Thermodynamics Introduction:

Thermal Physics has two approaches, the macroscopic Thermodynamics and the microscopic Statistical Mechanics.

In Thermodynamics we consider a **system**, with a **boundary** to it's **surroundings**. It is the properties of the boundary that decide what may be done on the system.

The system can be influenced via exchanging matter, doing work or transferring thermal energy. In an **Open System** energy and matter can be exchanged. In a **Closed System** mass cannot be exchanged but energy can, this type of system can have stationary or movable boundaries. In a **Thermally Isolated System** thermal energy cannot be exchanged but work can be done on the system. In a **Fully Isolated System** no energy or matter can be exchanged, and there are stationary boundaries so no work may be done.

Zeroth Law Of Thermodynamics:
"If A and C are in thermal equilibrium with B, then A is also in thermal equilibrium with C"

This can be demonstrated if one considers the system shown on the right. In the top diagram A and B are insulated form eachother but are both in thermal equilibrium with C. In the bottom diagram, A and B are then brought in to contact via a diathermic boundary, however no change of state occurs in A and B since they were already in thermal equilibrium with eachother via C. This demonstrates the Zeroth Law of Thermodynamics, if S(A)=S(C) and S(B)=S(C) then S(A)=S(B).
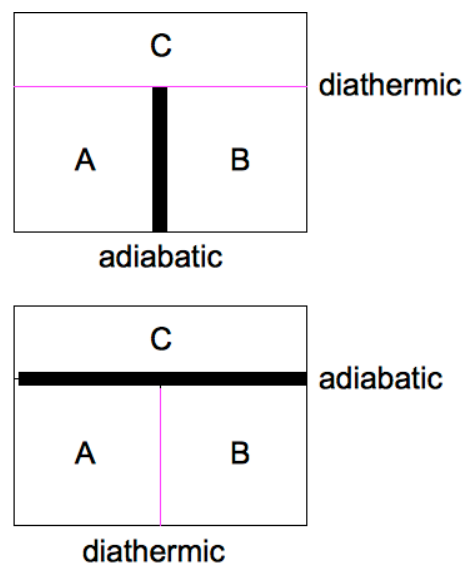
Molar Mass and Avogadro's Constant:

Avogadro's Number is the number of molecules/atoms in one moles, and is given as 6.022×10^{23} mol^{-1} .The molar mass of a molecule may be calculated by summing the atomic molar masses of its elements, which are provided on the Periodic Table. With these two pieces of information we can calculate the total mass of a given number of moles of a substance.

Thermodynamics and Boundaries:

A system is in **thermodynamic equilibrium** when no further change takes place with respect to it's surroundings. Two systems are in **thermal equilibrium** with each other when there is no change between them.

Boundary properties:
**Adiabatic** – Perfectly insulating.
Diathermic – Perfectly conducting.

Note that for thermal equilibrium the two states of the systems needn't be equal, but merely constant. If the systems have an Adiabatic boundary then one could be at 500K and the other at 1K and they could still be in thermal equilibrium.

Thermometers and Temperature Scales:

For a thermometer to be good it must have a thermometric property, reproducible and unique readings (i.e. a one to one function for the thermometric property against the temperature) , a wide range of temperature readings, and be small (so that it doesn't modify the heat of the considered system too much).

Constant-Volume Gas Thermometer:
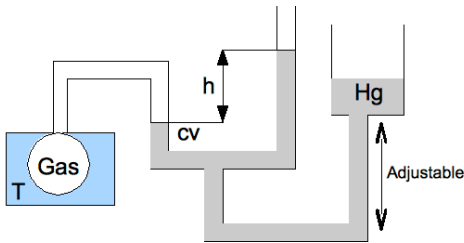
A gas of low density is used (it doesn't matter which at these low densities, although Helium provides the best temperature range), this means that $T=kP$. The height of the mercury reservoir is adjusted until the meniscus is at the constant volume mark, and P is measured since $P=\rho\, gh$. Two systems can then be compared since $\dfrac{T_B}{T_A}=\dfrac{P_B}{P_A}$. The Triple-Point of water is used as a standard since it occurs only at a specific temperature and pressure. So in calibration: $T=T_{TP}\dfrac{P}{P_{TP}}$. In practicality, the CV Gas Thermometer is slow and cumbersome to use and so is only used for calibration purposes (i.e. it is the Primary standard).
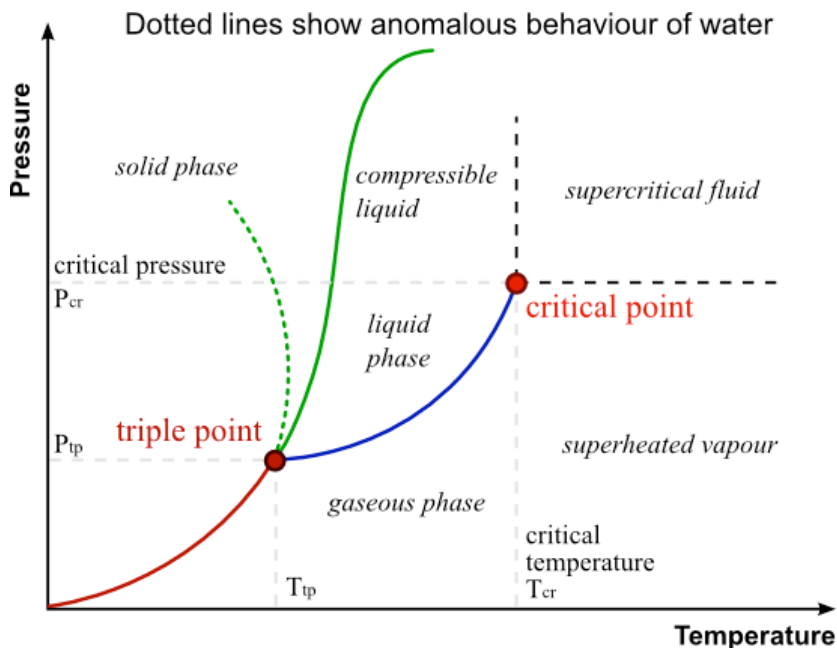
Platinum Resistance Thermometer:
A piece of platinum wire is heated.
  $R(T)=R_0(1+\alpha T+\beta T^2)$ where T is in $0-850°C$
R_0 is the resistance at T=0, and α and β are coefficients determined from experiment.

Thermocouples:
Two metals are joined together, and the difference in their reaction to the temperature difference produces an EMF.
  $\epsilon(T)=C_0+C_1 T+C_2 T^2+...$
Not as accurate as Pt resistance, but cheaper.

Radiation Thermometer:

Based on Planck's Law for black-body radiation, $\lambda_{max} = \dfrac{b}{T}$.

Temperature can be deduced from emission spectrum, does not need physical contact, useful for astronomical objects.

Ideal Gas Laws:

$$pV = nRT$$

Alternate Forms:

$$n = \frac{m}{M} \quad \text{so:} \quad P = \frac{\rho}{M} RT$$

$$n = \frac{N}{N_A} \quad \text{so:} \quad PV = NkT \quad \text{where} \quad k = \frac{R}{N_A} = 1.381 \times 10^{-23} \ J \ K^{-1} \quad \text{Boltzmann constant}$$

Calculating the variation of atmospheric pressure with height:
Assuming g and T are constant:

$$dP = \rho g \, dz \quad \text{but:} \quad \rho = \frac{PM}{RT} \quad \text{so:} \quad dP = \frac{PM}{RT} g \, dz \quad \therefore \quad \frac{dP}{P} = \frac{gM}{RT} dz$$

Integrating this:

$$\int_{P_0}^{P} \frac{dP}{P} = \frac{gM}{RT} \int_{z_1}^{z_2} dz \quad \therefore \quad \ln\left(\frac{P}{P_0}\right) = \frac{gM(z_2 - z_1)}{RT} \quad \therefore \quad \frac{P}{P_0} = e^{\frac{-gMh}{RT}} \quad \therefore \quad P = P_0 e^{\frac{-gMh}{RT}}$$
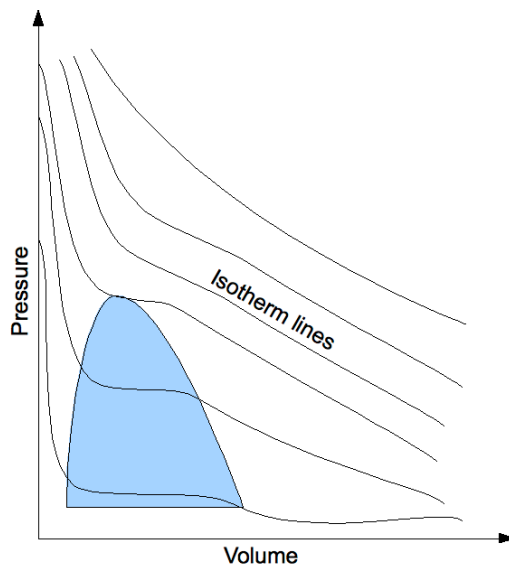
P-V diagrams:
Have series of lines corresponding to constant temperatures. The ideal gas is always in the gas phase and so doesn't model real gases, the critical temperature is the temperature above which the gas cannot be liquified by pressure alone. Approximations to the behaviour of real gases include the Van der Waal's equation for state and the virial equation of state.

Ideal gas equation of state: $\quad PV = nRT \quad$ or $\quad \dfrac{PV}{nRT} = 1$

Van der Waal's equation of state: $\quad \left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT \quad$, the constants a and b are determined

from experimentation. The nb term takes in to account the volume of the molecules, the an^2/V^2 term takes in to account the intermolecular attractions.

Virial equation of state: $\quad \dfrac{PV}{nRT} = 1 + B\left(\dfrac{n}{V}\right) + C\left(\dfrac{n}{V}\right)^2 + D\left(\dfrac{n}{V}\right)^3 + ... \quad$ the virial coefficients, B, C and

D (functions of T) are specific for each gas.

Critical Temperature – Temperature above which gas cannot be liquified by pressure alone.

The ideal gas is always a gas, whereas the real gas may change phase.

The PV diagram shows the Isotherm lines, and the critical temperature/condensation phase (shown in blue).

Equation of state for simple solids:
Solids also have equations of state:

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

where $\beta = \dfrac{\Delta V / V_0}{\Delta T}$ (coefficient of volume expansion, P is const.), $k = \dfrac{\Delta V / V_0}{\Delta P}$ (k is isothermal compressibility, T is const)

From Properties Of Matter:

$L \approx L_0 + \alpha L_0 \Delta T$ where $\alpha = \dfrac{\Delta L}{L_0 \Delta T}$ and $V \approx V_0 + \beta V_0 \Delta T$ and $\beta = 3\alpha$

Heat Transfer:
Heat is defined as the energy in transit between the system and its surroundings, solely due to a temperature difference.

$Q = mc \, \Delta T$ where c is the specific heat capacity.

A system is in **steady state** if the state properties (i.e. temperature) do not change in time. (i.e. H is constant). i.e. In steady state a constant work may be provided and so the rate of heat transfer will be constant although the state variables will still be changing.

A system is in **thermal equilibrium** a single temperature and pressure can be attributed to the whole system. (i.e. H is 0)

Heat transfer: $H = \dfrac{dQ}{dt}$

Conduction:

$$H = \kappa \, A \dfrac{(T_2 - T_1)}{L}$$, in general: $H = \dfrac{dQ}{dt} = -\kappa \, A \dfrac{dT}{dx}$

where k is the thermal conductivity.

The thermal resistance, R, $R = \dfrac{L}{k}$.

Convection:
Defines as heat transfer by free motion. Convection is an important heat transfer mechanism in

fluids.

Forced Convection: Externally generated flow.
Free convection: Flow generated by thermally-induced density gradients.

Radiation:
Heat transfer by electromagnetic radiation. Can occur in vacuum.

$$\lambda_{max} T = b \quad \text{(Wien's Law)}$$

The rate of energy radiation from a surface area A is given by:

$$H = e \sigma A T^4$$

where e is the emissivity (a value between 0 and 1), σ is the Stefan-Boltzmann constant (5.67×10^{-8} $Wm^{-2}K^{-4}$). T is the absolute temperature (in Kelvin).

If the surroundings are at a temperature T_S, then they will also radiate due to the same law. The considered body, will absorb some of this radiation and the net rate of radiation will be:

$$H_{net} = e \sigma A (T^4 - T_S^4) \qquad H_{net} > 0 \text{ means a net heat flow out of the body}$$

Thermodynamic Processes:
Thermodynamic process :- A change in the state variables of the system.

Quasi-static (or quasi-equilibrium) process :- A process during which the system is always infinitesimally close to the thermodynamic equilibrium (an idealisation).

Reversible process :- A process which is performed in such a way that, at the end of it, both the system and the surroundings may be restored to their initial states, <u>without any changes</u>.
(So all Reversible processes are Quasi-static and vice versa)

Irreversible :- does not fulfil the above requirement. Cannot be reversed by small change of conditions.

All natural processes are irreversible – from the second law of thermodynamics.

Isochoric – Constant Volume. (Decreasing pressure, decreases the temperature).
Isobaric – Constant Pressure. (Increasing volume whilst mantaing pressure, increases temperature)
Isothermal – Constant temperature. (Pressure and Volume change to maintain a constant temperature)
Adiabatic – No heat transfer. No state variable is constant.

Work-Energy Theorem: $W_{tot} = \Delta E_K$

Work is the energy transfer between a system and its surroundings by any means which is independent of the temperature difference between them.

Work is the energy transfer which is not heat.

When Q is positive there is heat flow **in** to the system (gas). When W is positive there is work done **by** the system (gas).

$$\text{Work:} \quad W = \int_{V_1}^{V_2} P(V)\,dV$$

Isochoric processes: $\quad \Delta V = 0 \quad \therefore \quad W_V = 0$

Isobaric processes: $\quad$ P is const. $\quad \therefore \quad W_P = P_0(V_2 - V_1)$

Isothermal process: Ideal gas: $\quad P(V) = \dfrac{nRT}{V} \quad \therefore \quad W = \int_{V_1}^{V_2} \dfrac{nRT}{V}\,dV = nRT \ln\!\left(\dfrac{V_2}{V_1}\right)$

and since: $\quad \dfrac{V_2}{V_1} = \dfrac{P_1}{P_2} \quad \therefore \quad W_T = nRT \ln\!\left(\dfrac{P_1}{P_2}\right)$

Adiabatic process: $\quad PV^\gamma = K$, where $\quad \gamma = \dfrac{C_P}{C_V}$, ratio of molar heat capacities.

where K is a constant.

$$W_Q = \int_{V_1}^{V_2} K V^{-\gamma}\,dV = \dfrac{K}{1-\gamma}\left(V_2^{-\gamma+1} - V_1^{-\gamma+1}\right) = \dfrac{P_1 V_1}{\gamma-1}\left[1 - \left(\dfrac{V_1}{V_2}\right)^{\gamma-1}\right] = \dfrac{1}{\gamma-1}(P_1 V_1 - P_2 V_2)$$

For ANY IDEAL GAS: $\quad dU = n C_v dT$

For Adiabatic processes: $\quad dU = -W = -pdV \Rightarrow nC_v dT = -pdV$

Rearranging: $\quad nC_v dT + \dfrac{nRT}{V}dV = 0 \quad \Rightarrow \quad \dfrac{dT}{T} + \dfrac{R}{C_V}\dfrac{dV}{V} = 0$

But: $\quad R = C_p - C_V \quad$ and $\quad \gamma = \dfrac{C_p}{C_v} \quad$ so $\quad \dfrac{R}{C_v} = \dfrac{C_p - C_v}{C_v} = \gamma - 1$

$\dfrac{dT}{T} + (\gamma-1)\dfrac{dV}{V} = 0 \quad$ Which integrates to: $\quad \ln(T) + (\gamma-1)\ln(V) = K \quad$ which can be rearranged to
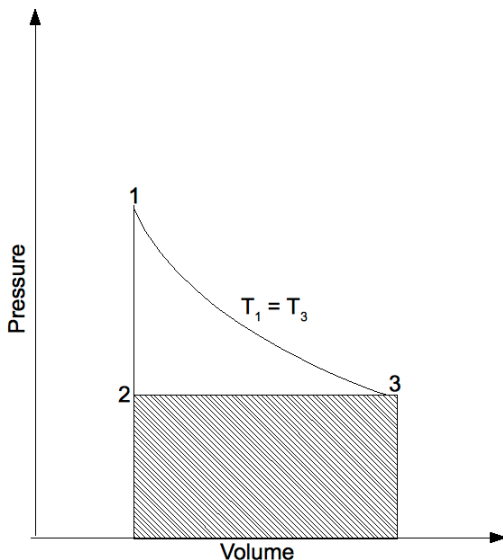
get: $\quad \ln(T) + \ln(V^{\gamma-1}) = \ln(TV^{\gamma-1}) = K \quad$ and raising to exponential: $\quad TV^{\gamma-1} = K \quad$ as K is just an arbitrary constant.

Using $\quad T = \dfrac{PV}{nR} \quad$ from the Ideal Gas Law we get $\quad \dfrac{PV}{nR}V^{\gamma-1} = K \quad$ we can multiply both sides by nR and still stay with K as n and R are both constants and K is just a constant so $\quad PV \times V^{\gamma-1} = K \quad$ and therefore $\quad PV^\gamma = K$

Also $\quad W = -nC_v(T_2 - T_1) = nC_v(T_1 - T_2) \quad$ but $\quad nT = \dfrac{pV}{R} \quad$ from ideal gas law so:

$$W = \dfrac{C_v}{R}(P_1 V_1 - P_2 V_2) \quad \text{but} \quad \dfrac{C_v}{R} = \dfrac{C_v}{C_p - C_v} = \dfrac{1}{\gamma-1}$$

$$\text{so} \quad W = \dfrac{1}{\gamma-1}(P_1 V_1 - P_2 V_2)$$

Work is path-dependent:
Path 1-2-3 is isochoric and then isobaric.
$\quad W_{1\to2\to3} = W_V + W_P = 0 + \text{hatched area}$

Path 1-3 is isothermal:
$\quad W_{1\to3} = W_T + \text{hatched area} + \text{blank area}$

So difference: $W_{1\to3}-W_{1\to2\to3}=blank\ area$

So heat content of a system and work of a system cannot be consistently defined, work can be extracted in a cyclic process.

First Law Of Thermodynamics:

$\Delta U=Q-W$, although Q and W are both path dependent, ΔU is path independent.

$$dU=\bar{d}Q-\bar{d}W$$

Applications:

Cyclic Process: $\Delta U=0 \quad Q=W$
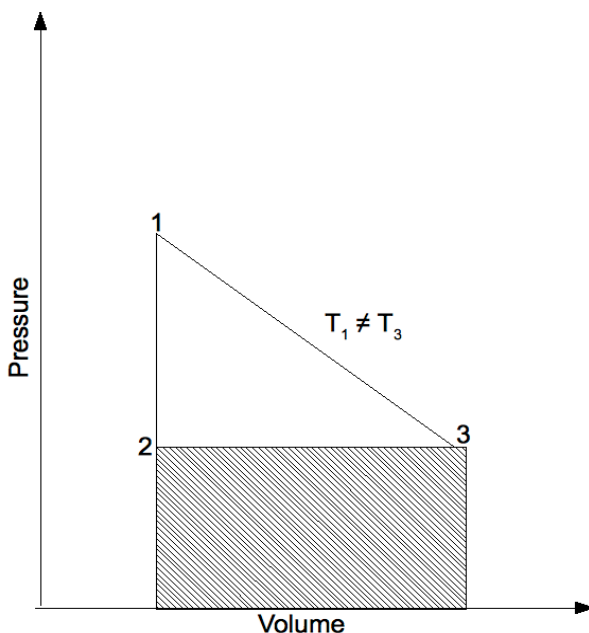
Isolated system: $Q=W=0 \quad \Delta U=0$

Isochoric process: $\Delta V=0 \quad W_V=0 \quad \Delta U=Q_V \quad Q_V=c_V m\Delta T$

Isobaric process: $\Delta U=Q_P-W_P \quad W_P=P_0(V_2-V_1) \quad Q_P=c_P m\Delta T$

Adiabatic Process: $Q=0 \quad \Delta U=-W_Q$

Adiabatic processes are realized in good insulation and rapid change.

Isothermal process: $Q=0 \quad W=0 \ \to \ U_1=U_2$

Considering the cyclic process: 1-3-2-1.

The temperature change from 1-3 is not clear since it is neither an adiabatic, isothermal, isobaric, or isochoric process.

The Heat Transfer in the process 1-3 can be calculated by first working out the work done in each process, and the heat transfer done in process 2-1 and 3-2. Using the fact that the internal energy change over the entire cyclic process must be 0, the thermal energy change in process 1-3 can be determined.

i.e. when the cycle is traversed in an anti-clockwise direction, work is done on the gas, and so heat is released from the gas and it acts as a heat engine. When the cycle is traversed in a clockwise direction, work is done by the gas, and so the system absorbs heat, acting as a refridgerator.

Statistical Mechanics:

Kinetic theory of gases:

Assume:
- A container of volume, V, contains a very large number, N, of identical molecules, each with mass m.
- The molecular radius is small compared to the average distance between molecules and the size of the container.
- The molecules are in constant motion ad obey Newton's laws. Their motion is random.
- There is no force acting on molecules except during collisions. The molecules collide with eachother and with the walls of the container. All collisions are perfectly elastic.
- The container walls are perfectly rigid and infinitely massive.
- The gas is in equilibrium.

In an elastic collision with a vertical wall, the particle's x momentum is reversed. So the change in momentum is $2mv_x$.

Molecules within the distance $dx = v_x dt$ to the wall will strike the wall during the time interval dt. So the number of molecules hitting the wall, of cross-sectional area A, will be $\frac{N}{V} A v_x dt$.

However, since the motion is random, on average half of the molecules will be moving away from the wall (and half towards), so the number of collisions is $\frac{1}{2}\left(\frac{N}{V}\right) A v_x dt$, since $\frac{N}{V}$ is the average density of molecules in the container.

This can be used to calculate pressure since the change in momentum per collision was found to be $2mv_x$. And so: $F_x = \frac{dp_x}{dt} = \left(\frac{NA}{V}\right) m v_x^2$, therefore $P = \frac{F}{A} = \left(\frac{N}{V}\right) m v_x^2$.

Generalizing velocity:

The average of the squared speeds, in the x-direction, is $\langle v_x^2 \rangle$.

Taking the modulus of the velocity: $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$

But since the motion is random: $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$

So: $\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$

And so: $PV = \frac{1}{3} N m \langle v^2 \rangle$

Note that $\sqrt{\langle v^2 \rangle} = v_{rms} \neq \langle v \rangle$ is called the root mean square speed, and is **NOT** the same as the average speed.

Interpretation of Temperature:

$\frac{1}{3} N m \langle v^2 \rangle = NkT$ so: $\frac{1}{2} m \langle v^2 \rangle = \langle E_{kinetic} \rangle = \frac{3}{2} kT$ where $k = \frac{R}{N_A} = 1.38 \times 10^{-23} J K^{-1}$.

Internal energy of an ideal gas:

$U = N \langle E_{kinetic} \rangle = \frac{3}{2} NkT = \frac{3}{2} nRT$ assuming there are no intermolecular forces and no rotational or vibrational kinetic energy.

Equipartition of energy:

Each degree of freedom is associated with $\frac{1}{2}kT$ of the total average kinetic energy.

A polyatomic molecule will have translational, rotational and vibrational degrees of freedom.

i.e. for a molecule with v degrees of freedom: $\langle E \rangle = v \left(\frac{1}{2} k T \right)$

E.g. in a diatomic molecule there are three translational degrees of freedom (x, y and z), two rotational degrees of freedom (around the x-axis and y-axis, twisting about the z-axis is prohibited due to quantum reasons, the z-axis rotational energy level is above the dissociation level of the molecule) and no vibrational degrees of freedom.

So in this case: $E = E_K = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2$

So: $\langle E_K \rangle = \frac{5}{2} kT$ in this case, where there is no vibrational energy since at room temperature there is not enough energy to excite vibrational motion.

Vibrational motion provides 2 degrees of freedom, one from the kinetic energy and one from the potential energy. Only energies with squared terms are taken in to account, i.e. the gravitational potential, mgh, is not taken in to account since it lacks a squared term.

The degrees of freedom are defined as "*each independent quantity that must be specified to determine the energy of the molecule*".

Heat capacities in ideal gases:

Molar heat capacity: $C = \frac{1}{n} \frac{dQ}{dT}$

First Law of Thermodynamics: $dU = dQ - PdV$ For monatomic, ideal gases: $U = \frac{3}{2} nRT$

At Constant Volume: $dV = 0$ so $dQ_V = dU$ And so: $C_V = \frac{1}{n} \frac{dU}{dT}$

$\frac{dU}{dT} = \frac{3}{2} nR$ And so $C_V = \frac{3}{2} R$

At Constant Pressure: $dQ = dU + PdV$, but $PdV = nRdT$

So $C_P = \frac{1}{n} \left(\frac{dU}{dT} + \frac{PdV}{dT} \right) = \frac{1}{n} \left(\frac{dU}{dT} + \frac{nRdT}{dT} \right) = \frac{1}{n} \left(\frac{3}{2} nR + nR \right) = \frac{5}{2} R$

$\gamma = \frac{C_P}{C_V} = \frac{5}{3} = 1.67$

Polyatomic gases:

$\langle E \rangle = v \frac{1}{2} kT$, $U = N \langle E \rangle = N v \frac{1}{2} kT = n v RT$

And so: $C_V = \left(\frac{dU}{dT} \right) \frac{1}{n} = \frac{v}{2} R$

$$C_P = C_V + R = \left(1 + \frac{v}{2}\right)R$$

$$\gamma = \frac{C_P}{C_V} = \frac{2+v}{v}$$

Note that experimentally the values for γ are consistently lower than expected for polyatomic and diatomic gases due to quantum theory.

The molar heat capacity is **not** constant with changing temperature, as would be expected from classical theory, but varies due to the energy needed to 'unlock' the different energy levels.

Adiabatic processes in ideal gases:

$dQ = 0$ since adiabatic so no heat transfer, $dU + PdV = 0$ but $dU = nC_V dT$, $P = \frac{nRT}{V}$

So: $\frac{dT}{T} + \frac{R}{C_V}\frac{dV}{V} = 0$, $\frac{R}{C_V} = \frac{C_P - C_V}{C_V} = \frac{C_P}{C_V} - 1 = \gamma - 1$

So: $\frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$, solving: $\ln(T) + (\gamma - 1)\ln(V) = c$, $TV^{\gamma-1} = c$

Using ideal gas equation $PV = nRT$ can also obtain expressions: $PV^{\gamma} = c$, $T^{\gamma}P^{1-\gamma} = c$

Work done: $W_Q = -\Delta U = -nC_V \Delta T = nC_V(T_1 - T_2) = \frac{1}{\gamma - 1}(P_1 V_1 - P_2 V_2)$ using the ideal gas equation of state.

Can also be shown that: $W_Q = \int_{V_1}^{V_2} PdV = \frac{P_1 V_1}{\gamma - 1}\left[1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}\right]$

It can be shown that these two expressions are equivalent.

Statistical Mechanics

Discrete distributions

$f_i = \frac{n_i}{N}$ where f_i is the probability of getting a certain value from the distribution (e.g. the proportion of students with a certain mark) and n_i is the number of students that have a certain mark and N is the total number of students.

Where $n_i(s_i)$ and $f_i(s_i)$ are distribution functions:

$$\sum_i f_i = \sum_i \frac{n_i}{N} = \frac{1}{N}\sum_i n_i = 1 \quad \langle s \rangle = \frac{1}{N}\sum_i n_i s_i = \sum_i s_i f_i \quad \langle s^2 \rangle = \frac{1}{N}\sum_i s_i^2 n_i = \sum_i s_i^2 f_i$$

$$s_{rms} = \sqrt{\langle s^2 \rangle}$$

Continuous distributions

f(h)dh: the probability of a person having a height between h and h+dh

$$dP = \frac{dN}{N} = f(h)dh$$

f(h): distribution function

dN = Nf(h)dh: number of people with height between h and h+dh

$$\int f(h)dh = \int dP = 1 \qquad \langle h \rangle = \int h f(h)dh \qquad \langle h^2 \rangle = \int h^2 f(h)dh \qquad \langle g(h) \rangle = \int g(h) f(h)dh$$

Maxwell-Boltzmann Distribution
We expect from the Maxwell-Boltzmann distribution(as it is in equilibrium):
Mean $v_x = 0$ (no convection), No. of molecules with v_x = No. of molecules with -v_x, No. of molecules with $v_x \to \pm\infty$ is negligible.

Let f(v_x) be the velocity distribution function. Then the probability that the molecule will have velocity between v_x and (v_x + dv_x) is:

$$dP_{v_x} = \frac{dN}{N} = f(v_x)dv_x$$

Then the number of molecules with velocity between v_x and (v_x +dv_x) is:

$$dN = Nf(v_x)dv_x \qquad \int dN = \int_{-\infty}^{\infty} N f(v_x)dv_x = N \int_{-\infty}^{\infty} f(v_x)dv_x = N \qquad \int_{-\infty}^{\infty} f(v_x)dv_x = 1$$

$f(v_x) = A e^{-Bv_x^2}$ satisfies our three expectations, A determines the height and B is inversely related to the width

Normalisation

$$\int_{-\infty}^{\infty} f(v_x)dv_x = \int_{-\infty}^{\infty} A e^{-Bv_x^2} dv_x = 1 \qquad A = \sqrt{\frac{B}{\pi}} \quad \text{given} \quad \int_{-\infty}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

Physical meaning of B

Calculate $\langle v_x^2 \rangle$: $\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)dv_x$

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)dv_x = \sqrt{\frac{B}{\pi}} \int_{-\infty}^{\infty} v_x^2 e^{-Bv_x^2} dv_x$$

Given that: $\int_{-\infty}^{\infty} x^2 e^{-\beta x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\beta^3}}$ we obtain $\langle v_x^2 \rangle = \frac{1}{2B}$

but $\langle E_x \rangle = \frac{1}{2}m\langle v_x^2 \rangle = \frac{1}{2}kT$ so $B = \frac{m}{2kT}$, $B \propto \frac{1}{T}$

For the distribution function we have:

$$f(v_x) = A e^{-Bv_x^2} = \left(\frac{m}{2\pi k T}\right)^{\frac{1}{2}} e^{\frac{-mv_x^2}{2kT}}$$

Therefore in three dimensions:
The probability a molecule will have velocity between v_x and (v_x+dv_x) , v_y and (v_y + dv_y), v_z and (v_z +dv_z) is:

$$dP_{v_x, v_y, v_z} = \frac{dN}{N} = f(v_x)dv_x f(v_y)dv_y f(v_z)dv_z = f(v_x)f(v_y)f(v_z)dv_x dv_y dv_z$$

$$dP_{v_x, v_y, v_z} = \left(\frac{m}{2\pi k T}\right)^{\frac{3}{2}} e^{-m\frac{(v_x^2+v_y^2+v_z^2)}{2kT}} dv_x dv_y dv_z = f_1(v)dv_x dv_y dv_z$$
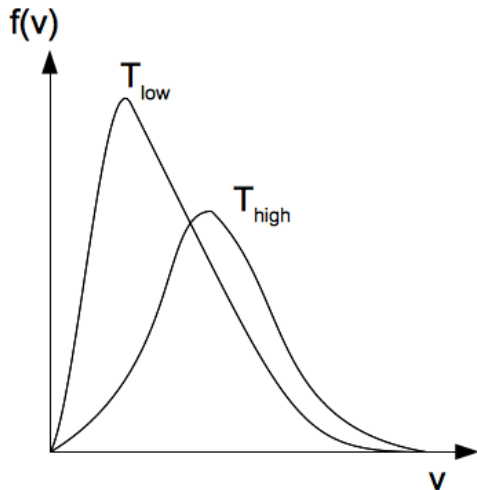
$$dP_v = f_1(v) 4\pi v^2 dv \quad \text{from multiple integration.}$$

$$dP_v = 4\pi \left(\frac{m}{2\pi k T}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kt}} dv$$

and thus via generalising in three dimensions we obtain the speed (directions are lost) distribution function:

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kt}}$$

Effect of Temperature:

$$f(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{\frac{-mv^2}{2kt}}$$

As the temperature increases the speed distribution curve flattens and the peak moves towards high speeds.

1) Mean (average) speed: $\langle v \rangle = \int_0^\infty v f(v) dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty v^3 e^{\frac{-mv^2}{2kT}} dv$ so $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}}$

2) Root Mean Square (rms) speed: $\langle v^2 \rangle = \int_0^\infty v^2 f(v) dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_0^\infty v^3 e^{\frac{-mv^2}{2kT}} dv$ so

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

3) Most probable speed: occurs at $\frac{df(v)}{dv} = 0$ so $v_{mp} = \sqrt{\frac{2kT}{m}}$

Note that $v_{mp} < \langle v \rangle < v_{rms}$

ADD Derivation of energy distribution function from velocity distribution function

Collisions between molecules:
Considering N spherical molecules with radius r in a volume V. The cylinder volume is
$4\pi r^2 \langle v \rangle dt$. The number of molecules with centres in the cylinder is $dN = \frac{N}{V} 4\pi r^2 \langle v \rangle dt$ so

the number of collisions per unit time is $\frac{dN}{dt} = \frac{N}{V} 4\pi r^2 \langle v \rangle$

A correction is required for when all molecules are moving: $\frac{dN}{dt} = \frac{N}{V} 4\pi r^2 \sqrt{2} \langle v \rangle$

The average time between collisions: **Mean free time**: $t_{mean} = \frac{V}{4\pi \sqrt{2} r^2 \langle v \rangle N}$

Average distance between collisions, **Mean free path**: $\lambda = \langle v \rangle t_{mean} = \frac{V}{4\pi \sqrt{2} r^2 N}$

Remember $\langle v \rangle = \text{mean speed} = \sqrt{\frac{8kT}{\pi m}}$

Using the equation of state for an ideal gas at equilibrium, $PV = NkT$, we find:

$$\lambda = \frac{kT}{4\pi\sqrt{2}\,r^2 P} \quad \text{and so} \quad \lambda \propto T,\ \lambda \propto \frac{1}{P}$$

The viscosity (momentum transfer), thermal conductivity (energy transfer) and the coefficient of diffusion (mass transfer) can all be explained in terms of transport of a property across a surface by the gas molecules.

Kinetic theory of thermal conductivity:

$$H = \frac{dN_+}{dt}\langle E_1\rangle - \frac{dN_-}{dt}\langle E_2\rangle = \frac{dN}{dt}\left(\langle E_1\rangle - \langle E_2\rangle\right) = \frac{dN}{dt}\left(\frac{3}{2}kT_1 - \frac{3}{2}kT_2\right) = \frac{3}{2}k\frac{dN}{dt}(T_1 - T_2)$$

but $T_1 = T(x-\lambda)$, $T_2 = T(x+\lambda)$ so $T_1 - T_2 = T(x-\lambda) - T(x+\lambda) = -\frac{dT}{dx}2\lambda$

so $H = -3k\lambda\frac{dN}{dt}\frac{dT}{dx}$ but must find expression for $\frac{dN}{dt}$.

$$dN = \frac{1}{6}\frac{N}{V}\times(cylinder\ volume) = \frac{1}{6}\frac{N}{V}A\langle v\rangle dt \quad so \quad \frac{dN}{dt} = \frac{1}{6}\frac{N}{V}A\langle v\rangle$$

$$H = -3k\lambda\frac{dN}{dt}\frac{dT}{dx} = -\frac{1}{2}k\lambda\frac{N}{V}A\langle v\rangle\frac{dT}{dx} \quad but \quad H = -\kappa A\frac{dT}{dx}$$

so $\kappa = \frac{1}{2}k\lambda\frac{N}{V}\langle v\rangle$ but $C_v = \frac{3}{2}R + \frac{3}{2}kN_A$ so $\kappa = \frac{1}{3}C_v\lambda\frac{n}{V}\langle v\rangle$

so $\lambda \propto \frac{T}{r^2 P} \propto \frac{V}{r^2 N}$, $\langle v\rangle \propto \sqrt{\frac{T}{m}}$ so $\kappa \propto \frac{V}{r^2 N}\frac{N}{V}\sqrt{\frac{T}{m}} \propto \frac{1}{r^2}\sqrt{\frac{T}{m}}$ density-independent.

The Second Law Of Thermodynamics:
Second Law – Spontaneous processes only occur to increase entropy (reducing order), never increasing the order in a system.

Irreversible processes – Finite changes in the state variables, presence of dissipative forces such as friction. **All real processes are irreversible**.

Reversible processes – idealisation, well defined locus on the P-V diagram, can be retraced so that the system **and** the surroundings are restored.

The Carnot cycle:
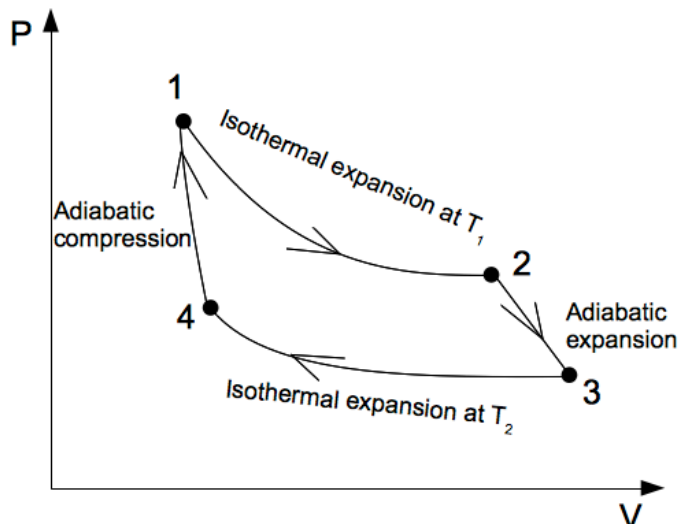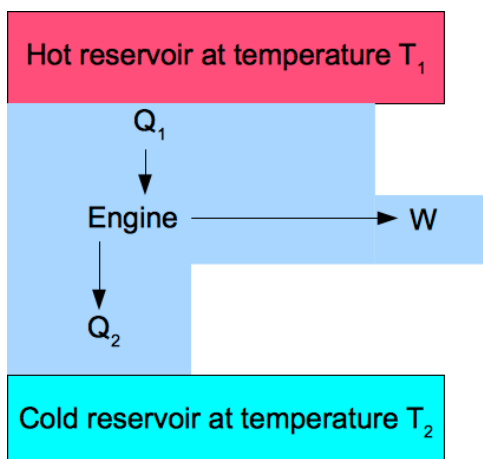
$$\Delta U = Q - W \qquad\qquad W = Q$$
$$\Delta U_{cyc} = 0 \qquad\qquad W = Q_1 + Q_2 = Q_1 - |Q_2|$$
$$Q = Q_1 + Q_2 = Q_1 - |Q_2| \qquad\qquad \eta = \frac{W}{Q_1} \quad \text{thermal efficiency of the engine}$$
$$W = W_{1 \to 2} + W_{2 \to 3} + W_{3 \to 4} + W_{4 \to 1}$$

So Thermal Efficiency: $\eta = \dfrac{W}{Q_1} = \dfrac{Q_1 - |Q_2|}{Q_1} = 1 - \dfrac{|Q_2|}{Q_1}$, it is impossible to achieve a thermal

efficiency of 1 (100% of heat converted in to work), due to the dissipative forces present.

Kelvin formulation of Second Law: *No process is possible whose **sole** result is the extraction of heat from a single reservoir and the performance of an equivalent amount of work.*

Thermal Efficiency of the Carnot Cycle:
If the working substance is an Ideal Gas:

$$\eta = 1 - \frac{|Q_2|}{Q_1} \qquad\qquad \Delta U = Q - W$$

For $1 \to 2$: $\quad \Delta U_{1 \to 2} = 0 \qquad Q_1 = W_{1 \to 2} = nRT_1 \ln\left(\dfrac{V_2}{V_1}\right)$

For $3 \to 4$: $\quad \Delta U_{3 \to 4} = 0 \qquad Q_2 = W_{3 \to 4} = nRT_2 \ln\left(\dfrac{V_4}{V_3}\right) = -nRT_2 \ln\left(\dfrac{V_3}{V_4}\right)$

$$\frac{|Q_2|}{Q_1} = \frac{T_2}{T_1} \frac{\ln\left(\dfrac{V_3}{V_4}\right)}{\ln\left(\dfrac{V_2}{V_1}\right)}$$

For $2 \to 3$: $\quad T_1 V_2^{\gamma - 1} = T_2 V_3^{\gamma - 1} \qquad$ For $4 \to 1$: $\quad T_1 V_1^{\gamma - 1} = T_2 V_4^{\gamma - 1} \quad$ so $\quad \left(\dfrac{V_2}{V_1}\right)^{\gamma - 1} = \left(\dfrac{V_3}{V_4}\right)^{\gamma - 1}$

so $\quad \dfrac{V_2}{V_1} = \dfrac{V_3}{V_4}$, $\quad \dfrac{|Q_2|}{Q_1} = \dfrac{T_2}{T_1} \dfrac{\ln\left(\dfrac{V_3}{V_4}\right)}{\ln\left(\dfrac{V_2}{V_1}\right)} = \dfrac{T_2}{T_1}$ so $\quad \eta = 1 - \dfrac{|Q_2|}{Q_1} = 1 - \dfrac{T_2}{T_1}$

Carnot Cycle as a Refrigerator:
Refrigerators extract heat from a colder reservoir and transfer it to a hotter reservoir. This always requires work.

$$\eta_R = \frac{|Q_2|}{|W|} \quad \text{coefficient of performance for refrigerators}$$

$$\eta_{HP} = \frac{|Q_1|}{|W|} = 1 + \eta_R \quad \text{for heat pumps}$$

Clausius Formulation of Second Law: *No process is possible whose **sole** result is the removal of heat from a reservoir at one temperature and the absorption of an equal quantity of heat by a reservoir at a higher temperature.*

No engine can be more efficient than a Carnot engine operating between the same two temperatures as the practical engine. i.e. $\eta = 1 - \dfrac{T_2}{T_1}$ gives the **maximum efficiency** of a practical engine.

Note that the thermal efficiency of the Carnot Cycle is independent of the working substance, depends only on the reservoir temperatures, T_1 and T_2, gives the maximum possible efficiency of any practical engine and is equal to the efficiency of any other **reversible** heat engine (i.e. considering other reversible cycles yields the same result).

Note that when $\eta=1$, $T_2=0$ and so the Second Law of thermodynamics prohibits the attainment of absolute zero.

Entropy (it's not what it used to be)
Any reversible cyclic process can be approximated via an infinite number of Carnot cycles: We can sum Q/T for these: $\displaystyle\sum_i \frac{Q_i^{(R)}}{T_i} = \oint \frac{\bar{d}\,Q^{(R)}}{T} = 0$ for any reversible cyclic process.
As it equals zero about a closed loop it is an exact differential therefore if we say
$dS = \dfrac{\bar{d}\,Q^{(R)}}{T}$ then $\bar{d}\,Q^{(R)} = T\,dS$ where S is the entropy (reversible only!)

As dS is an exact differential, the entropy S is a function of state. The change in entropy between two states is dependent solely by the initial and final equilibrium states and not by the path between them i.e. path-independent. $\Delta S = S_2 - S_1 = \displaystyle\int_{(1)}^{(2)} \frac{\bar{d}\,Q^{(R)}}{T}$

For an irreversible heat engine $\displaystyle\oint \frac{\bar{d}\,Q^{(I)}}{T} < 0$ and for reversible $\displaystyle\oint \frac{\bar{d}\,Q^{(R)}}{T} = 0$

So in general $dS \geq \dfrac{\bar{d}\,Q}{T}$ (equality only applies for reversible processes)

For a system which is thermally isolated (or completely isolated) $\bar{d}\,Q = 0$ so $dS \geq 0$
The entropy of a thermally isolated system cannot decrease!
Entropy distinguishes between reversible and irreversible processes.
It helps determine the direction of natural processes and equilibrium configuration of a thermally isolated system: maximal entropy.
Provides a natural direction to the time sequence of natural events.

In a thermally isolated system spontaneous processes proceed in the direction of increasing entropy. Processes such as irreversible heat flow or free expansion of a gas result in increased disorder.

E.g. for the reversible isothermal expansion of an ideal gas:
$dU = 0 \Rightarrow \bar{d}\,Q = \bar{d}\,W = P\,d\,V = nRT \dfrac{dV}{V} \Rightarrow \dfrac{dV}{V} \propto \dfrac{\bar{d}\,Q}{T} = dS$ therefore $\dfrac{dV}{V} \propto dS$ and both $\dfrac{dV}{V}$
and dS are measures of the increase in disorder.

Microscopically, the entropy of a system is a measure of the degree of molecular disorder existing

in the system. $S = k \ln \Omega$ Where S is the entropy, k is the Boltzmann Constant and omega is the thermodynamic probability. The thermodynamic probability is a measure of the number of micro-states that result in a given macro-state e.g. for the result of three coin flips: Tail Tail Head it is 3 as TTH HHT and THT are all valid, whereas for Head Head Head it is 1 as only HHH is valid.

Therefore, in a (thermally) isolated system only processes leading to greater disorder (or no change or order) will be possible since the entropy must increase or remain constant. $dS \geq 0$

<u>The fundamental thermodynamic relationship</u>
   $dU = \bar{d} Q - \bar{d} W$ is **always** true.
   $\bar{d} W = P \, dV$ Is true for reversible cases.
   $\bar{d} Q = T \, dS$ Is true for reversible cases.
   $dU = T dS - P dV$ Here all the variables are functions of state so that all the differentials are exact. Therefore it is true for all processes. But we have only included mechanical work whereas more generally you would add additional terms for the work against the surface tension, electric fields etc. in appropriate cases.