1. Introduction

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Consider a volume of gas. We know that <u>real</u> systems are made up of molecules or atoms (particles) which are in a state of constant <u>random</u> motion e.g. Brownian motion. It is the motions of these individual particles which give rise to the <u>bulk</u> quantities we use in thermodynamics, e.g. Pressure, Internal Energy, etc.

1.1 Bulk Properties of a Gas

- Volume
- Pressure → Force per unit area. Arises from random motions.
 A particle collides with the wall of the container it rebounds so there is a change in momentum. Therefore it exerts a force on the wall. If we sum up all such individual forces over a period of time ∆t we get the total force on the wall and hence the pressure.
- Temperature \rightarrow related to random motions. High temperature \rightarrow we have particles with large E_k so they are moving at high speed. In solids, vibrational energy is important.
- Internal Energy U \rightarrow the sum of the energies associated with all the individual particles (Translational, rotational, vibrational, E_{n})

$$U = \sum \frac{mv^2}{2}$$

These quantities define the <u>state</u> of the <u>system</u> we are studying. The system is the thing we are studying (usually a mass of gas). Everything else is the <u>surroundings</u>.

A system can be <u>open</u> (physically connected to the surroundings) or <u>closed</u> (Not open; no physical exchange with the surroundings). It can also be <u>thermally isolated</u>, when it cannot exchange heat with the surroundings (aka <u>adiabatic</u>), or <u>thermally contacted</u> where it can exchange heat with the surroundings.

1.2 Equation of State

This is an equation which describes the state of the system in terms of bulk parameters (state variables). E.g.:

$$pV = nRT = Nk_BT$$

the Ideal Gas equation, or Van der Waal's equation:

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

where a and b are empirical constants, i.e. the values depend on the particular gas in the system.

A simple equation of state for a solid is

$$V = V_0 (1 + \beta (T - T_0) - k (P - P_0))$$

where β and k are constants which depend on the material.

<u>Simple</u> systems can be fully defined if we know any two of the state variables. The equation of state will give us the third providing the system is <u>thermal equilibrium</u>.

1.3 Standard Temperature and Pressure (STP)

This is when $T = 0^{\circ}C = 273.15k$ $P = 1atm = 10^{5}Pa$



1.5 Heat Capacities

This is the heat absorbed per unit rise in temperature (Kelvin)

Specific heat capacity $-c - JK^{-1}kg^{-1}$

Molar heat capacity $-C - JK^{-1}mol^{-1}$

1.6 Thermal Equilibrium

For a system in thermal equilibrium:

- Temperature does not vary with time

- Temperature is constant throughout the system

This implies that there is <u>no</u> current (flow) of heat through the system.



This also implies that there is no bulk movement of particles.



This strict definition of nothing changing makes it difficult in practice to achieve thermal equilibrium, e.g. the Earth's atmosphere. However, we can "zoom in" on a relatively small part of the atmosphere where thermal equilibrium is near enough true.

Thermal equilibrium is important as it means, provided pressure and volume are well defined, we can use equations of state (e.g. pV = nRT) to analyse the system.

On the microscopic level, thermal equilibrium means that the system is in a state of maximum randomness – this means we can apply statistical arguments to predict large scale behavior by considering individual particles and then averaging over large numbers.

2. Probability Distribution Functions

Say we are studying a volume of gas at thermal equilibrium. We know that particles in that gas are moving with random speeds and in random directions, sharing or transferring energy by collision. How can we find the average speed of a molecule or the average E_{μ} ?

If we know how E_k is distributed between molecules then we can find the total internal energy U.

We can look at an example which has nothing to do with thermal physics, to show how statistics can be applied to a whole range of problems, not just those presented in this course.

2.1 Gaussian Distribution

Say we are interested in the height of people. It is impractical to measure the height of everyone in the world so we take a sample – say 100. From this we can make a histogram to see what this tells us. We can group data into "bins". To start with, we will use 2cm wide bins. The letters below correspond with those on the graphs on pages 3 and 4 of Handout 1.

- a)We can see from the histogram that the mean height is ~ 180cm, and the graph is <u>not</u> smooth. Very few people are either very tall or very small.
- b)This shows us a larger sample. It shows that if we use a much larger sample, the slope of the histogram becomes smoother. N here = 1,000,000. Notice that the y-axis scale has changed.
- c)Instead of plotting frequency on the y-axis we could plot the probability that any one

measurement would lie in a particular bin, i.e. $y = \frac{N_i}{N} = P_i$ where N_i is the number of

measurements in the i^{th} bin, N the total number of measurements and P_i the probability that the measurement is in the i^{th} bin.

This graph looks the same as (b) apart from the numbers in the y-axis.

We say that the histogram has been <u>normalised</u> to a population of 1. (If we calculate the area under the histogram it equals 1).

- d)What happens if we use a bin size of 0.5cm? The bins get narrower and there are fewer measurements in each bin. We still have a very large number of measurements so the histogram looks smaller than the previous one but the y-axis numbers have changed compared to (b).
- e)Plot probability instead of frequency this means we have a graph which is still independent of the number of measurements, but we are still dependent on the bin size.
- f) It is more useful to plot the histogram so that the y-axis gives us the probability that a measurement lies in a bin of unit width (i.e. 1cm). We still have 0.5cm bins but even if we used 2cm bins again the y-axis stays the same.
- g)We can now make the bins infinitesimally small (providing N is still large) the histogram becomes a smooth line.

Note that the y-axis is the same as (f).

Now we are independent of N and Δh (bin size). If we know the function for this curve then we can apply the probabilities to any other ample of heights, e.g. if we have N=1000 measurements we could predict how many would lie in any given range of heights. In this case:

$$P(h) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\left(\frac{(h-\bar{h})^2}{2\sigma^2}\right)}$$

where P(h)dh is the probability that any one person has height in the range $h \rightarrow h + dh$.

P(h) is the probability per unit bin width. It has a unit of cm⁻¹.

The function has several names – the Normal, Gaussian or Bell curve. Any function which describes the probabilities for a particular situation is called a <u>probability distribution function</u>.

The properties of a probability distribution function P(x) can be summarised as follows: 1. The probability that a measurement of the quantity x will fall in the range of values

 $x_1 \rightarrow x_1 + dx$ is $P(x_1)dx$.

- 2. If we make N measurements of x then the number of these measurements which will fall into the range $x_1 \rightarrow x_1 + dx$ is $NP(x_1)dx$.
- 3. The probability that a measurement of x will have some value between $-\infty$ and $+\infty$ is 1 it definitely has some value!

This means that

$$\int_{-\infty}^{\infty} P(x) dx = 1$$

The area under the curve = 1

The sum of the individual probabilities = 1.

4. P(x)dx is dimensionless <u>but</u> the function P(x) has units $(x)^{-1}$.

Such a function is said to be normalised. We can normalise a function as follows:

Say
$$f(x) = Ae^{-\frac{(x-\bar{x})^2}{2\sigma^2}}$$

Let $\int_{-\infty}^{\infty} f(x) dx = 1$
 $\int_{-\infty}^{\infty} Ae^{-\frac{(x-\bar{x})^2}{2\sigma^2}} dx = 1$

Substitute $(x - \overline{x}) = u$ (to simplify the algebra) and use the standard integral

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

We get $A \int_{-\infty}^{\infty} e^{-\frac{u^2}{2\sigma^2}} du = 1$
Hence $A \sqrt{\frac{\pi}{\left(\frac{1}{2\sigma^2}\right)}} = 1$ so $A = \frac{1}{\sqrt{2\pi\sigma}}$.

2.2 Mean value

We know that the average or mean value of a set of measurements is given by

$$\overline{x} = \frac{1}{N} \sum x_i$$

(sum over all measurements), e.g. in heights example

$$\overline{h} = \frac{1}{100} \sum_{i=1}^{100} h_i$$

This quickly becomes impractical when N is large. We bin the data into bins of width Δx and find the mean value from

$$\overline{x} = \frac{1}{N} \sum \left(x_j N_j \right)$$

This time the sum is over the number of bins x_j is the average in the jth bin, and N_j is the number of measurements in the jth bin.

If we know the probability distribution function P(x) then $N_j = P(x_j)N\Delta x$.

The mean value of x is

$$\overline{x} = \frac{1}{N} \sum x_j N_j$$
$$= \frac{1}{N} \sum x_j N P(x_j) \Delta x$$
$$= \sum x_j P(x_j) \Delta x$$

If N is very large and we make the bins very small $(\Delta x \rightarrow dx)$

$$\overline{x} = \int_{-\infty}^{\infty} x P(x) dx$$

Note – in real situations we often only need to evaluate the integral from $0 \rightarrow \infty$, e.g. the heights example. There is no such thing as a negative height so

$$\overline{h} = \int_0^\infty h P(h) dh$$

This works for any function of P(x) e.g. we want to find $\overline{x^2}$.

$$\overline{x^2} = \int_{-\infty}^{\infty} x^2 P(x) dx$$

This works because P(x) is the same as $P(x^2)$.

2.3 Variance and Standard Deviation

We start by noting that any one measurement of a quantity x will differ from the mean value of a sample of N measurements by an amount $(x - \overline{x}) = d$. We can find the average value of this difference from

$$(\overline{d}) = S = \frac{1}{N} \sum_{i=1}^{N} (x_i - \overline{x})$$

However this is not a very practical way to measure the average difference since the positive and negative values of d will cancel each other out. Instead we consider the square of the difference

$$S^{2} = \frac{1}{N} \sum_{i=1}^{N} \left(x - \overline{x} \right)^{2}$$

If we let $N \rightarrow \infty$ then this quantity S^2 is usually called σ^2 – the <u>Variance</u> of the distribution. 68% of all measurements of x will lie within $\pm \sigma$ of \overline{x} . σ is called the <u>Standard Deviation</u>.

$$\sigma^{2} = \frac{1}{N} \sum_{i=1}^{N} \left(x_{i}^{2} - 2x_{i}\overline{x} + \overline{x}^{2} \right) = \frac{1}{N} \sum x_{i}^{2} - \frac{1}{N} \sum 2x_{i}\overline{x} + \frac{1}{N} \sum \overline{x}^{2}$$
$$= \overline{x^{2}} - \frac{2\overline{x}}{N} \sum x_{i} + \frac{1}{N} \left(N\overline{x}^{2} \right)$$
$$= \overline{x^{2}} - 2\overline{x}^{2} + \overline{x}^{2} = \overline{x^{2}} - \overline{x}^{2}$$
Note $\overline{x^{2}} \neq \overline{x}^{2}$.

2.4 Probability Distribution Functions

Now we look at some useful distribution functions which can be applied to situations in all areas of physics (not just thermal physics) and you will probably see them in lab.

2.4.1 Gaussian Distribution

$$P(x) = \frac{1}{\sqrt{2\pi\sigma}} e^{-\left(\frac{\left(x-\bar{x}\right)^2}{2\sigma^2}\right)}$$

Remember a normalised distribution function has $\int_{-\infty}^{\infty} P(x) dx = 1$.

This is used when x is a real number (not an integer), and any single measurement of x is

as likely to be larger than smaller than x.

See Page 6, Handout 1 for graphs of this distribution.

2.4.2. Binomial Distribution

This applies to processes which can have two possible outcomes, which are usually called "true" or "false". The classic example would be tossing a coin. Heads \rightarrow true, tails \rightarrow false. P = 0.5 for both.

 $P_{true} = 0.5$

Binomial also applies just as well in cases where $P_{true} \neq 0.5$ e.g. throwing a dice:

Let true be a $1 \rightarrow P_1 = \frac{1}{6}$.

Let false be 2,3,4,5, or 6 (i.e. false, not 1). $P_{\text{false}} = \frac{5}{6}$.

Binomial can tell us what to expect if we have more than one throw (trial). Say we throw six times. What is the probability that we throw exactly two ones? We split the problem into two parts – firstly combinations i.e. the number of ways to throw two ones from six throws.

TTFFFF TFTFFF TFFTFF Ftc

There are 15 ways in total. In shorthand we write:

 ${}^{n}C_{r} \rightarrow$ The number of ways to get r true results from n trials.

$${}^{n}C_{r} = \frac{n!}{r!(n-r)!}$$

In our example:

$${}^{6}C_{2} = \frac{6!}{2!(6-2)!} = 15$$

Secondly find the probability that we actually get one of these combinations.

One way e.g. is TTFFFF. Probability = $\frac{1}{6}x\frac{1}{6}x\frac{5}{6}x\frac{5}{6}x\frac{5}{6}x\frac{5}{6}$ ie. $P_{true}{}^{r}x(1-p_{true})^{(n-r)}$

In our case:
$$\left(\frac{1}{6}\right)^2 \left(\frac{5}{6}\right)^4 = 0.01339$$

Finally we combine the first and second steps to get the probability of obtaining exactly r successes (true outcomes) from n trials is

$$\mathbf{P}(r/n;p) = {}^{n}C_{r}p^{r}(1-p)^{\left[n-r\right]}$$

In our example $P(2/6; \frac{1}{6}) = {}^{6}C_{2}(\frac{1}{6})^{2}(\frac{5}{6})^{4} = 0.2$.

See page 7 of Handout 1 for graphs of this function. Note as n increases the shape of P(x) becomes more Gaussian-like. In the second column true is throwing a 2,3,4,5 or 6.

2.4.3. Poisson distribution

$$P(r;\lambda) = \frac{\lambda^r e^{-\lambda}}{r!}$$

This is a mathematical approximation to the Binomial distribution in the case where $n \rightarrow \infty$, $P \rightarrow 0$ (but *np* stays constant).

$$P(r) \to \frac{n^2}{r!} p^r e^{-np}$$

If we write $np = \lambda$ (= mean value) then we get the Poisson distribution.

An example would be detecting radiation:

We know a source emits 10 γ rays per second. We don't know n – the number of times the atom has tried to emit a γ ray.

$$P(0) = \frac{1xe^{-10}}{1} = 4.5x10^{-5}$$
$$P(12) = \frac{10^{12}e^{-10}}{12!} = 0.09$$

NB: Poisson \rightarrow Gaussian for large λ .

2.5 Central Limit Theorem (CLT)

Or why everything in lab is Gaussian. Suppose we are measuring the current in a circuit using an analogue ammeter. There are several factors which affect our measurement of *I* : A) Parallax error in reading small needle position

B) Needle wobbles

C) Rounding error etc.

$$I = I_{true} + A + B + C + \dots$$

Our value of I contains a combination of all these effects. To find the uncertainty in I we should consider the uncertainly of each factor and combining them using error propagation formula.

The central limit theorem tells us that a measurement which depends on lots of independent factors will tend to follow a Gaussian distribution. If we plot several measurements of I the distribution curve would have a Gaussian shape. This is true even if the individual effects don't have a Gaussian distribution.

The CLT also states that:

$$\overline{x} = \sum \mu_i$$

where μ_i is the mean value of the ith factor.

$$\overline{I} = \left(I_{true} + \overline{A} + \overline{B} + \overline{C}\right)$$

2.6 Two or more independent probabilities

Suppose we consider a particle with velocity

 $\underline{v} = v_x \hat{\underline{i}} + v_y \hat{\underline{j}} + v_z \hat{\underline{k}}$

What is the probability that the particle has speed v_x in the x-direction and, v_y in the y-

direction <u>and</u> v_{z} in the z-direction?

(By v_x we actually mean the velocity is in the range $v_x = v_x + dv_x$ etc.)

We note that v_x , v_y and v_z are independent.

$$P(\underline{v})d\underline{v} = P(V_x, V_y V_z)dv_x dv_y dv_z = P(v_x)dv_x P(v_y)dv_y P(V_z)dv_z$$

We can separate the total probability of three things into the product of the three (or n) separate probabilities.

e.g. in Binomial Distribution:

Probability of TTFFFF = $\frac{1}{6} \frac{1}{6} \frac{5}{6} \frac{5}{6} \frac{5}{6} \frac{5}{6}$. Each of the six throws is independent so the total probability is equal to the product of each individual probability.

probability is equal to the product of each individual probability.

3. Boltzmann Distribution

3.1 Boltzmann Factor

This distribution is particularly important in thermal physics – it tells us how the energies of particles in a system <u>at thermal equilibrium</u> are distributed. The probability that a particle in such a system (e.g. air in a beaker etc.) has energy E (in the range $E_1 \rightarrow E_1 + dE$) depends on:

The number of ways the particle can have this energy (these ways are called states)
 The probability that it is in a certain state

E.g. in a simple monatomic system the particles all have E_k given by $E_k = \frac{1}{2}m\underline{v}^2$. There are

many ways (states) that it can have this energy – depending on the direction of \underline{v} .

 \underline{v}_1 and \underline{v}_2 represent two different states, but if $|\underline{v}_1| = |\underline{v}_2|$ then $E_1 = E_2$.

The probability that a particle has energy $E \rightarrow P(E)dE$ decreases as E increases and increases as T increases.

Boltzmann showed that $P(E) \propto e^{-\frac{E}{kT}}$.

The term e^{-kT} is called a Boltzmann factor.

E can be any type of energy – translational, rotational, vibrational, potential, gravitational, electrical etc.

k is Boltzmann's constant, and has a value of $1.38 \times 10^{-23} J k^{-1}$

T is the temperature of the system in <u>Kelvin</u>.

3.2 Boltzmann Distribution

$$P(E)dE \propto e^{-\frac{E}{kT}}dE$$

We can use this relation to investigate the way that the speeds of molecules are distributed. We know the particles have E_k due to the random motion and also have E_p due to

interactions with other particles, also excited states – extra energy is stored in the excited state.

Here we consider an ideal gas, therefore there is no intermolecular energies etc. All the energy is $E_{\kappa} = \frac{1}{2}mv^2$. We know that the speed of a molecule can vary continuously and is independent of position. The probability that a particle has energy E is proportional to the Boltzmann Factor $P(E) \propto e^{-\frac{E}{kT}}$.

One way the particle has this energy is if its velocity components are v_{x1}, v_{y1}, v_{z1} and

$$E_{1} = \frac{1}{2}mv_{1}^{2} = \frac{1}{2}m(v_{x1}^{2} + v_{y1}^{2} + v_{z1}^{2}).$$

Thus $P(E_{1})dE \propto P(E_{x1}, E_{y1}, E_{z1})dE_{x}dE_{y}dE_{z}.$
$$e^{-\frac{E_{1}}{kT}}dE \propto e^{-\frac{mv_{1}^{2}}{2kT}}dE = e^{-\frac{mv_{x1}}{2kT}}e^{-\frac{mv_{y1}}{2kT}}e^{-\frac{mv_{z1}}{2kT}}dE_{x}dE_{y}dE_{z}.$$

If we are only interested in the speed in the x-direction, we can separate this part out – because x, y and z directions are independent of each other.

$$P(E_x)dE_x \propto e^{-\frac{mv_{x1}^2}{2kT}}dE_x$$

Hence $P(v_{x1})dv_x \propto e^{\frac{-mv_{x1}^2}{2kT}}dv_x = Ae^{-\frac{mv_{x1}^2}{2kT}}dv_x$ Normalise to find $A = \sqrt{\frac{m}{2\pi kT}}$

Therefore
$$P(v_x)dv = \sqrt{\frac{m}{2\pi kT}}e^{-\frac{mv_x^2}{2kT}}dv_x$$

Note that this function has the form of a Gaussian centred on $v_x = 0$. $\sigma = \sqrt{\frac{kT}{m}}$

- \rightarrow Most probable value of v_x is 0.
- \rightarrow Mean value of $v_x = 0$ (Particle is as likely to be moving in +x as -x direction)
- → Large positive or negative values of v_x are unlikely (few molecules have very high speeds) → If T increases then more molecules will have higher speeds (σ increases).

→ The mean value of $v_x^2 \neq 0$ which means that the mean KE (from motion in x direction) $\neq 0$ Similarly:

$$P(v_y)dv_y = Ae^{-\frac{mv_y^2}{2kT}}dv_y$$
$$P(v_z)dv_z = Ae^{-\frac{mv_z^2}{2kT}}dv_z$$
where $A = \sqrt{\frac{m}{2\pi kT}}$ in each case.

Thus the probability that the particle is in the particular energy state E_1 defined by a velocity vector \underline{v}_1 is:

$$P(v_x, v_y, v_z) dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} dv_x dv_y dv_z$$

(Remember that there are other states with the same energy but different velocity vectors) The Boltzmann Distribution also applies to situations involving gravitational potential energy. E.g. consider a column of gas in thermal equilibrium at the Earth's surface.



What is the distribution of molecules as a function of height z? Provided z is small compared to the radius of the Earth, we can write the E_P of a molecule at height z above the earth's surface as E = mgz.

Boltzmann Factor is
$$e^{-\frac{mgz}{kT}}$$

The probability that one particular molecule is at height z_1 therefore $E_1 = mgz_1$

is
$$P(z_1)dz = Ae^{-\frac{mgz}{kT}}dz$$
.
We can normalise to find A.
$$\int_{-\infty}^{\infty} Ae^{-\frac{mgz}{kT}}dz = 1$$
$$A = \frac{mg}{kT}$$

$$P(z)z = -\frac{mg}{kT}e^{-\frac{mgz}{kT}}dz$$

This is an exponential distribution.

We can take this further and investigate how the density of the gas varies with height. The number of molecules which lie in a small slab of gas, dz thick, at height z_1 is given by the total number of molecules in the column N times the probability that the molecule has height z_1 .

$$N_{z_1} = N \frac{mg}{kT} e^{-\frac{mgz_1}{kT}} dz$$

Density is $\rho = \frac{Nm}{V}$, so in our slab of gas (volume = Adz) which is

$$\rho(z_1) = \frac{N_z m}{A dz} = \frac{N m g}{kT} e^{-\frac{m g z_1}{kT}} dz \frac{m}{A dz}$$

Now find $\rho(z=0)$.

$$\rho(0) = \frac{N \frac{mg}{kT} dz \frac{m}{Adz}}{\frac{mg}{kT}} = \rho_0$$

Hence $\rho_z = \rho_o e^{-kT}$ (Also exponential as expected)

<u>3.3 Scale Height</u>

We can define the scale height of our model atmosphere to be

$$z_o = \frac{kT}{mg}$$
, then $\rho(z) = \rho_o e^{-\frac{z}{z_o}}$.

If we compare the density at z with the density at $(z + z_0)$ then

$$\frac{\rho(z+z_o)}{\rho(z)}=e^{-1}.$$

I.e. density drops by a factor e for every rise z_o in the height.

Now we calculate pressure (p) as a function of height (z).

Firstly we note that p(z) > p(z + dz) because there is an extra layer dz thick pressing down.

This layer adds an amount of pressure dp.

The mass of gas in this layer is p(z)V = p(z)Adz. Hence the force exerted

is
$$F = mg = \rho(z) A dzg$$
.

Pressure
$$\left(P = \frac{F}{A}\right)$$
 contributed by this layer is $dp = \rho(z)gdz$.

Now we can calculate the total pressure at height z from the sum of all contributions to the pressure from heights > z.

$$p(z) = \int_{z}^{\infty} dp = \int_{z}^{\infty} \rho(z) g dz = \rho_{o} g \int_{z}^{\infty} e^{\frac{-mgz}{kT}} dz = \rho_{o} g \left[\frac{-kT}{mg} e^{-\frac{mgz}{kT}} \right]_{z}^{\infty} = \rho_{o} g \frac{kT}{mg} e^{-\frac{mgz}{kT}} = \frac{kT}{m} \rho(z) \operatorname{No}$$

w substitute $\rho(z) = \frac{N_z m}{V}$.

i.e.
$$p = \frac{kT}{m} \frac{Nm}{V}$$

pV = NkT - ideal gas equation of state, as expected for an ideal gas in thermal equilibrium.

3.4 A Quantized Example of the Boltzmann Distribution

The Boltzmann Distribution works just as well for quantized systems (e.g. electron levels in a Hydrogen atom).

Here we consider a very simple quantized system. Each particle can take one of three possible energy levels.

 $E_o = 0$ $E_1 = \frac{1}{2}eV$

 $E_2 = 1 eV$

We can predict the properties of this system using the Boltzmann Distribution. Assume the system is in thermal equilibrium at T = 6000k (e.g. sun's surface). So

$$P(E) = Ae^{-\frac{E}{kT}}$$

Here kT = 0.5175 eV. This distribution is not normalised – we can't normalise by

using	P(E)dE = 1, because E does not vary continuously – instead use	P(E) = 1.
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Level	Energy (eV)	$e^{-\frac{E}{kt}}$
E _o	0	1
E ₁	0.5	0.3806
E ₂	1	0.1448

Therefore
$$\sum P(E) = A + 0.3806A + 0.1448A = 1.5254A = 1, A = 0.656$$

Now we can calculate P(E) for each level.

n	P(E)	EP(E)
0	0.656	0
1	0.250	0.125
2	0.094	0.094

We can calculate $\overline{E} = \sum EP(E) = 0.219eV$.

Note – most particles do not have enough energy to be in n = 2 or n = 1 levels. In general we only get significant excitation of an energy level if $kT \approx (E_n - E_o)$.

(In this case $kT \approx 0.51 \approx E_1 - E_0$ so the first level is starting to become populated.)

We can find the total internal energy U of the system from U = NE. If we have 1 mole of this stuff at T = 6000k then U = 21kJ.

The relative population densities can be found as follows: for N molecules

$$N(0) = NP(0) \propto Ne^{-\frac{E_0}{kT}}$$
$$N(1) = NP(1) \propto Ne^{-\frac{E_1}{kT}} = Ne^{-\frac{(E_o + \Delta E)}{kT}}$$

where ΔE is E(1) - E(0).

So
$$\frac{N(0)}{N(1)} = e^{\frac{\Delta E}{kT}}$$

As we add heat at a constant rate more particles will move into n=1 level so $\frac{N(0)}{N(1)}$ will

decrease.

This type of system can help us to understand some other types of physical phenomena, e.g. chemical reactions. Often a reaction only occurs if the reacting molecule is in a certain excited state. We can make the reaction go faster by increasing T - this increases the number of reacting molecules in the excited state.

4. Maxwell Boltzmann Speed Distribution

It was originally thought that all particles in a gas at Thermal Equilibrium, at temperature T, had the same speed. In 1859 Maxwell analysed the collision processes and derived the speed distribution function. In 1877 Boltzmann used statistical mechanics to get the same result (from the distribution of energies).

A molecule in a gas at Thermal Equilibrium has three independent E_k components associated with the translational motion (in x, y and z directions); 3 degrees of freedom. We can write down the probability that a particle has velocity component v_x ;

$$P(V_x)dv_x = Ae^{-\frac{mv_x}{2kT}}dv_x$$

and similarly

$$P(V_{y})dv_{y} = Ae^{-\frac{mv_{y}}{2kT}}dv_{y}$$
$$P(V_{z})dv_{z} = Ae^{-\frac{mv_{z}}{2kT}}dv_{z}$$

Remember that $A = \sqrt{\frac{m}{2\pi kT}}$.

We can now write the probability that a molecule has a particular velocity vector $\underline{v} = v_x \hat{\underline{i}} + v_y \hat{j} + v_z \hat{\underline{k}}$;

$$P(\underline{v})dv_{x}dv_{y}dv_{z} = A^{3}e^{-\frac{mv^{2}}{2kT}}dv_{x}dv_{y}dv_{z}$$

 $(dv_x dv_v dv_z \text{ is sometimes written } d^3v)$

In this section we are only interested in the speed of the molecule, not the direction. If we plot every possible vector with magnitude $v = |\underline{v}|$ then these vectors will map out a sphere of radius v. This tells us that the number of different velocity vectors with the same magnitude v is proportional to the surface area of the sphere $4\pi v^2$. Since we actually mean vectors with speed in the small range $v \rightarrow v + dv$ so in this case vectors map out a spherical shell of thickness dv. Therefore the number of vectors is proportional to $4\pi v^2 dv$.

The probability that a particle has speed v is given by the number of ways times the probability of one way.

$$P(v)dv = B4\pi v^2 A^3 e^{-\frac{mv^2}{2kT}}dv.$$

We can normalise to find (A^3B) to get

$$P(v)dv = \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\frac{mv^2}{2kT}} dv.$$

This function is <u>not</u> symmetric, centred on zero or Gaussian. See Handout 2, Page 3 for a spherical polar coordinate derivation of this.

4.1 Most Probable Speed

To do this, find v at the top of the curve. So we want to calculate $\frac{dP}{dv} = 0$ and check $\frac{d^2P}{dv^2} < 0$.

Simplified,
$$P(v) = Av^2 e^{-Bv^2}$$
.

$$\frac{dP}{dv} = Av^2 (-2Bv) e^{-Bv^2} + A2v e^{-Bv^2} = 0$$

$$v_{mp}^2 = 1$$

$$v_{mp} = \sqrt{\frac{1}{B}} = \sqrt{\frac{2kT}{m}}$$

Example for student to prove that $\frac{d^2 P}{dv^2} < 0$.

 $\frac{4.2 \text{ Mean Speed}}{\overline{v} = \int_0^\infty v P(v) dv} = \int_0^\infty A v^3 e^{-Bv^2} dv$

Substitute
$$x = v^2$$

 $\overline{v} = \frac{A}{2} \int_0^\infty x e^{-Bx} dx$
Integrate by parts:
 $u = x$
 $dw = e^{-Bx} dx$
 $\frac{A}{2} \left[\frac{-x}{B} e^{-Bx} \right]_0^\infty + \frac{A}{2B} \int_0^\infty e^{-bx} dx = \frac{A}{2B^2} = \sqrt{\frac{8kT}{\pi m}}$

Example for student to check this. Note that this is different to the most probable speed.

$$\frac{\sqrt{v^2}}{v^2} = \int_0^\infty v^2 P(v) dv = \int_0^\infty A v^4 e^{-Bv^2} dv$$

See tutorial sheet for maths.

$$\overline{v^2} = \frac{3kT}{m}$$
$$\sqrt{\overline{v^2}} = v_{rms} = \sqrt{\frac{3kT}{m}}$$

In a simple system, particles all have the same mass so we can find the average E_k in a gas.

$$\overline{E_{\kappa}} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

E.g. For argon at room temperature 293K (atomic weight 40):

 $v_{mp} = 348 m s^{-1}$

$$v = 393 m s^{-1}$$

 $v_{rms} = 426 m s^{-1}$

http://lorax.chem.upenn.edu/Education/MB/applet.html

4.4 Observation of MB Distribution

The Maxwell-Boltzmann distribution can be measured directly as follows:

An oven heats some solid material until it vaporises – to give a Maxwell-Boltzmann distribution of speeds. Particles have a known mass, and the gas is at a known temperature. The particles escape in a beam through a small hole in the oven. The beam will contain particles with a range of speeds. (Note this is actually not Maxwell-Boltzmann – see section 8 – effusion). The entire apparatus is in a vacuum to avoid the particles in the beam scattering off air molecules.

Beam hits a rotating wheel A. A small burst of particles will get through the slit. This burst still contains a full range of speeds. The burst travels distance L and hits wheel B, which also has a slit offset by angle θ from A. Most particles hit B but a few get through the slit. This happens

when $t_{AB} = \frac{L}{V} = \frac{\theta}{\omega}$ i.e. $V = \frac{L\omega}{\theta}$. So by varying ω we can measure the number of particles in

the beam with speed v, and plot N_V vs. V.

See page 2, Handout 2 for a picture of this setup.

5. Thermal Radiation and the Planck Distribution

Any body or system contains moving particles, therefore there are accelerating charges. We know that an accelerating charge emits EM radiation, so any system of particles with T > 0k will emit EM radiation. The spectrum of this radiation depends on the temperature of the system and the nature of the surface.

Terminology:

 $I(\lambda)$ - Spectral emittance or spectral energy density. It has units of Power/Unit area/Unit

wavelength.
$$(Wm^{-2})$$

 $I = \int_0^\infty I(\lambda) d\lambda$ - Intensity. It has units of power / unit area. (Wm^{-2})

A black body is a perfect emitter and absorber of radiation.. Any other body will emit / absorb less efficiently. To make one, get a cavity at temperature T and make a <u>small</u> hole through which radiation can escape without affecting the thermal equilibrium. At room temperature the hole would look black because the peak intensity (spectral emittance) emitted is $\sim \lambda = 10 \mu m$.

5. 1 Stefan's Law

In 1879, Stefan found that the total power emitted per unit area by a black body (intensity) is $I = \sigma T^4$ where $\sigma = 5.67 \times 10^{-8} W k^{-4} m^{-2}$ - Stefan's constant.

We can assume that the sun is approximately a black body with a surface temperature of about 5800K. The intensity at the sun's surface is

$$I = \sigma T^4 = 64.2 MW m^{-2}$$

The total power emitted by the sun is

$$P_{\odot} = I4\pi R_{\odot}^{2} = I$$
 times the surface area = $3.9x10^{26}W$.

At a distance of $1AU = 1.5 \times 10^{11} m$ the intensity of the sun's radiation is

$$\frac{P_{\odot}}{4\pi r^2} = \frac{I4\pi R_{\odot}^2}{4\pi r^2} = \frac{IR_{\odot}^2}{r^2} = 1.4 kW m^{-2}.$$

5.2 Wien's Law

Wien's Law (1893): as T increases, λ_m decreases (λ_m is the wavelength at the peak of the intensity distribution) such that $\lambda_m T = 2.9 \times 10^{-3} K.m$

If the temperature of the sun is about 5800K , we can find out $\lambda_{max} = 500 nm$,

5.3 Rayleigh – Jeans Approximation

1899 – The shape of $I(\lambda)$ as a function of wavelength was deduced experimentally but could not be explained theoretically.

In 1900, Rayleigh modelled black body radiation using standing waves. The method he used is as follows:

Step 1; find the number of waves in the black-body cavity per unit wavelength.

In a cavity of length a, waves with $\lambda = \frac{2a}{m}$ are allowed (see Page 5, handout 2). In a 3D cavity,

$$n = \left(\frac{8\pi V}{\lambda}\right) d\lambda \, .$$

n is the number of waves with a wavelength between λ and $\lambda + d\lambda$. The number of these waves which escape the black body cavity is given by the <u>Effusion</u> formula (Section 8).

The rate is

$$\frac{1}{4}n_d$$
cdA

 n_d - Number density of waves

c - Speed of Light

dA - Area of the hole through which they escape.

The number that escape per unit time per unit area is

$$\frac{1}{4}n_{d}c = \frac{1}{4}\left(\frac{8\pi}{\lambda^{4}}\right)cd\lambda$$

Step 2; Find the energy associated with each wave

Rayleigh assumed that the Theory of Equipartition (Section 6) holds for waves. This leads to the result that the energy in one wave = kT.

Step 3;

Putting the results from the first two steps together gives;

$$I_{RJ}\left(\lambda\right) = \frac{2\pi ckT}{\lambda^4} d\lambda$$

This works well to high frequencies, but does not work for low (< 60 microns) wavelength as it tends to infinity (the Ultraviolet catastrophe).

$$I_{RJ} = \int_0^\infty I_{RJ}(\lambda) d\lambda \to \infty$$

This means that you can't get Stefan's law. Also $I_{R,I}(\lambda)$ does not have a maximum, so

Wien's law cannot be derived from it. See pages 5 and 6, Handout 2.

5.4 Planck

Planck asked himself what the simplest mathematical change to this theory which would give the correct function for $I(\lambda)$. His answer was to quantize the energy in a wave, i.e.:

$$E = nhf$$
.

h was a "fudge factor" to get the numbers to come out right.

$$\overline{E} = \frac{hc}{\lambda} \left[e^{\frac{hc}{\lambda kT}} - 1 \right]^{-1}.$$

This gives us the Planck Distribution Function.

$$I(\lambda)d\lambda = \frac{2\pi hc^2}{\lambda^5} \left(\exp\left(\frac{hc}{\lambda kT}\right) - 1 \right)^{-1} d\lambda$$

See Page 4, Handout 2.

To derive Stefan's law from this, integrate the Planck function to find *I*.

$$I = \int_{0}^{\infty} \frac{2\pi hc^{2}}{\lambda^{5}} \left[e^{\frac{hc}{\lambda kT}} - 1 \right]^{-1} d\lambda$$

$$z = \frac{hc}{\lambda kT}$$

$$\lambda = \frac{hc}{zkT}$$

$$\frac{dz}{d\lambda} = -\frac{hc}{\lambda^{2}kT} = \frac{z}{\lambda}$$

$$d\lambda = -\frac{\lambda}{z} dz = \frac{-hc}{z^{2}kT} dz$$

$$I = 2\pi hc^{2} \int_{z=\infty}^{z=0} \left(\frac{kTz}{hc} \right)^{5} \left[e^{z} - 1 \right] \left(\frac{-kc}{z^{2}kT} \right) dz = 2\pi hc^{2} \left(\frac{kT}{hc} \right)^{4} \int_{z=0}^{z=\infty} z^{3} \left[e^{z} - 1 \right]^{-1} dz$$
Use the standard integral
$$\int_{0}^{\infty} z^{3} \left(e^{z} - 1 \right) dz = \frac{\pi^{4}}{15}$$

$$I = 2\pi hc^{2} \left(\frac{kT}{hc} \right)^{4} \frac{\pi^{4}}{15}$$

$$= \left(\frac{2}{15} \pi^{5} \frac{k^{4}}{h^{3}c^{2}} \right) T^{4}$$

$$= \sigma T^{4}$$

$$\sigma = 5.67 \times 10^{-8} Wm^{2} K^{-4}$$

To derive Wien's law, differentiate to find λ_{max} .

$$\frac{dI}{d\lambda} = \frac{2\pi hc^2}{\lambda^6} \left(e^{\frac{hc}{\lambda kT}} - 1 \right) \left[\frac{hc}{\lambda kT} e^{\frac{hc}{\lambda kT}} \left(e^{\frac{hc}{\lambda kT}} - 1 \right) - 5 \right]$$
$$\frac{dI}{dt} = 0 \text{ at } \lambda = \lambda_{max}.$$

$$\frac{1}{d\lambda} = 0$$
 at $\lambda = \lambda_{max}$

Therefore we need the square bracket to equal 0.

Use the substitution $z = \frac{hc}{\lambda_m kT}$ to get $z = 5 - 5e^{-z}$ after some algebra. It is easiest to solve this by trial and error.

We find

$$z = \frac{hc}{\lambda_m kT} = 4.965 \; .$$

Therefore

 $\lambda_{max}T = \frac{hc}{4.965k} = 2.9x10^{-3}mK$ Which is Wien's Law.

6. Classical Equipartition of Energy

Degrees of Freedom of a particle are the independent factors which define how this particle is. For example, in a monatomic ideal gas a particle can be defined by its position (x, y, z) and its velocity. (v_x, v_y, v_z) . This means there are 6 separate independent values to describe the particle – in other words, 6 degrees of freedom.

Only quadratic degrees of freedom can contribute to energy, therefore

$$E_{k} = \frac{1}{2}mv^{2} = \frac{1}{2}mv_{x}^{2} + \frac{1}{2}mv_{y}^{2} + \frac{1}{2}mv_{z}^{2}.$$

Each of these contributes $\frac{1}{2}kT$ to the particle.

 $E_P = mgz$ is not a quadratic term, so does not contribute to Equipartition. For a monatomic ideal gas, e.g. He, we have 3 degrees of freedom which contribute quadratic energy terms. Each one contributes $\frac{1}{2}kT$ to the mean thermal energy of a He atom.

$$\overline{E_k} = 3\frac{1}{2}kT = \frac{3}{2}kT$$
 (per atom)

Note: this is the same result which we derived in Section 4.

The total internal energy of a gas of He atoms is just $N\overline{E_k} = \frac{3}{2}NkT$. Note U depends only on T for an ideal gas.

We can use Equipartition to predict heat capacities. From Gases, Liquids and Solids:

$$C = \frac{dQ}{dT}$$

At constant volume;

$$C_{v} = \frac{\partial Q}{\partial T} \bigg|_{V} = \frac{dU}{dT}$$

For one mole of an ideal gas:

$$U = \frac{3}{2}N_A kT = \frac{3}{2}RT$$

So
$$C_V = \frac{3}{2}R$$
 (for one mole)

If we measure the molar heat capacities for monatomic gases this seems to work. What about diatomic gases, e.g. ${\sf H}_2.$



Model this as a rigid dumbbell.

Again we expect 3 degrees of freedom from translational E_k . We also now have rotational degrees of freedom.

$$E_{k,rotation} = \frac{1}{2}I\omega^2$$
.

The molecule can rotate independently about x, y and z axis, therefore

$$E_{k,rot} = \frac{1}{2}I_{x}\omega_{x}^{2} + \frac{1}{2}I_{y}\omega_{y}^{2} + \frac{1}{2}I_{z}\omega_{z}^{2}$$

For an ideal gas we have point masses, so $I_x = 0$. Therefore for an ideal gas

$$\boldsymbol{E}_{k,rot} = \frac{1}{2}\boldsymbol{I}_{y}\left(\boldsymbol{\omega}_{y}^{2} + \boldsymbol{\omega}_{z}^{2}\right)$$

Note: $I_v = I_z$ by symmetry.

Therefore $2\frac{1}{2}kT$ is contributed to the mean energy of the particle. So for one molecule of a diatomic ideal gas (e.g. H₂):

$$\overline{E_k} = \frac{5}{2}kT$$
$$U = \frac{5}{2}NkT = \frac{5}{2}RT$$

for one mole.

Therefore the molar heat capacity $C_v = \frac{5}{2}R$.

For polyatomic molecules, we expect to get rotational contributions to Equipartition from

rotation about all three axes. Therefore we expect $C_v = 3R\left(U = \frac{6}{2}kT\right)$.

Some species do give $C_v = 3R$ but again there are exceptions. See Handout 3, Page 2.

There is another problem for classical Equipartition – measured values of C_v for hydrogen vary with temperature (Handout 3, Page 3). Part of the solution to these discrepancies is vibrational energy. For example, a diatomic model can be viewed as two masses joined by a spring.

Vibration will give $\frac{1}{2}mv^2$ and $\frac{1}{2}kx^2$ i.e. 2 degrees of freedom, therefore $2x\frac{1}{2}kT$ available for Equipartition (we used this in RJ derivation).

Therefore if we include vibrational degrees of freedom we get:

$$U = \underbrace{3x\frac{1}{2}kT}_{translational} + \underbrace{2x\frac{1}{2}kT}_{rotational} + \underbrace{2x\frac{1}{2}kT}_{vibrational}.$$

For a system of N molecules, $U = \frac{7}{2}kT$ and $C_v = \frac{7}{2}R$.

Polyatomic molecules also give additional contributions from other vibrational modes.

To summarise; Classical Equipartition seems OK for monatomic (ideal) gases, but there are problems for diatomic or polyatomic gases and we need to find an explanation for variation of C_V with T.

7. Equipartition and Quantum Physics

Either Equipartition is wrong, or classical physics is wrong. We go back to the Boltzmann Distribution – the probability that a particle has energy E (i.e. $E \rightarrow E + dE$) is;

$$P(E)dE = Ae^{-\frac{E}{kT}}dE .$$

We can normalise to find A:

$$A\int_{-\infty}^{\infty} e^{-\frac{E}{kT}} E = 1$$
$$A = \frac{1}{\int_{0}^{\infty} e^{-\frac{E}{kT}} dE}$$

This is fine for translational terms since $E_{k,translational} = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$ and v_x can

vary from $-\infty$ to ∞ etc. However, Quantum Physics tells us that energies are quantised; they can only take discrete values. Therefore strictly speaking we can't normalise by integrating. The principle of Equipartition only works classically when energy varies continuously. See page 4, Handout 3.

a) Closely spaced energy levels.

There are many levels within kT. This means that, on the scale of kT, the energies look continuous. Remember that the Boltzmann Factor deals with energy in units of kT.

b) Widely spaced energy levels. Levels look discrete on the scale of kT.

If we increase T slightly, we also increase kT slightly;;

a) We excite several new energy states.

b) The increase is not enough to excite new energy states.

In (a) we find some particles now have the new higher energy levels.

In (b) none of the particles can reach the next energy level.

Looking now at rotational energy levels; Quantum Mechanics tells us that angular momentum is quantised.

$$E_{rot} = \frac{L^2}{2m} = \frac{n(n+1)\hbar^2}{2I}$$

n is an integer – quantum number.

 $\hbar = \frac{n}{2\pi}$, *I* is the moment of inertia.

Level spacing is:

$$\Delta \boldsymbol{E} = \boldsymbol{E}_{n+1} - \boldsymbol{E}_n = \frac{(n+1)\hbar^2}{I}$$

Consider the rigid dumbbell model of H₂.



 $r \sim 10^{-10} m$ $m \sim 1.67 \times 10^{-27} kg$

$$I_y = I_z = \frac{mr^2}{2} \approx 8.35 \times 10^{-48} \, kgm^2$$

$$\Delta E_{0\to 1} = 1.3 x 10^{-21} J = 0.008 eV$$

At room temperature $kT \sim 0.025 eV$.

Therefore $kT > \Delta E$ so at room temperature we would expect many molecules to be rotating (about the y and z axis).

What about rotation about x-axis? Moment of inertia for a sphere about its diameter

is
$$I = \frac{2}{5}mr^2$$
. For H₂, $I = \frac{4}{5}mr^2$. Now $r \sim 10^{-15}m$ so $I_x = 1.3x10^{-57}kgm^2$.

$$\frac{I_x}{I_y} \sim \frac{10^{-57}}{10^{-47}} \sim 10^{10}$$

So for $E_{o \to 1}$, we would need $\frac{\hbar^2}{I_x} = \frac{\hbar^2}{10^{-10}I_y} \sim 8x10^7 eV$ i.e. $E_{rot,x} >> kT$ at room temperature.

Therefore we don't expect to find molecules rotating about the x-axis at room temperature. So at room temperature, H₂ has 5 degrees of freedom, therefore $U = \frac{5}{2}kT$.

Degrees of freedom which are inaccessible because kT is too small are said to be <u>frozen out</u>. Quantum Mechanics tells us that the vibrational energy is also quantised, for harmonic vibrations: $\Delta E = \hbar \omega$. At room temperature $\Delta E >> kT$ for H₂. Vibrational modes are frozen out. If we increase T by enough then we start to get vibrational modes being excited (but note at high enough temperature the molecular bonds will break).

The common exception is Cl₂, which has a very low value of ω , hence ΔE_{vib} is also low and Cl₂ molecules do vibrate at room temperature, hence $C_v = 3R$ at room temperature. As a rule of thumb for gases:

0		
	$\frac{\Delta E}{k}$	
Translations	10 ⁻¹⁸ k	$T >> \frac{\Delta E}{k}$
Rotations	1 <i>k</i>	$T > \frac{\Delta E}{k}$ usually
Vibrations	1000 <i>k</i>	$T < \frac{\Delta E}{k}$ usually

In solids, the mean positions of atoms are fixed, so we don't have translational or rotational degrees of freedom. However the atoms are free to vibrate in 3D, therefore Equipartition tells us that we have 6 degrees of freedom (3 kinetic, 3 potential – one of each due to each direction the molecule can vibrate). Therefore for one mole of a pure element it should have thermal (internal) energy $3N_AkT = 3RT$ and $C_V = 3R$. This is known as the Law of Dulong and Petit.

Experimentally, this holds well at room temperature.

At low temperatures, kT becomes small compared to ΔE_{vib} and the Law of Dulong and Petit fails. At high temperatures kT becomes large enough to break interatomic bonds and the solid will melt.

8. Kinetic Theory of Gases

8.1 Basic Assumptions:

- 1. Gases contain very large numbers of molecules.
- 2. The volume occupied by the molecules is small compared to the volume of the gas.
- 3. The molecules are in continual, rapid, random motion colliding with each other and the container walls.
- 4. The pressure on the container walls arises from the change in momentum as molecules hit the wall and rebound. The impacts are numerous and one individual impact is not important compared to the total number of impacts at the same time interval.

Simplifying assumptions for an Ideal Gas:

- 5. Volume occupied by the molecules is negligible.
- 6. Intermolecular forces are negligible.

This has a useful result:

A

Consider a container of gas, number density n_d . $\frac{1}{6}$ of the particles are moving with \overline{v} towards surface A.



In some time t, all particles within a distance vt of the wall will strike (cross) the surface. The total number of particles which cross area A in time t is:

$$\frac{1}{6}n_{d}vtA$$

Therefore the number of particles which cross unit area (A = 1) in unit time (t = 1) is $n_{d} v$ (8.1).

8.2 Mean Free Path

This is the average distance a molecule travels before bumping into another molecule (λ) .

Mean speed is $\overline{v} = \sqrt{\frac{8kT}{\pi m}}$. In 1 second a molecule will travel a distance \overline{v} and collide with all

the molecules in a cylinder of volume $\pi d^2 v$

The number of molecules it collides with is $n_a \pi d^2 v$ in time t = 1s. Therefore the average

distance between collisions is $\lambda = \frac{\overline{v}}{n_d \pi d^2 \overline{v}} = \frac{1}{n_d \pi d^2}$ (8.2)

Note: actually we have assumed that the other molecules are not moving. Therefore it is better to use the mean relative speed to get the number of collisions. $\overline{v}_{rel} = \sqrt{2}\overline{v}$ which

gives
$$\lambda = \frac{1}{\sqrt{2}n_d\pi d^2}$$
.

See Handout 3, Page 5.

8.3 Pressure in an ideal gas

This is due to collisions with the container wall. A simple model e.g. GLS or Young and Freedman.

Assume the number density of gas is n_d . Say $\frac{1}{6}$ of molecules are travelling in each of $\pm x, \pm y, \pm z$ directions with mean speed \overline{v} .

From (8.1) $\frac{1}{6}n_d v$ (8.3) molecules will hit unit area on one side of the box in unit time. Each molecule has a change in momentum of 2mv. Therefore the total change in momentum per unit time per unit area is $2mv \frac{1}{6}n_d v = \frac{1}{3}n_d mv^2$

I.e. pressure = $\frac{1}{3}n_d mv^2$.

This happens to give (approximately) the right answer because two wrongs make a right! <u>But</u> this method can give completely wrong results for similar problems.

Correct Derivation:

 n_d molecules per unit volume. The probability that a molecule has velocity component v_x in the x-direction is $P(v_x)dv_x$. From (8.1) $v_xn_dP(v_x)dv_x$ is the number of molecules with velocity component v_x which hit unit area in unit time.

The change of momentum of one molecule which hits the wall is $2mv_x$. Therefore total change in momentum due to all molecules with velocity component v_x is

 $2mv_x n_d v_x P(v_x) dv_x$ per unit area per unit time = $2mn_d v_x^2 P(v_x) dv_x$. We integrate over all values of v_x to find the total change of momentum per unit area per unit time.

$$\int_{0}^{\infty} 2m n_{d} v_{x}^{2} P(v_{x}) dv_{x}$$
 (Note integral limits only include +x direction).

$$2mn_d \int_0^\infty v_x^2 P(v_x) dv_x$$

Note that this is an even function. Therefore we can write this equal to

$$2mn_{d} \frac{1}{2} \int_{-\infty}^{\infty} v_{x}^{2} P(v_{x}) dv_{x} = mn_{d} \overline{v_{x}^{2}}$$

Therefore pressure = $mn_d \overline{v_x^2} = \frac{1}{3} mn_d \overline{v^2}$ (8.4)

since;

$$\frac{v^{2} = v_{x}^{2} + v_{y}^{2} + v_{x}^{2}}{v^{2} = v_{x}^{2} + v_{y}^{2} + v_{y}^{2}} + v_{x}^{2}}$$
$$\overline{v_{x}^{2} = v_{y}^{2} = v_{x}^{2}}$$

8.4 Effusion

See Handout 3, page 6.

Suppose we have a sealed container full of gas in lower pressure environment. If we make a large hole in the container, the gas will flow out until the pressures are equalised. However, if the hole is small $(\leq \lambda)$ then the gas inside the container 'doesn't know' about the lower pressure outside. Molecules will only escape if they happen to head in the direction of the hole in their random motion, and they do not collide with any other molecules before they escape. This also implies that the pressure inside the container does not change. This process is called <u>effusion</u>. At STP, $\lambda \sim 100 nm$. At $10^{-5} Nm^{-2}$, $\lambda = 10,000m$. We calculate the rate of effusion as follows. Start with the number density n_d and (from the previous derivation) the number of molecules with velocity component v_x which hit (cross) unit area in unit time is $n_d v_x P(v_x) dv_x$. To get the total number of molecules which hit unit

area in unit time we integrate over all values of v_x .

$$\int_0^\infty n_d v_x P(v_x dv_x)$$

We have an <u>odd</u> function this time so we cannot use the same trick as in the pressure derivation. Instead we remember that $P(v_x)dv_x = Ae^{-Bv_x^2}dv_x \left(A = \sqrt{\frac{m}{2\pi kT}}, B = \frac{m}{2kT}\right)$

This gives
$$An_d \int_0^\infty v_x e^{-Bv_x^2} dv_x$$
. Substitute;
 $u = v_x^2$
 $du = 2v_x dv_x$
So $\frac{An_d}{2} \int_0^\infty e^{-bu} du = \frac{n_d A}{2} \left[-\frac{1}{B} e^{-Bu} \right]_0^\infty = \frac{n_d A}{2B} = \frac{n_d}{2} \sqrt{\frac{2kT}{\pi m}} = \frac{n_d}{4} \sqrt{\frac{8kT}{\pi m}} = \frac{$

If our hole has area A then the number of molecules which escape per unit time is

$$\frac{n_d}{4}\bar{v}A = \frac{\rho vA}{4m} \quad (8.5)$$

Note: rate of effusion depends on $\frac{n_d}{\sqrt{m}}$ therefore if we have a mixture of gases the lighter gas (smaller m) will effuse more quickly.

$$\frac{dN}{dt} = \frac{n_d v dA}{4} \propto \frac{n_d}{\sqrt{m}}$$
$$\left(\frac{n_1}{n_2}\right)_{after} = \left(\frac{n_1}{n_2}\right)_{before} \sqrt{\frac{m_2}{m_1}}$$

Effusion continues until $\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$

8.5 Examples of Effusion:

Uranium Enrichment.

Suppose we have a mixture of UF_6 gas such that we have 0.7% $^{235}UF_6$ and 99.3% $^{238}UF_6$. The lighter gas $^{235}UF_6$ will effuse more quickly so we can boost the proportion of $^{235}UF_6$ by allowing the gas to effuse. In unit time N_{235} and N_{238} molecules will have effused through the hole.

$$\frac{N_{235}}{N_{238}} = \left(\frac{n_{d,235}}{n_{d,238}}\right)_{effused} = \left(\frac{n_{d,235}}{n_{d,238}}\right)_{original} \sqrt{\frac{m_{238}}{m_{235}}}$$

The ratio $\sqrt{\frac{m_{238}}{m_{235}}}$ is called the <u>enrichment factor</u> of the effused gas and in this case it is equal

to 1.004 (fluorine has mass 19)

9. Transport Phenomena

9.1 Diffusion

Diffusion occurs if the gas is not in thermal equilibrium such that the number density of molecules in the gas varies. We consider a simple example where the number density is a

function of position along the z-axis, $\frac{dn_d}{dz} = const.$ and n_d decreases as z increases.



Note this means $\frac{dn_d}{dz}$ is a negative. The flow of molecules is in the +z-direction. It is found experimentally that the rate at which molecules cross unit area in unit time (of a plane perpendicular to the z-axis) is

$$J(z,t) = -D\frac{dn_d(z,t)}{dz}$$

where D is the coefficient of diffusion. We can find an expression for D using a simple kinetic theory model. Start by assuming at any time $\frac{1}{6}$ of the molecules are moving in each direction along each axis, each with speed \overline{v} (Note warning in Pressure derivative). Firstly we look at molecules crossing the z_0 plane in the +z direction. Using result 8.1, the number of molecules crossing unit area of the $z = z_0$ plane in unit time, coming from the $z = z_0 - \lambda$

plane (λ is the mean free path) = $\frac{1}{6}n_d(z_o - \lambda, t)\overline{v}$



We can write $n_d(z_o - \lambda, t) = n_d(z_o, t) - \lambda \frac{dn_d(z_o, t)}{dz}$ so we get $\frac{1}{6}vn_d(z_o, t) - \frac{1}{6}v\lambda \frac{dn_d(z_o, t)}{dz}$. Similarly, for molecules crossing the $z = z_o$ plane from $z = z_o + \lambda$ moving in the -z direction The number per unit area per unit time is $\frac{1}{6}vn_d(z_o, t) + \frac{1}{6}v\lambda \frac{dn_d(z_o, t)}{dz}$. To get the total flux of molecules in the +z direction we take the contribution from the $z = z_o - \lambda$ plane, and we subtract the contribution from the $z = z_o + \lambda$ plane (since these are

going the other way). Therefore the total flux at $z = z_o$ plane is equal

to
$$-\frac{2}{6}v\frac{dn_d}{dz} = -\frac{1}{3}v\lambda\frac{dn_d}{dz}$$
. Note again that this is a positive number since $\frac{dn_d}{dz}$ is negative.
Hence the diffusion coefficient is $D = \frac{1}{2}v\lambda$.

9.2 Viscosity

Transfer of momentum.

Imagine that at z = 0 a flat sheet is moving through a gas with speed u in the x-direction. Molecules next to the sheet will pick up an extra speed u. These collide with molecules in the

next layer and transfer some of this extra x-momentum. We say u(z,t) and $\frac{du}{dz}$ is a negative constant.

9.3 Conduction

This time T varies as a function of z such that $\frac{dT}{dz}$ is a negative constant. Temperature

increases the lower down you go.

From experiment, the heat current $H = \frac{dQ}{dt} = \frac{kA\Delta T}{L}$.

If we heat one end of a bar, these atoms gain vibrational energy – this extra energy is passed from atom to atom in a heat current. ΔT is the temperature difference across length L. k is the constant – thermal conductivity.

9.4 Convection

In this case energy is transported by a flow of molecules from hotter to cooler. E.g. central heating systems:

Radiators – heat up air next to it – sets up a convection current – hot air rises – cooler air forced down – circular flow is set up. Difficult to model but via experiment we find that:

1) $\frac{dQ}{dt} \propto A$ - larger surface area radiator is a more efficient heater.

2) Convection slows down near stationary surfaces because of viscosity.

3) Heat current $\frac{dQ}{dt} \propto \Delta T^{\frac{5}{4}}$ where ΔT is the temperature difference between the surface of the heater and the main body of the convecting fluid.

9.5 Radiation

Heat transported by EM waves e.g. sun feels warm. We have seen that for black bodies

$$\frac{dQ}{dt} = A\sigma T^4$$
 (Stefan's law $I = \sigma T^4$)

For non black bodies $\frac{dQ}{dt}$ also depends on the nature of the surface, described by e – emissivity. $0 \le e \le 1(1 \text{ for a black body})$. e tends to be larger for darker surfaces and for dull surfaces. In general $\frac{dQ}{dt} = Ae\sigma T^4$. This s the only way to transport heat across a vacuum. Summery on page 7, Handout 3.

10. Temperature and the Zeroth Law of Thermodynamics

See Handout 4 and GLS.

The Zeroth Law: "If two systems are separately in thermal equilibrium with a third system then they must be in thermal equilibrium with each other."

11. Work, Energy and the First Law of Thermodynamics

See Handout 4, page 4.

By definition, thermodynamics is the study of the relationship between heat and mechanical work.

Heat is a disordered form of energy with random motions, whereas work is an ordered form of energy e.g. pushing a piston. The first law of thermodynamics is a statement that energy is conserved.

 $\Delta \boldsymbol{U} = \boldsymbol{Q} + \boldsymbol{W}$

 ΔU is the change in U of a system.

Q is the heat added to the system (Q < 0, heat is removed from the system) W is work done on the system (W < 0, system does work on the surroundings)

<u>11.1 Work</u>

In general $dW = \underline{F} \cdot \underline{dx}$. To find the total work done $W = \int \underline{F} \cdot \underline{dx}$

In thermodynamics we look at change in volume: V is important in defining the state of a system. We look at work done when we change the volume of a gas. Consider a volume of gas in a cylinder, cross-sectional area A, confined by a (frictionless) piston. If no force is applied to the piston, the pressure inside will equal the pressure outside. The gas in the cylinder exerts a force F = pA on the piston. If we now compress the gas by applying a force to the piston to move it through a distance dx we do work against this force F. dW = -Fdx = -pAdx = -pdV where dV = Adx is the change in volume of the gas. Note dW > 0 since dV is negative since the volume has decreased. dW is incremental. To get total work we integrate. $W = \int_{V}^{V_2} -pdV$. Usually p is a function of V. e.g. if we compress

isothermally then pV = nRT = const. $P = \frac{nRT}{V}$. Therefore $W = \int_{V}^{V_2} -\frac{nRT}{V} dV$

<u>State</u> of a system – we define the state of a simple thermodynamic system by two variables (p, V or T). We can always calculate the other parameters of the system (provided we are in thermal equilibrium) using the equation of state – e.g. pV = nRT.

Simple system has 2 degrees of freedom.

If we change the state of our system, we transfer energy (Q, W) and change some or all of p, V and T. We can go from the initial state (1) to the final state (2) in various different ways or paths. We can plot the path of a thermodynamic process on a pV diagram <u>if</u> at every point on the path the system is in thermal equilibrium (because then we can use pV = nRT to

plot(p,V). The amount of work done in each path is given by $W = \int -pdV$. The amount of work done in each case is different – it depends on the path. We write dW = -pdV (d-bar).

E.g. isothermal
$$W = -\int p dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

Isobaric: $W - p \Delta V$ (Pressure constant) Isochoric: W = 0 (Volume constant)

<u>11.2 Heat</u>

Similarly we can add heat to a system in different ways. In general, dQ = cdT (c is the heat capacity) (or dQ = CndT - C is molar heat capacity). e.g. (a):



OR same change in state but by free expansion



No heat has escaped and no work has been done (if it is an ideal gas). Experiments show that T is constant for an ideal gas undergoing free expansion. Therefore the final state is the same as for (a) but the amount of heat added is different.

We define the two principle heat capacities:

- c_v constant volume
- c_p constant pressure

 $c_p > c_v$ for gases because to keep p constant we need to do work against the surroundings.

11.3 Internal energy

We know that U is the sum of all the energies from random motions of molecules in the system. If we change the state of a system then we change U by $\Delta U = U_f - U_i$. In

general $\Delta U = Q + W$. But we have seen that Q and W depend on path. Is it true that ΔU is independent of path? Joule experimented on a thermally isolated system by adding energy in different ways. He found that for a given amount of energy added to the system, the change in state was always the same, i.e. ΔU is independent of path. It is a function of state. For an ideal gas Joule found that U only depends on temperature. From free expansion experiments Q = 0, W = 0 therefore $\Delta U = 0$ and T is constant, therefore any two states at the same temperature have the same U (Joule's Law).

From the differential form of the first law dU = dQ + dW.

If we change the state at constant volume $dU = c_v dT$

If we go from the same initial to final state some other way, dU is still $c_v dT$ since it is path

independent. $dU = c_v dT$ is <u>always</u> true for an ideal gas.

To find the total change in U:

$$\Delta U = \int_{T_1}^{T_2} c_v dT$$

If c_v is constant, then $\Delta U = c_v \Delta T$.

Reminder: we used $c_v = \frac{dU}{dT} = \frac{a}{2}nR$ where a is the number of degrees of freedom.

(Equipartition $\frac{1}{2}kT$ of energy per degree of freedom).

$$U = \frac{3}{2} nRT \text{ for a monatomic gas}$$
$$\frac{dU}{dt} = \frac{3}{2} nR = c_v \text{ for a monatomic gas.}$$

Also note since c can be a function of T, always use dQ = cdT and integrate: $Q = \int cdT$.

We can derive a relation between c_v and c_p using Joule's Law:

Suppose we change state from (1) to state (2) and we do this at constant pressure. From the first law, dU = dQ + dW. At constant pressure, $dU = c_p dT - p dV$. We know that $dU = c_v dT$.

Therefore $c_v dT = c_p dT - p dV$. Now use pV = nRT so $V = \frac{nRT}{p}$ and differentiating with

respect to T gives $dV = \frac{nR}{p} dT$.

Substituting gives

 $c_v dT = c_p dT - nRdT$

$$c_v = c_p - nR$$

$$c_p - c_v = nR$$

Note that $c_p > c_v$ as expected.

Also,
$$\frac{c_p}{c_v} = \gamma = \frac{5}{3}$$
 for a monatomic gas.

$$\begin{pmatrix} c_v = \frac{3}{2}nR \\ c_p = \frac{5}{2}nR \\ \therefore \gamma = \frac{5}{3} \end{pmatrix}$$

For a diatomic gas, $\gamma = \frac{7}{5}$, etc.

11.4 Adiabatic Processes

No heat exchange. dQ = 0.

If we compress a gas adiabatically p, V and T all change. We want to find an equation

relating p and V (same as $P = \frac{nRT}{V}$ for isotherm).

From 1st law:

 $dU = dQ + dW = 0 - pdV = c_v dT$

 $c_v dT = -pdV$

We want to eliminate T.

We differentiate pV = nRT.

$$p\frac{dV}{dT} + v\frac{dP}{dT} = nR$$
$$dT = \frac{pdV + vdP}{nR}$$

Note: differentiated by parts since p and V are both functions of T. Now substitute for dT in our equation:

$$\frac{c_v}{nR}(pdV - vdP) = -pdV$$
$$\frac{c_v}{c_p - c_v}(pdV + Vdp) = -pdV$$
$$c_vpdV + c_vVdp = -c_ppdV + c_vpdV$$

$$c_v V dp = -c_p p dV$$

Rearranging to get p's on one side and all the V's on the other side:

$$\frac{c_{p}}{c_{v}} \frac{dV}{V} = \frac{dp}{p} = \gamma \frac{dV}{V}$$

$$\gamma \int_{V_{1}}^{V_{2}} \frac{dV}{V} = -\int_{p_{1}}^{p_{2}} \frac{dp}{p}$$

$$\gamma \ln\left(\frac{V_{2}}{V_{1}}\right) = \ln\left(\frac{p_{1}}{p_{2}}\right)$$

$$\ln\left(\left(\frac{V_{2}}{V_{1}}\right)^{\gamma}\right) = \ln\left(\frac{p_{1}}{p_{2}}\right)$$

$$\left(\frac{V_{2}}{V_{1}}\right)^{\gamma} = \left(\frac{P_{1}}{P_{2}}\right)$$

$$p_{1}V_{1}^{\gamma} = p_{2}V_{2}^{\gamma}$$

 $pV^{\gamma} = const.$

This is the equation for an adiabat.



We can find similar equations relating p,T and V,T by using pV = nRT and substituting for p or V in $pV^{\gamma} = const$.

 $TV^{(\gamma-1)} = const.$

 $T^{\gamma} p^{(1-\gamma)} = const.$

When we compress a gas adiabatically T increases, therefore p increases more quickly than for an isothermal compression.

Adiabat:
$$p \propto \frac{1}{V^{\gamma}}$$

Isotherm: $P \propto \frac{1}{V}$

12. Heat Engines and Refrigerators

12.1 Reversible Processes

We have seen that provided a system is in thermal equilibrium, we can plot its state on a P-V diagram. If we change its state very slowly, so that it is at all times in thermal equilibrium, then we can plot the path from the initial to the final state e.g. going from T_1 to T_2 if we place

the system in thermal contact with a series of heat reservoirs each at dT more than the last one. In principle we can reverse the path, i.e. go from the final to the initial temperature. In practice, this is impossible, <u>but</u> it is a good model approximation and allows us to model thermodynamic systems accurately.

Reversible (Equilibrium) processes:

- Heat flow across an infinitesimal gradient dT.
- Slow adiabatic expansion.
- Irreversible processes:
- Heat flow across a finite gradient ΔT .
- Free expansion of a gas.
- Conversion of work to heat by friction.

12.2 Heat Engines

A heat engine is a device which extracts an amount of heat Q_H from a hot reservoir at T_H . It

converts some of Q_H into work W_E , and the rest Q_C is expelled into a cold reservoir at T_C in one engine cycle.

See Page 3, Handout 5 for a diagram of this.

We can apply the 1st law of thermodynamics over one cycle. The system is the engine itself. Over one cycle it goes through a series of thermodynamic processes which return to its initial state at the end of the cycle. So $\Delta U = Q + W = 0$.

Total Q is $Q_H - Q_C$.

Total W is $-W_{F}$ (Since work is done on the surroundings)

$$\therefore \Delta U = Q_H - Q_C - W_E$$
$$Q_H - Q_C = W_E$$

Ideally we would convert all of Q_H into W_E and Q_C would be 0. In practice this is impossible. We can define the efficiency of a heat engine:

$$e = \frac{W_E}{Q_H} = \frac{What you get}{What you pay}$$
$$e < 1$$

$$e = \frac{W_E}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

Example: an aircraft engine does 9000J of work and discards 6400J of heat each cycle. How much heat is supplied to the engine in each cycle? $\label{eq:Q_H} \begin{aligned} \mathbf{Q}_{H} &= \mathbf{W}_{E} + \mathbf{Q}_{C} = 15400 J \; . \end{aligned}$ What is the efficiency of this engine?

$$e = \frac{W_E}{Q_H} = 0.58$$
 (This is actually pretty good!)

12.3 Refrigerator

A refrigerator is just a heat engine in reverse. It takes heat Q_c from the cold reservoir (T_c)

and expels heat Q_H to a hot reservoir (T_H) . The engine requires work W_E to do this. Again over one cycle $\Delta U = 0$ and from the 1st Law:

$$\Delta \boldsymbol{U} = \boldsymbol{Q} + \boldsymbol{W}$$

$$= Q_C - Q_H + W_E = 0$$

 $W_F = Q_H - Q_C$

This is the same as for the heat engine. The equivalent of efficiency is the coefficient of performance:

$$k = \frac{Q_C}{W_E} = \frac{What you get}{What you pay}$$
$$k = \frac{Q_C}{Q_H - Q_C}$$

12.4 Carnot Cycle

What is the most efficient heat engine possible? We know that e = 1 is impossible (i.e. all heat changed to work). For maximum efficiency we need to avoid irreversible processes. Therefore we want to avoid heat flow across a finite temperature gradient, In the Carnot cycle, heat flow only occurs during isothermal processes, which are not across a heat gradient. This means that when the engine takes Q_H from the hot reservoir, the working substance of the engine (system) is also at T_H . Similarly when Q_C is expelled to the cold reservoir the working substance is at T_C . All other processes must avoid heat flow, therefore they must be adiabatic, to take the working substance from T_H to T_C and back again. Finally we should also ensure that all these processes are entirely reversible; they must be done slowly enough that the working substance is always in thermal equilibrium. Engine:

 $\begin{array}{cccc} Q_C & Q_C \\ T_H & \rightarrow & T_H & \rightarrow & T_C & \rightarrow & T_C & \rightarrow & T_H \\ isothermal & Adiabatic & Isothermal & Adiabatic \end{array}$

See Handout 5, Page 4.

If we run the cycle anti-clockwise, it operates as a refrigerator. Note dW = -pdV. Therefore:

W = the area under the curve.

 $W_{\rm F}$ = the area enclosed by the cycle.

We can analyse each step of the cycle. 1-2 Isothermal: $\Delta U = Q + W = nC_{,,}\Delta T = 0$ so Q = -W.

$$p = \frac{nRT}{V}$$
 so $W = \int_{V_1}^{V_2} -pdV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT_H \ln\left(\frac{V_1}{V_2}\right)$

This is < 0 i.e. the system does work on the surroundings – expansion.

Therefore
$$Q = Q_H = -nRT_H \ln\left(\frac{V_1}{V_2}\right) = nRT_H \ln\left(\frac{V_2}{V_1}\right).$$

2-3 Adiabat: $Q = 0 \cdot \Delta U = W$.

Since
$$pV^{\gamma} = const$$
 $W = -\int_{V_2}^{V_3} p dV = -\int_{V_2}^{V_3} \frac{k}{V^{\gamma}} dV = \frac{1}{1 - \gamma} \left[p_3 V_3 - p_2 V_2 \right]$

,

Again W < 0 as expected.

Alternatively
$$\Delta U = nc_V \Delta T = nc_V (T_C - T_H) < 0$$
.

3-4 Isothermal: $\Delta U = 0, Q = -W$

$$W = nRT_{C}\ln\left(\frac{V_{3}}{V_{4}}\right) > 0$$

Work done on the system, gas is compressed.

 $Q = -W \therefore Q < 0$ i.e. heat expelled.

 $Q_{\rm C}$ flows out of the system.

4-1 Adiabatic: Q = 0, $\Delta U = W$

$$W = \frac{1}{\gamma - 1} \left[p_1 V_1 - p_4 V_4 \right]$$
$$\Delta U = n c_v \left(T_H - T_C \right) > 0$$

Therefore work is done on the system.

Over one complete cycle:

The system is returned to its original state. Therefore $\Delta U = 0$.

 $\begin{array}{cccc} 1-2 & 2-3 & 3-4 & 4-1 \\ \Delta U = 0 + nc_v \left(T_C - T_H\right) + & 0 + & nc_v \left(T_H - T_C\right) = 0 \end{array}$

 W_E = total work done by the engine:

$$\frac{1-2}{nRT_{H}}\ln\left(\frac{V_{1}}{V_{2}}\right) + \frac{1}{\gamma-1}\left[P_{3}V_{3} - P_{2}V_{2}\right] + nRT_{C}\ln\left(\frac{V_{3}}{V_{4}}\right) + \frac{1}{\gamma-1}\left[P_{1}V_{1} - P_{2}V_{2}\right]$$

.

The efficiency of the engine is:

$$e = \frac{W_E}{Q_H} = \frac{Q_H - Q_C}{Q_H} = \frac{nRT_H \ln\left(\frac{V_2}{V_1}\right) - nRT_C \ln\left(\frac{V_3}{V_4}\right)}{nRT_H \ln\left(\frac{V_3}{V_1}\right)} = \frac{T_H \ln\left(\frac{V_2}{V_1}\right) - T_C \ln\left(\frac{V_3}{V_4}\right)}{T_H \ln\left(\frac{V_2}{V_1}\right)}$$

.

This can be simplified using the Adiabatic relation $TV^{\gamma-1} = const$ Therefore:

2-3
$$T_H V_2^{\gamma - 1} = T_C V_3^{\gamma - 1}$$

4-1 $T_C V_4^{\gamma - 1} = T_H V_1^{\gamma - 1}$
 $\frac{V_2}{V_1} = \frac{V_3}{V_4}$

So
$$e = \frac{T_H \ln\left(\frac{V_2}{V_1}\right) - T_C \ln\left(\frac{V_2}{V_1}\right)}{T_H \ln\left(\frac{V_2}{V_1}\right)} = \frac{T_H - T_C}{T_H}$$

Similarly the coefficient of performance for the Carnot refrigerator is:

$$K = \eta = \frac{Q_C}{Q_H - Q_C} = \frac{T_C}{T_H - T_C}$$

http://www.phy.ntnu.edu.tw/java/carnot/carnot.html http//www.rawbw.com/~xmwang/myGUI/CarnotG.html http//www.rawbw.com/~xmwang/myGUI/OttoG.html http//www.rawbw.com/~xmwang/myGUI/DieseIG.html

<u>12.5 Example of Carnot Cycle</u>

Carnot engine with working substance 1 mole of ideal gas, operating between $T_H = 400K$ and $T_C = 300K$. Initial pressure of 10atm and the volume doubles during isothermal expansion.

a) Find the pressure and volume at each corner of the cycle.

1:
$$T = T_{H} = 400K$$
, $p_{1} = 10atm = 10^{\circ}Pa$
 $V_{1} = \frac{nRT_{H}}{P_{1}} = 3.326 \times 10^{-3} m^{3}$
2: $T = T_{H} = 400k$, $V_{2} = 2V_{1} = 6.65 \times 10^{-3} m^{3}$
 $P_{2} = \frac{nRT_{H}}{V_{2}} = \frac{nRT_{H}}{2V_{1}} = \frac{P_{1}}{2} = 5 \times 10^{5} Pa$
3: $T = T_{C} = 300k$

2-3 is an adiabatic process therefore $TV^{\gamma-1} = const$. For an ideal monatomic gas $\gamma = \frac{5}{3}$.

$$V_{3} = V_{2} \left(\frac{T_{H}}{T_{C}}\right)^{\frac{1}{\gamma-1}} = 1.024 \times 10^{-2} m^{3}$$
$$p_{3} = \frac{nRT_{C}}{V_{3}} = 2.436 \times 10^{5} Pa$$

4: $T = T_c = 300k$

4-1 is adiabatic so $TV^{\gamma-1} = const$.

$$V_4 = V_1 \left(\frac{T_H}{T_C}\right)^{\frac{1}{\gamma - 1}} = \frac{V_3}{2} = 5.12 \times 10^{-3} \, m^3 \, .$$
$$P_4 = \frac{nRT}{V_4} = 2P_3 = 4.871 \times 10^5 \, Pa \, .$$

b) Find Q, W and ΔU for each leg of the cycle:

1-2 Isothermal

 $\Delta \boldsymbol{U} = \boldsymbol{0} = \boldsymbol{Q} + \boldsymbol{W}$

 $W = \int_{V_1}^{V_2} -pdV = \int_{V_1}^{V_2} -\frac{nRT_H}{V}dV = nRT_H \ln\left(\frac{V_1}{V_2}\right) = -2305J$ Q = -W = 2305J $Q_{H} = 2305J$ (Added to engine) 2-3 Adiabat Q = 0. $\Delta U = W$ $\Delta U = c_{v} \Delta T = -1247J$ (Remember $c_p - c_v = nR$ and $\frac{c_p}{c} = \gamma = \frac{5}{3}$) $c_{v} = 12.47$ W = -1247J (work done by system) (Or use $pV^{\gamma} = k, W = \int_{2}^{3} \frac{-k}{V^{\gamma}} dV$) 3-4 Isothermal Use the same method as 1-2 $\Delta U = 0$. $W = \int_{V_4}^{V_4} -pdV = 1729J$ Work is done on the system. Q = -W = -1729J therefore heat is removed from the system. $Q_{C} = 1729J$ 4-1 Adiabat Same as 2-3. Q = 0, $\Delta U = W = 1247J$ c) Find the total W_{F} and ΔU over one cycle. ΔU over one complete cycle = 0 W_F = output from engine = -W $W = W_{12} + W_{23} + W_{34} + W_{41}$ = -2305 - 1247 + 1729 + 1247= -576J $W_{F} = 576J$ Efficiency $e = \frac{W_E}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 0.25$ Because this is a Carnot engine we could also use:

$$e = \frac{T_H - T_C}{T_H} = 0.25$$

13. The Second Law of Thermodynamics

This law can be stated in various ways. They all boil down to the idea that thermodynamic processes have a natural direction.

The Engine Statement

It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts it completely into mechanical work with the system ending in exactly the same state in which it began.

The Refrigerator Statement

It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.

To show that these two statements are equivalent, suppose we have a heat engine and we run it in conjunction with a workless refrigerator (i.e. violates the refrigerator statement). The heat engine converts Q_h into $W_E + Q_C$. The workless refrigerator returns Q_C from the cold

reservoir to the hot reservoir. The net effect is to remove heat $Q_H - Q_C$ from the hot reservoir

and convert it <u>completely</u> into work W_F . Therefore we have violated the engine statement.

Any device which violates one form of the second law can be used to make a device which violates the other form, <u>or</u>, if violations of one form of the second law are impossible then so are violations of the other form.

According to the Second Law, no engine can have 100% efficiency and we know that the Carnot Cycle gives the maximum possible efficiency.

"No engine can be more efficient than a Carnot engine operating between the same two temperatures."

Suppose that we have a Carnot refrigerator extracting Q_{c} from a cold reservoir at

temperature T_C , and expels Q_H to a hot reservoir at T_H . To do this requires work W_E on the refrigerator. The Carnot fridge works in tandem with a super-efficient heat engine which exhausts Q_C to the cold reservoir. This engine is more efficient than the Carnot engine which would operate between the same two temperatures, i.e. it violates the Carnot statement of the Second Law. This engine takes in and converts $Q_H + \Delta - Q_C$ into work. An amount W_E of this work is used to drive the Carnot refrigerator, which leaves an amount Δ of work still available. Therefore the net effect is to remove Δ from the hot reservoir and convert it totally into work. We know from the engine statement of the second law that this is impossible.

Example:

An inventor claims to have designed a heat engine which takes in $11x10^7 J$ at 400K and exhausts $5x10^7 J$ at 200K, delivering 16.67kWhrs of work.

 $W_F = 16.67 kW hrs(x1000x3600) = 6x10^7 J$.

From the First Law, $\Delta U = 0 = Q + W$

$$Q = -W (W = -6x10^7 J)$$

 $11x10^7 - 5x10^7 = 6x10^7$ This satisfies the first law.

Second law:
$$e = \frac{W_E}{Q_{\mu}} = \frac{6}{11} = 0.545$$

Carnot engine
$$e = 1 - \frac{T_C}{T_U} = 1 - \frac{200}{400} = 0.5$$

This engine therefore violates the second law.

15. Entropy

15.1 Introduction

So far we have stated the second law in various forms of words – each basically a statement of impossibility. We introduce the concept of entropy to lead us to a mathematical version of the second law.

When we add heat to a system we effectively increase the amount of disorder in the system: each particle has more energy available to it therefore there are more states available to it. Entropy is a way of quantifying this increase in disorder (connects micro and macro). Consider an infinitesimal isothermal expansion of an ideal gas i.e. we add heat dQ to the gas at constant temperature so the gas expands isothermally, therefore dU = 0 (dU depends on dT). If we add dQ we must get work out: dU = 0 = dQ + dW.

Work done by the system = $-dW = +pdV = \frac{nRT}{V}dV = dQ$. Rearrange to get:

 $\frac{dV}{V} = \frac{1}{nR} \frac{dQ}{T}$ $\frac{dV}{dV}$ is the frac

 $\frac{dV}{V}$ is the fractional increase in volume.

The gas is more disordered since the volume has increased - it has a larger volume to move

around in. We note that
$$\frac{dV}{V} \propto \left| \frac{dQ}{T} \right|$$

Definition of entropy:

For an infinitesimal reversible process:

$$dS = \frac{dQ}{T}$$
.

For a reversible, isothermal process

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

For any reversible process:

$$\Delta S = \int_{1}^{2} \frac{dG}{T}$$

Note: entropy is a function of state. So ΔS does <u>not</u> depend on path from initial to final state.

e.g. 1kg of water is heated from $0^{\circ}C$ to $100^{\circ}C$. What is the change in entropy?

This is not a reversible process but we can use the fact that entropy is a function of state so the actual path does not matter. We consider a series of infinitely small temperature increases, each of which is reversible.

For each step
$$ds = \frac{dQ}{T} = \frac{mcdT}{T}$$

(Note the integration is now in terms of T and two constants) Therefore:

$$\Delta S = \int_{T=0}^{T=100} mc \frac{dT}{T} = mc \int_{273}^{373} \frac{dT}{T} = mc \ln\left(\frac{373}{273}\right)$$

$$c = 4190 J k g^{-1} k^{-1}$$

$$\Delta S = 1.31 x 10^3 J k^{-1}$$

15.2 Entropy and the Second Law

Reversible processes $\Delta S_{total} = 0$

Irreversible processes $\Delta S_{total} > 0$

This means that the entropy of the universe is increasing (becoming more random) with time.

e.g. 300ml glass of water is taken outside on a warm $(20^{\circ}C)$ day and allowed to warm up.

what is the total change in entropy of the universe?

This is not a reversible process. Therefore find ΔS_{water} by considering a series of infinitesimal (reversible) increases in T.

$$\Delta S_{water} = \int_{1}^{2} \frac{dQ}{T} = mc \ln \frac{293}{273} = 89 J k^{-1}$$

We must also include ΔS_{air} - we assume T_{air} is constant.

Therefore
$$\Delta S_{air} = \frac{\Delta Q}{T_{air}}$$

 $\Delta Q = mc\Delta T_{water} = 0.3x4190x20 = 25140J$

$$\Delta S_{air} = \frac{-25140}{T(=293k)} = -86Jk^{-1}$$

-Q because heat flows out of air i.e. entropy of air has decreased.

$$\Delta S_{total} = \Delta S_{water} + \Delta S_{air} = 3Jk^{-1}$$

15.3 Entropy and the Carnot Cycle

Entropy is a function of state, therefore in one complete cycle $\Delta S = 0$! Since we end up in the same state as we started in. Analyse each leg separately:

1-2: Reversible isotherm

$$\Delta S_{12} = \frac{Q_H}{T_H}$$

2-3 Adiabatic

$$Q = 0 \therefore S_{23} = 0$$

3-4 Isothermal $-Q_c$

$$\Delta S_{34} = \frac{1}{T_c}$$

$$\Delta S_{41} = 0$$

Therefore for one cycle:

$$\Delta S_{total} = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

Therefore
$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

Put in numbers from example in section 13: Q = 2305 I

= 0

$$Q_{H} = 2305J$$

$$Q_{C} = 129J$$

$$T_{H} = 400k$$

$$T_{C} = 300k$$

$$\Delta S = \frac{Q_{H}}{T_{H}} - \frac{Q_{C}}{T_{C}} = 5.76 - 5.76$$

We showed that $e = \frac{Q_H - Q_C}{Q_H} = \frac{T_H - T_C}{T_H}$ This involved analysing the cycle using the first law and the equation for the adiabat. $TV^{\gamma-1} = const.$

We can also derive this result much more easily using:

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

$$Q_C = \frac{Q_H T_C}{T_H}$$

$$e = \frac{Q_H - Q_C}{Q_H} = \frac{Q_H - Q_H T_C}{Q_H} = 1 - \frac{T_C}{T_H}$$