frac{3}{2} N k_B T$, and the ideal gas equation of state can also be written in terms of the number of particles:

Ideal gas equation

$$\boxed{PV = N k_B T}$$

The equation above establishes directly the relationship between *microscopic* behaviour of individual gas particles and the *macroscopic* bulk properties of matter. What's more, the ideal gas equation of state that was initially established through empirical means (experimentally), has now been derived purely from classical mechanics and kinetic theory.

3 *First Law of Thermodynamics*

3.1 *Thermodynamic terminology*

THERMODYNAMICS IS A PURELY MACROSCOPIC THEORY OF THE PROPERTIES OF MATTER. The first law of thermodynamics is a statement of the principle of conservation of energy for thermodynamical systems. As such, it may be expressed by stating that **the change in energy of a system during any process is equal to the amount of energy the system receives from its' surroundings**
We will proceed to examine what this means mathematically but before doing so, more precise definitions of 'system', 'surroundings', and 'process' are required.

* *System* = a collection of particles (usually atoms or molecules) whose properties we are interested in
* *Surroundings* = anything outside of the system
* *Process* = means by which a system changes from one equilibrium to another

The interface between the system and surroundings is called a **boundary**. An **open system** is one in which both matter and energy (such as heat) can flow between the system and surroundings. A **closed system** is one in which matter cannot be exchanged between the system and its' surroundings; however, *energy* can still flow. An **isolated system** is one in which neither matter nor energy flows. In a purely mechanically conserved system, the energy is equal to the sum of the kinetic and potential energies. If left alone (that is, if external conditions remain unchanged) it will settle into equilibrium whereby macroscopic properties (e.g. P, T) do not change. In fact **thermodynamic equilibrium** refers to a condition in which equilibrium exists wrt P, T, and concentration. For instance, a gas enclosed within a container of constant volume is in equilibrium when the pressure of the gas is constant and the temperature of the gas is equal to that of it's surroundings. We can deduce therefore that the energy of a system is basically a function of its' dynamical state.

Often we will consider a process that takes a system from an initial state to a final state through a succession of intermediate states; it is said to be **reversible** when the successive states are at equilibrium and also differ by infinitesimal amounts. In practice this can be realised by changing the external conditions so slowly that the system has time to adjust itself gradually to the altered conditions. For example, we could produce a reversible compression of a gas by en-

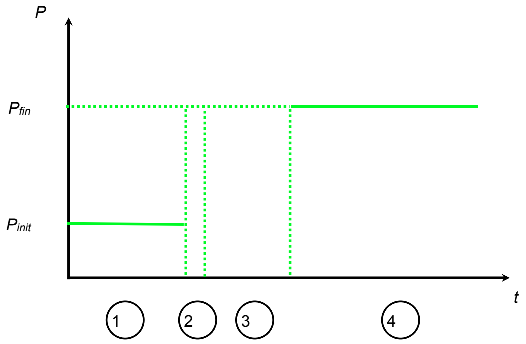

Figure 4: Rapid compression 1. initial equilibrium, 2. rapid compression, 3. gas settles into equilibrium, 4. new equilibrium

closing it in a cylinder with a movable piston and shifting the piston inward very slowly. Under such conditions this process is known as a **quasistatic process**.

The system might not necessarily be in equilibrium *during* a process however, consider our enclosed gas; if we were to shift the piston quickly, rapid compression heating of the gaseous mass would occur and the intermediate states would no longer be in equilibrium. This process therefore could not be considered reversible; it is illustrated in figure 4 where the system changes during stages 2-3 and is now non-uniform → P not well defined.

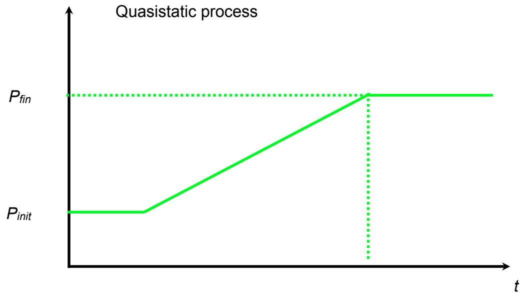

Figure 5: Quasistatic process: system stays approximately in equilibrium e.g. very slow compression (pushing a piston slowly)

3.2 Zeroth Law of Thermodynamics

The zeroth law can be stated as follows: *If a system C is in thermal equilibrium with both system A and system B, then system A is also in thermal equilibrium with system B.*

The zeroth law tells us that we can determine if two systems are in thermal equilibrium without bringing them into contact. It allows T dependent devices (thermometers) to define an absolute scale of temperature - since the device once in equilibrium with system, also measures the temperature of the system.

3.3 Heat

If two systems are in contact but are not in thermal equilibrium (i.e. there is a temperature difference), then heat will *flow* across the boundary between them. Heat always flows spontaneously from regions of high temperature to regions of low temperature. If the temperature of the surroundings is lowered during a process then Q is positive; if it is raised, Q is negative. It is common to think that if Q is positive, heat is withdrawn from the surroundings and deposited into the system, and vice-versa. There are three methods of heat transfer:
(1) conduction heat transported via collisions of particles.

$$\boxed{\frac{\Delta Q}{\Delta t} = \frac{\kappa\, A\, \Delta T}{L}}$$

κ= thermal conductivity $(Wm^{-1}K^{-1})$, A = cross-sectional area, and L = length of conductor.

(2) convection - hot material carries energy with it as it moves - some of which is transferred upon collision with container walls or other particles [there is no simple formula which describes this process].

(3) radiation - All matter emits electromagnetic radiation when it has a temperature above absolute zero. This (black body) radiation represents a conversion of thermal energy into electromagnetic energy, and is therefore called **thermal radiation**.

$$\boxed{\frac{\Delta Q}{\Delta t} = \epsilon_s \sigma A \left(T^4 - T_0^4\right)}$$

Stefan-Boltzmann Law

ϵ_s = emissivity (takes values from 0 to 1), σ = Stefan-Boltzmann constant (5.67×10^{-8} J s^{-1} m^{-2} K^{-4}), A = area of radiating (or absorbing) surface, T_0 = temperature of surroundings.

For ordinary temperatures (less than red hot"), the radiation is in the infrared region of the electromagnetic spectrum. Joule showed that **heat** causes the same change in temperature as **work done** on the system (mechanical, electrical...) by equating the temperature change caused by both methods on water. *heat is therefore a form of energy.*

$m\,c\,\Delta T = \Delta Q$ or ΔW.

c is the *specific heat capacity* (or simply specific heat) and is sometimes replaced by the molar heat capacity C_m [we will explore this in section 3.3],

$\therefore \quad \Delta Q = N_m C_m \Delta T.$

To raise the temperature of 1kg of water by 1°C requires 4,200 J, so $c = 4.2 \times 10^3$ J kg^{-1} K^{-1}.

3.4 *First Law of Thermodynamics*

A more concise statement of the first law can now be formulated as follows:

$$\boxed{\textit{The internal energy, U, of an isolated system is constant}}$$

This might seem strange as it suggests that nothing happens in an isolated system. However, when a system is in contact with it's surroundings then the changes in U of both system *and* surroundings must be taken into account, and so ΔU_{total} is given by:

$$\boxed{\Delta U_{total} = \Delta U_{system} + \Delta U_{surroundings} = 0}$$

Therefore the first law becomes $\Delta U_{system} = -\Delta U_{surroundings}$. For any decrease of U_{system}, $U_{surroundings}$ must increase by *exactly* the same amount. For a closed system in which no chemical reactions or phase changes occur, energy can enter or leave a system in two ways (summarised below) and in both cases, energy spreads to other particles via collisions:

1. **Work**, W e.g. piston: Gas particles collide with moving piston → KE increases → energy into gas i.e. work = energy transfer due to *ordered* particles motion.
2. **Heat**, Q (place in contact with something hot): Gas particles collide with wall, some particles KE increases, some decrease, on average KE equalises with KE of container particles→ if container hotter, gas gains energy, if container cooler, gas loses energy.

Note the sign of the energy flow:
ΔQ = heat flow **INTO** system [$\Delta Q <$ 0 heat flows out of system.]
ΔW = Work done **ON** system [$\Delta W <$ system does work on outside world]
some disciplines (e.g. engineering) write ΔW = work done by system, i.e. $\Delta U = \Delta Q - \Delta W$

If the amount of energy (either work or heat or combination of both) put into a system is the same, then the temperature change and hence internal energy only depends on the initial and final states (i.e. $\Delta U = U_{fin} - U_{init}$), otherwise one could devise a perpetual motion machine! [Nb. We use ΔU without subscript to indicate a change in internal energy of the system]. This is a statement of energy conservation, therefore:

$\Delta U = \Delta Q + \Delta W$ 1^{st} Law of Thermodynamics

$$\boxed{\mathrm{d}U = \text{đ}Q + \text{đ}W}$$

differential form of the 1^{st} Law

3.5 *Quasistatic work*

THE FIRST LAW CAN ALSO BE EXPRESSED FOR AN IDEAL GAS. For *quasistatic compression* (see fig. 6): $F = (P + \Delta P)\,A$, where ΔP is average pressure change as piston moves an infinitesimally small distance Δx

$\Delta W = F\,\Delta x = P\,A\,\Delta x + A\,\Delta P\,\Delta x$

Take the limit $\Delta x \rightarrow dx$, then ignore 2nd term (2nd order of smallness), and using : $A\,\mathrm{d}x = -\mathrm{d}V$

$\mathrm{d}W = -P\,\mathrm{d}V$

For piston moving a finite distance, P changes throughout the compression, so

$$W_{\text{done on gas}} = -\int_{V_{\text{init}}}^{V_{\text{fin}}} P\,\mathrm{d}V$$

So for gases the first law becomes;

$$\boxed{\mathrm{d}U = \mathrm{d}Q - P\,\mathrm{d}V}$$

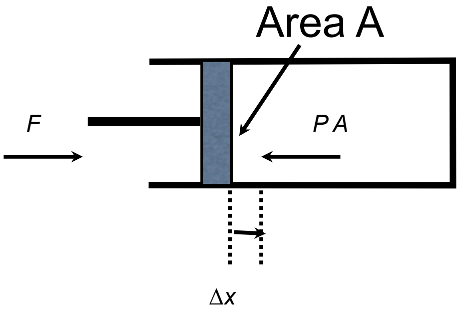

Figure 6: Piston, equilibrium $F = P * A$