TKP Revision Notes

NB. The following is a review of the seven sets of lecture notes that are available on the web. Those full notes take up 259 pages and cover the course material in great detail. This review is supplementary to the full notes and should be used with those notes, the weekly exercises and their solutions (also available on the web) for revision purposes.

1.   Introduction & Temperature.

Internal Energy, Zeroth law of thermodynamics, Temperature scales and Gas scale. Functions of state, state variables. Ideal gas system, equation of state.

Equations of state and internal energy

For an ideal monatomic gas it is relatively straightforward to demonstrate that the **internal energy**, U is related to pressure and volume by;

$$PV = \frac{2}{3}U \qquad\qquad U = \frac{3}{2}PV$$

Internal energy for an ideal gas (no potential energy interactions) is the sum of all of the kinetic energies of the constituent atoms

$$U = \sum_{n=0}^{N} \frac{1}{2}mv_n^2$$

From equipartition of energy considerations, for a single atom the average kinetic energy is

$$KE = \frac{1}{2}m\vec{v}^2 = \frac{3}{2}k_BT$$

Recall $\frac{1}{2}k_BT$ *per degree of freedom*

For a collection of N atoms

$$U = \frac{3}{2}Nk_BT$$

$$PV = Nk_BT = nRT$$

In the above n is the number of moles of a substance forming the system being described.

The above include several **equations of state.** The EoS specifies the relation between **state variables** or **functions of state** such as **P, V** and **T** of which (any) two are independent variables the other being a dependent variable.

It is to be noted that if a process occurs where the temperature remains constant throughout the process then $dU = \frac{3}{2}Nk_BdT = \frac{3}{2}nRdT = 0$ ie. if the temperature is held constant throughout any change in state (change in P or V in the gas paradigm) then there is no change in internal energy.

i) *For an isothermal process the internal energy remains unchanged.*
ii) *The change in internal energy in going from one equilibrium state to another is a constant irrespective of how the change in state was effected. This is because the internal energy is a state variable.*
iii) *If a system is taken around a closed cycle there is no change in internal energy. This also follows from the fact that the internal energy is a state variable.*

The Zeroth Law

The temperature introduced above is the absolute temperature and needs careful definition beginning with the zeroth law.

The zeroth law of thermodynamics is simply stated;
If system A is in equilibrium with system B and system A is in equilibrium with system C then it follows that system B is in equilibrium with system C.

This is important for thermometry as temperature is defined for thermal equilibrium and system A would be the thermometer in the above telling us whether or not system A and C have a common temperature.

Thermometry

Empirical temperature scales involve an observable that is different for different equilibrium states

$$T_X = 273.16\left(\frac{X}{X_{TP}}\right)$$

X is a thermometric property (there are many) and X_{TP} is the value of that property at a fixed point (usually the triple point of water). The value 273.16 is there for historical reasons that sought to align the Kelvin scale (above) with the Celsius scale.

An ideal gas provides a perfect thermometric property as we see by the equation of state. Either pressure or volume is held constant and the other varies linearly with temperature if the gas is ideal. It is easiest to hold volume constant and a constant volume gas thermometer gives temeprature by measuring P and using this as the thermometric property in the previous equation

$$T_{Gas} = 273.16\left(\frac{P}{P_{TP}}\right)$$

The gas will approximate more closely an ideal gas as it becomes more dilute reducing any potential interactions and so the accurate definition of the gas temperature is

$$T_{Gas} = 273.16 \lim_{P_{TP} \to 0}\left(\frac{P}{P_{TP}}\right)$$

The Celsius scale has two fixed points, the boiling and freezing points of water defined as 100 C and 0 C respectively. The other requirement of the Celsius scale (that follows directly) is that there are 100 subdivisions between the ice and boiling points.

$$T_X(^0C) = 100\left(\frac{X - X_{ice}}{X_{steam} - X_{ice}}\right)$$

In defining the Kelvin (absolute) scale using the gas thermometer it was decided to keep 100 degrees between the ice and boiling points. This lead to the appearance of the number 273.16.

2.   Partial Differentials.

Chain rule, reciprocal and cyclical relations, perfect differentials.
In thermodynamics we are dealing with systems that are described by several independent variables and dependent variables. Eg. for a gas we have the variables/physical quantities P, V and T and an equation of state describing the relationship amongst them. Two of these will be independent variables whilst the other will be a dependent variable depending on the problem we are trying to solve. Similarly we have U and many other variables. Other systems will have other variables and equations of state describing the relationship amongst them. To work mathematically in this circumstance we need to use the language of partial differentials and its rules and relations fully described in the coursenotes.

The chain rule.
If z = z(x, y) is a function which depends on two independent variables, x and y

$$\frac{dz(x, y)}{dx} = \frac{dz}{dy}\frac{dy}{dx}$$

The reciprocal relation.
Eg, When there are three variables, P, V, T to be considered

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V} \qquad \left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P} \qquad \left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\left(\frac{\partial P}{\partial V}\right)_T}$$

Taking the ideal gas equation of state for 1 mole $PV = RT$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \qquad \Rightarrow \qquad \left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V}$$

etc.

The cyclical relation.

$$\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = -1$$

An easy way to remember this relation is to take the following row of variables

$$\overset{\textbf{T} \quad \textbf{P} \quad \textbf{V} \quad \textbf{T}}{\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = -1}$$

Taking the ideal gas equation of state for 1 mole $PV = RT$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R} \qquad\qquad \left(\frac{\partial P}{\partial V}\right)_T = \frac{-RT}{V^2} \qquad\qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{R}\frac{-RT}{V^2}\frac{R}{P} = \frac{-PV}{V^2}\frac{V}{P} = -1$$

Perfect Differentials.

A differential is said to be perfect if when carrying out a path integral from an initial to final state it's value is independent of path. A test for the perfect differential as follows; Suppose z = z(x, y) is a function which depends on two independent variables, x and y.

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dz = a(x, y)dx + b(x, y)dy$$

For dz to be a perfect differential requires by definition that

$$\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

implying

$$\frac{\partial a(x, y)}{\partial y} = \frac{\partial b(x, y)}{\partial x}$$

If

$$\frac{\partial a}{\partial y} \neq \frac{\partial b}{\partial x}$$

Then the differential is imperfect and the integral of dz depends on the path. z is not a function of state.

Example; An ideal monatomic gas

$$U = \frac{3}{2}PV$$

(i) $\quad dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV = \frac{3}{2}\left(VdP + PdV\right)$

$$a = \frac{3}{2}V \qquad\qquad\qquad b = \frac{3}{2}P$$

$$\frac{\partial a}{\partial V} = \frac{3}{2} = \frac{\partial b}{\partial P} = \frac{3}{2}$$

dU is a perfect differential and U is a state function

(ii) $\quad$ dW $= -$PdV

First law $\quad dQ = dU - dW = \frac{3}{2}\left(VdP + PdV\right) + PdV = \frac{3}{2}VdP + \frac{5}{2}PdV$

$$a = \frac{3}{2}V \qquad\qquad\qquad b = \frac{5}{2}P$$

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$$\frac{\partial a}{\partial V} = \frac{3}{2} \neq \frac{\partial b}{\partial P} = \frac{5}{2}$$

đQ is not a perfect differential and Q is not a state function.

3. Heat & First Law.

Work, heat and first law. Isothermal and adiabatic processes. Calculations of heat and work flows on a PV indicator diagram.

Work
An ideal gas (later a real gas) is taken as the paradigm that illustrates much of the course and the operations of thermodynamics and its laws. We have internal energy and the equation of state in various forms already and now need to define work to continue. To define work we consider a gas being compressed or expanded. With an infinitesimal change in volume it is straightforward to show tah the infinitesimal work đW is given by

$$đW = -PdV$$

W is not a state variable and and as such the work done in expanding or compressing a gas *depends on how exactly the process is carried out* and not on the ammount of expansion/compression hence the line through the *d* of đ*W* to remind us of this. đ*W* is an example of an **imperfect differential**.

Sign convention;
Work done on the gas, compression, is counted as positive.
Work done by the gas, expansion, is counted as negative.
Noting the negative sign in the equation for đ*W* we can see that this sign convention is reflected there.

The course focussed on four primary processes involving expansion/compression;
      i)   Isochoric processes where volume remained constant while P and T were allowed to vary.

      ii)   Isobaric processes where pressure remained constant while V and T were allowed to vary.

      iii)   Isothermal processes where temperature remained constant while V and P were allowed to vary.

      iv)   Adiabatic processes where P, V and T were allowed to vary but the system was isolated and there was no energy (heat) allowed to enter or leave during the process.

These processes were dealt with in detail in lectures and in the coursenotes using PV diagrams and finding $\Delta W = \int_{i}^{f} đW = - \int_{V_i}^{V_f} PdV = 0$

The most important step in carrying out such integrals for the four processes is to write the pressure P as a function of V something that differs for each process. This is done in detail in the coursenotes but is as follows.

i) Isochoric processes; $dV = 0$ and

$$\unicode{x00111}W = -\int_{V_i}^{V_f} P dV = 0$$

ii) Isobaric processes $dP=0$ and

$$\unicode{x00111}W = -\int_{V_i}^{V_f} P dV = -P\int_{V_i}^{V_f} dV = -P\left(V_f - V_i\right)$$

iii) Isothermal processes $dT = 0$

Using the equation of state and the fact that T is a constant, $P = \dfrac{nRT}{V}$ and

$$\unicode{x00111}W = -\int_{V_i}^{V_f} P dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln\left(V_f - V_i\right) = -nRT \ln\frac{V_f}{V_i}$$

iv) Adiabatic processes need the concept of heat in order to be addressed along with the first law, $dU = \unicode{x00111}Q + \unicode{x00111}W = \unicode{x00111}Q - PdV$
It will be shown later that in an adiabatic process where $\unicode{x00111}Q = 0$

$$PV^{\gamma} = const$$

Where γ is the ratio of specific heat capacities $\gamma = {}^{c_P}\!\!\diagup\!\!{}_{c_V}$ and will depend on whether the gas is monatomic, diatomic etc.
We return to this later but for now

$$\unicode{x00111}W = -\int_{V_i}^{V_f} P dV = -const \int_{V_i}^{V_f} \frac{dV}{V^{\gamma}} = const \times \gamma\left(V_f^{-(\gamma+1)} - V_i^{-(\gamma+1)}\right)$$

$$\unicode{x00111}W = \gamma P_i V_i^{\gamma}\left(V_f^{-(\gamma+1)} - V_i^{-(\gamma+1)}\right)$$

First Law of Thermodynamics

Sticking with the paradigm of the ideal gas. The work done on/by a gas *depends on the details of the process* and not on the initial and final values of the state variables (eg P and V). But if we go from any equilibrium state (P_i, V_i) to any other (P_f, V_f) in any process other than an isothermal process the internal energy will change by an amount

$$\Delta U = \frac{3}{2}\left(P_f V_f - P_i V_i\right)$$

This depends only on the initial and final states and is independent of the process *because U is a state variable.* However, the work done, $\unicode{x00111}W$, will differ depending on the process therefore we cannot write

$$\Delta U = \unicode{x00111}W$$

as a general statement of energy conservation. The concept of heat is thus required and introduced into physics and The First Law returns energy balance to thermodynamics by taking into account the heat evolved in a process.

$$\Delta U = \unicode{x00111}Q + \unicode{x00111}W \qquad\qquad dU = \unicode{x00111}Q + \unicode{x00111}W$$

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Where $\bar{d}Q$ is the heat absorbed or expelled by the system and as $\bar{d}W$ is path dependent then so to must $\bar{d}Q$ be.

Heat
To find the heat absorbed or expelled by the system in any process we must use the First Law and calculations of ΔU and $\bar{d}W$ for the process of interest and then use the First Law $\bar{d}Q = \Delta U - \bar{d}W$.

Sign convention;
Heat absorbed the gas is counted as positive.
Heat expelled by the gas is counted as negative.

Adiabatic processes
In an adiabatic process there is no heat introduced to or extracted from the system under consideration, ie.

$$\bar{d}Q = 0 \qquad \Rightarrow \qquad \Delta U = \bar{d}W \qquad \textbf{and} \qquad dU = \bar{d}W \qquad \Rightarrow \qquad dU = -PdV$$

But the equation of state $U = \dfrac{3}{2}PV \quad \Rightarrow \qquad dU = \dfrac{3}{2}(PdV + VdP) = -PdV \qquad$ for   an adiabatic process

$$\frac{3}{2}VdP = -\frac{5}{2}PdV$$

$$\int_{P_i}^{P_f}\frac{dP}{P} = -\frac{5}{3}\int_{V_i}^{V_f}\frac{dV}{V} \qquad \Rightarrow \qquad \ln\left(\frac{P_f}{P_i}\right) + \ln\left(\frac{V_f}{V_i}\right)^{5/3} = const$$

$$\boxed{P_f V_f^{\gamma} = P_i V_i^{\gamma} = const = PV^{\gamma}}$$

For any **equilibrium state** (P,V) along a path on a PV diagram that represents an adiabatic process. $\gamma = \dfrac{5}{3}$ for a monatomic gas where the state equation $U = \dfrac{3}{2}PV$ applies. Using the equation of state $PV = nRT$ the adiabatic rule can be expressed as

or as

$$\boxed{\begin{array}{c} TV^{\gamma-1} = const \\[2mm] P^{1-\gamma}T^{\gamma} = const \end{array}}$$

Diatomic gases will have a slightly modified equation of state because there are more degrees of freedom (ways in which energy may be taken up) available to those molecules.

Heat Capacities
The introduction/abstraction of an ammount of heat, $\bar{d}Q$, into/from a system will be accompanied by a temperature rise/drop, ΔT and a quantity, the heat capacity may be defined as

$$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} = \frac{dQ}{dT}$$

It is defined when the change in temperature is a reversible one, that is to say at each intermediate temperature the new state is an equilibrium state obeying the state equation. In this case the input or output of heat will always raise or lower the temperature by the same amount. The value of the heat capacity will depend on the type of process in which the heat was transferred in one further way

Constant volume heat capacity when the volume of the system is held constant

$$C_V = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}\bigg|_{V=const}$$

At constant volume the First Law gives $dU = dQ - PdV = dQ \Rightarrow \Delta U = \Delta Q$

And in terms of state variables only we may express the constant volume heat capacity as;

$$C_V = \lim_{\Delta T \to 0} \frac{\Delta U}{\Delta T}\bigg|_{V=const} = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}nR$$

Where the equation of state for a monatomic gas, $U = \frac{3}{2}PV = \frac{3}{2}nRT$, was used.

Constant pressure heat capacity is defined when the heat is transferred whilst holding the pressure constant

$$C_P = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T}\bigg|_{P=const}$$

Tp proceed further a new state function, **Enthalpy** is defined

$$H = U + PV$$

and

$$dH = dU + PdV + VdP = dU + PdV = dQ$$

Allowing a definition of the heat capacity at constant pressure in terms of state variables alone

$$C_P = \lim_{\Delta T \to 0} \frac{\Delta Q_{Rev}}{\Delta T} = \lim_{\Delta T \to 0} \frac{\Delta H}{\Delta T}\bigg|_{P=const} = \left(\frac{\partial H}{\partial T}\right)_P$$

$$H = U + PV = \frac{3}{2}PV + PV = \frac{5}{2}PV = \frac{5}{2}nRT$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{5}{2}nR$$

We see that $\gamma = \frac{5}{3} = \frac{C_P}{C_V}$ from the adiabatic law.

It should be noted that all of the above only applies to a monatomic gas, (no potential, rotational or vibrational contributions to U) where $U = \frac{3}{2}PV = \frac{3}{2}nRT$.

Diatomic gases

Rigid diatomic gases have extra degrees of freedom as the molecule may rotate in two mutually orthoganal directions about the axis joining the atoms. This changes the equation of state

$$U = \frac{5}{2}nRT = \frac{5}{2}PV \qquad \Rightarrow \qquad H = U + PV = \frac{7}{2}PV$$

With a change to the expressions for the heat capacities

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{5}{2}nR$$

and

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{7}{2}nR$$

The adiabatic law becomes

$$P_f V_f^{7/5} = P_i V_i^{7/5} = const = PV^{C_P/C_V}$$

Non-Rigid diatomic gases have two further degrees of freedom as they may vibrate about the axis joining the atoms as well as rotate. The two extra degrees of freedom represent kinetic energy of vibration and potential energy

$$U = \frac{7}{2}nRT = \frac{7}{2}PV \qquad \Rightarrow \qquad H = U + PV = \frac{9}{2}PV$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{7}{2}nR$$

and

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{9}{2}nR$$

The adiabatic law becomes

$$P_f V_f^{9/7} = P_i V_i^{9/7} = const = PV^{C_P/C_V}$$

The Van der Waals gas

The best representation of a non ideal gas (one with potential interactions between the atoms/molecules is with the equation of state;

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

The pressure is modified with a term to account for these interactions and the volume term is modified to account for the fact that in a non-dilute gas the atoms themselves take up a volume thus reducing the free volume for the atoms of the system to move freely in.

The internal energy of the Van der Waals gas may be found as

$$U_{VdW} = \frac{3}{2}nRT - \frac{n^2 a}{V}$$

The heat capacity at constant volume

$$C_V(VdW) = \left(\frac{\partial U_{VdW}}{\partial T}\right)_V = \frac{3}{2}nR$$

An adiabatic law for the Van der Waals gas as

$$T^{3/2}(V - nb) = const$$

NB This is done in detail in the coursenotes.

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4.   Engines.

Heat Engine, Heat Pump and Refrigerator. Simple schematic diagrams with heat and work flows. Efficiency. Carnot engine.

In taking a fluid around a closed cycle on a PV diagram

(i)   The internal energy is unchanged, $\Delta U = 0$

(ii)   The work done on/by the system depends on the details of the path taken. In a clockwise cycle work is done by the system whereas the same cycle counter clockwise results in work done on the system.

(iii)   The heat flow into/from the system depends on the details of the path taken. In a clockwise cycle heat flows into the system whereas the same cycle counter clockwise results in heat flowing from the system.

(iv)   From the first law, $\Delta Q = -\Delta W$

Engine   Refrigerator   Heat Pump
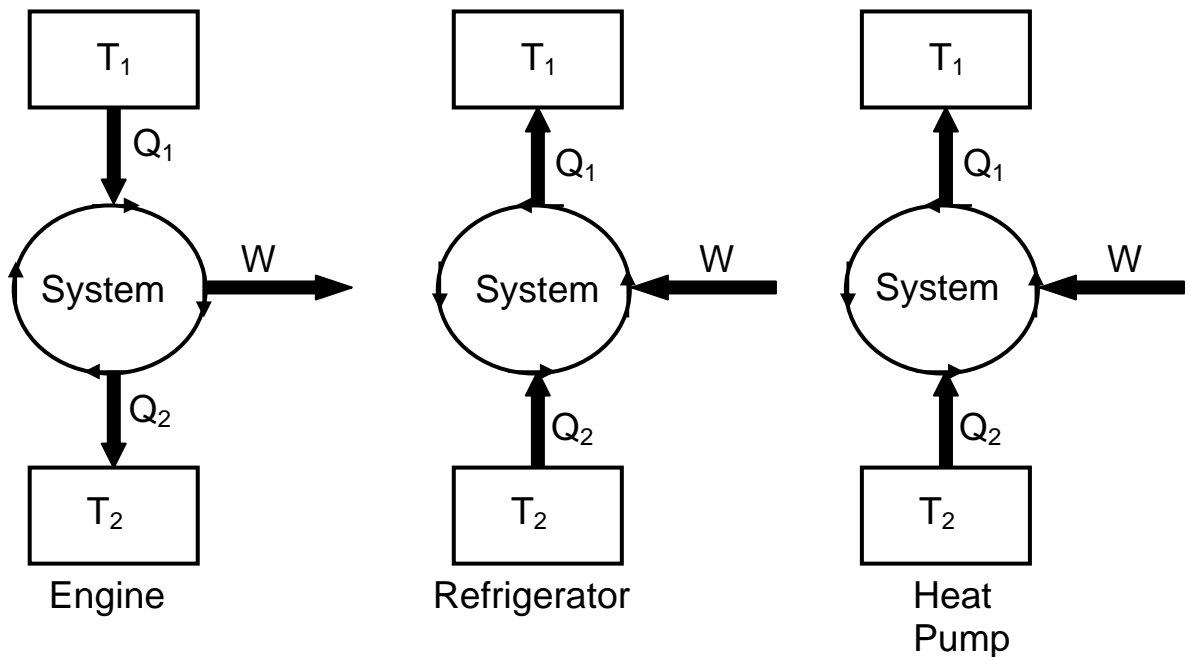
Heat Engines and Efficiencies

The efficiency of either an engine, refrigerator or heat pump may be defined in twords as

$$\eta = efficiency = figure \ of \ merit = \frac{What \ we \ get \ out}{What \ we \ put \ in}$$

i)   Engine; $\eta_E = \dfrac{What \ we \ want \ out}{What \ we \ put \ in} = \dfrac{W}{Q_1}$

From the diagram and the first law $W = Q_1 - Q_2$

$$\eta_E = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

ii)   Refrigerator; $\eta_R = \dfrac{What \ we \ want \ out}{What \ we \ put \ in} = \dfrac{Q_2}{W}$

From the diagram and the first law $W = Q_1 - Q_2$

$$\eta_R = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\dfrac{Q_1}{Q_2} - 1}$$

iii)   Heat Pump; $\eta_{HP} = \dfrac{What \ we \ want \ out}{What \ we \ put \ in} = \dfrac{Q_1}{W}$

$$\eta_{HP} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{1}{1 - \dfrac{Q_2}{Q_1}} = \frac{1}{\eta_E}$$

Ideal Engines and Carnot Cycle

Looking at the efficiency of an engine $\eta_E = 1 - \dfrac{Q_2}{Q_1}$ we answer the question "what form of engine will give the greatest efficiency"?

We need a cycle that will minimise the heat rejected to the low temperature reservoir, Q_2 at the same time maximising the heat into the system as extracted from the hot reservoir, Q_1. Carnot recognised that this would be a cycle in which any heat flows should take place with little or no temperature differences ***ie. the heat flows must be reversible.***

To achieve this he proposed a cycle composed of an isothermal expansion of the system at the temperature of the hot reservoir T_1 with heat transfer to the system from the reservoir with no temperature difference and an isothermal compression of this system at the temperature of the cold reservoir with heat transfer to that reservoir from the system at T_2. The two isotherms are joined by two adiabatic processes (no heat flow) taking the expanded substance from the high to the low temperature and taking the compressed substance from the low temperature to the high temperature.
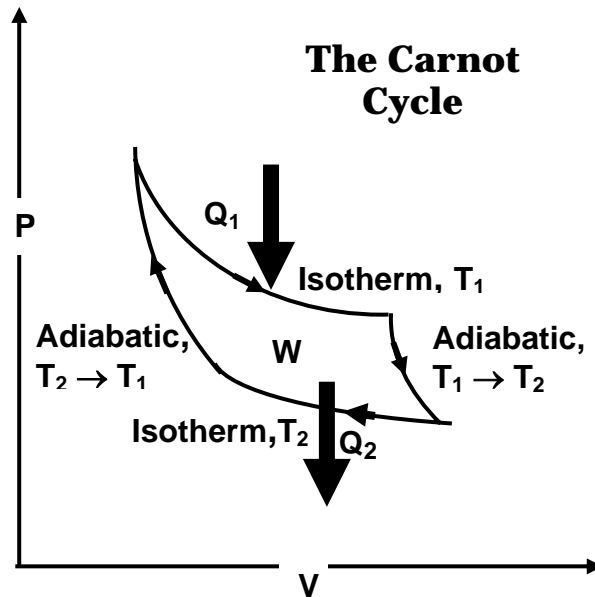
The Carnot Cycle

Carnot's system leads to two statements about the ideal engine;

i) Any Carnot cycle running between two heat reservoirs at temperatures T_1 and T_2 will have a greater efficiency than any other cycle running between those same two temperatures.

ii) The efficiency of any Carnot engine running between the same two heat reservoirs at temperatures T_1 and T_2 will be the same irrespective of the material from which the system is composed or its size. Ie. the efficiency of the Carnot engine depends only upon the temperatures of the two reservoirs.

Absolute Thermodynamic Temperature Scale

Kelvin realised that he could used the Carnot statements to define an absolute temperatuer scale independent of any system, material etc.

$$\eta_C = 1 - \frac{Q_2}{Q_1}$$

Independent of the material of the system and <u>dependent only upon the temperatures</u> of the two reservoirs.

Therefore define the thermodynamic temperature, θ , by

$$\frac{\theta_2}{\theta_1} = \frac{Q_2}{Q_1} = 1 - \eta_C$$

Fix the scale factor by defining $\theta_{Triple\ Point} = 273.16$ and θ is then an absolute (thermodynamic) temperature scale.

It is straightforward to demonstrate, by analysing the Carnot cycle, that $\theta \equiv T_{Gas}$.

$$\boxed{\eta_{CE} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\theta_2}{\theta_1} = 1 - \frac{T_2}{T_1}}$$

Ideal refrigerators and heat pumps may be defined around the Carnot cycle and have efficiencies

$$\eta_{CR} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} = \frac{1}{\frac{T_1}{T_2} - 1}$$

$$\eta_{CHP} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2} = \frac{1}{1 - \frac{T_2}{T_1}} = \frac{1}{\eta_{CE}}$$

NB.
i)   For an engine to have 100% efficiency the low temperatuer reservoir must be at absolute zero.
ii)   If the reservoir temperatures are very close then the heat pump and refrigerator

efficiencies become very large, in fact much greater than 1 but the engine efficiency

becomes very small approaching zero. **The same is true of non-Carnot systems.**

Second Law of Thermodynamics
First given in the form of empirical statements;
        (i)   The Kelvin-Planck Statement: *It is impossible to devise a device that , operating in a cycle, produces no other effect than the extraction of heat from a single body (a reservoir) with the production of an equivalent amount of work.*
        Heat cannot be converted into work with 100% efficiency.

        (ii)   The Clausius Statement: *It is impossible to devise a device that , operating in a cycle, produces no other effect than the transfer of heat from a cooler to a hotter body (reservoir).*
        Heat cannot flow spontaneously from a colder to a hotter body.

Both statements while seemingly different propositions concerning heat and work are equivalent and both statements of the Second Law.

5.   Entropy.

        Clausius inequality. Entropy as a new function of state. Boltzmann's microscopic description of entropy. Entropy calculations.

Clausius Inequality
From the Carnot cycle analysis we have

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \qquad \Rightarrow \qquad \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Clausius considered an arbitrary thermodynamic system undergoing a cycle including both heat flow and work processes and constraining all of the heat flows to be from a reversible Carnot engine operating from a hot reservoir at temperature T_0 . The arbitrary system at temperature T is supplied incremental heat $\delta Q(T)$ at that temperature by the Carnot engine at the same time causing the system to do incremental work δW_{Sys}. This will involve the Carnot engine extracting incremental heat $\delta Q(T_0)$ from the reservoir and doing incremental reversible work δW_{Rev} as shown in diagram. With reference to the diagram

Reservoir at

T_0
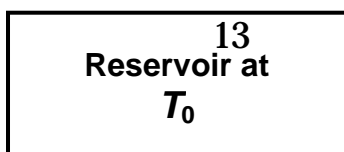
It is important to note that $dQ(T_0)$, $dQ(T)$ and dW_C are cyclical quantities wrt the Carnot engine but they are incremental quantities wrt the system and many Carnot engines drive a complete cycle of the system.

1. $dQ(T_0)$ **is the heat received from the reservoir by the Carnot engine during one or more complete cycles of the Carnot engine.**

2. $dQ(T)$ **is the heat rejected in one or more complete cycles of the Carnot engine consistent with constraints set by the requirements of the Carnot cycle,**

$$\frac{dQ(T_0)}{T_0} = \frac{dQ(T)}{T}$$

3. dW_C **is the work performed in one or more complete cycles by the Carnot engine consistent with constraints set by the requirements of the Carnot cycle,**

$$dW_C = dQ(T_0) - dQ(T)$$

4. dW_{Sys} **is the increment of work performed by the system as it executes a cycle**

For the Carnot engine we use the first law to obtain;

$$dW_C - dQ(T_0) + dQ(T) = 0$$

and

$$\frac{T}{T_0} = \frac{dQ(T)}{dQ(T_0)}$$

Eliminating $dQ(T_0)$ to obtain

$$dW_C = \left(\frac{T_0}{T} - 1\right) dQ(T)$$

The net work of the combined system and Carnot engine for one complete cycle is;

$$W_{Net} = \oint_{\substack{System \\ cycle}} dW_C + \oint_{\substack{System \\ cycle}} dW_{Sys}$$

The second term on the RHS relates to dQ(T) via the first law applied to the system alone

$$\oint_{\substack{System \\ cycle}} dW_{Sys} = \oint_{\substack{System \\ cycle}} dQ(T)$$

Make substitutions to obtain

$$W_{Net} = \oint_{\substack{System \\ cycle}} \left[\left(\frac{T_0}{T} - 1\right) dQ(T)\right] + \oint_{\substack{System \\ cycle}} dQ(T)$$

Which simplifies to

$$W_{Net} = T_0 \oint_{\substack{System \\ cycle}} \frac{dQ(T)}{T}$$

If W_{Net} is positive we have a compound system that violates the Kelvin-Planck statement ie.a device would exist whose sole effect is the exchange of heat with a single reservoir and the creation of an equivalent amount of work.
If W_{Net} is negative or zero no principles are violated as we can always convert work completely to heat as did Joule in his experiments demonstrating the first law.
Ie.

$$W_{Net} = T_0 \oint_{\substack{System \\ cycle}} \frac{dQ(T)}{T} \leq 0$$

This is **The Clausius Inequality**

Whenever a system executes a complete cyclic process the integral of $\delta Q / T$ around the cycle is less than or equal to zero.
T_0 is positive and the Clausius Inequality is usually stated as

$$\oint_{\substack{System \\ cycle}} \frac{dQ(T)}{T} \leq 0$$

For a reversible system cycle which we can go around the cycle in either sense with only the sign of the heat flow changing we have

$$\oint_{anticlockwise} \frac{dQ_R}{T} \leq 0 \qquad \text{and} \qquad \oint_{clockwise} \frac{-dQ_R}{T} \leq 0$$

Therefore

$$\oint_{Cycle} \frac{dQ_R}{T} = 0 \qquad\qquad \text{REVERSIBLE}$$

and

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$$\oint \frac{dQ}{T} < 0 \qquad\qquad \text{IRREVERSIBLE}$$

Note that the quantity $\dfrac{dQ_R}{T}$ is behaving exactly as a state function where its integral over a cycle sums to zero, cf U, H, P and V
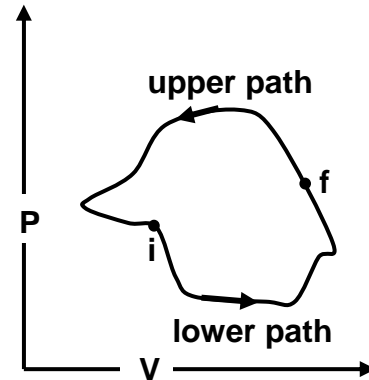
Entropy

To see the significance of $\dfrac{dQ_R}{T}$ we consider
an arbitrary closed reversible cycle and go from
an initial state i to a final state f via either the upper
or lower paths as shown in the diagram opposite.
Around the cycle we have

upper path

f

P

i

lower path

V

$$\int \frac{dQ_R}{T} = \int_{f_{upper}}^{i} \frac{dQ_R}{T} + \int_{i_{lower}}^{f} \frac{dQ_R}{T} = 0$$

or

$$\int_{i_{lower}}^{f} \frac{dQ_R}{T} = - \int_{f_{upper}}^{i} \frac{dQ_R}{T} = \int_{i_{upper}}^{f} \frac{dQ_R}{T}$$

$$\int_{i_{lower}}^{f} \frac{dQ_R}{T} = \int_{i_{upper}}^{f} \frac{dQ_R}{T}$$

The path integral of $\dfrac{dQ_R}{T}$ ***from an initial to a final equilibrium state is independent***

of the path taken (or process used) unlike the path integral of dQ_R. The quantity $\dfrac{dQ_R}{T}$

again displays the property associated with a function of state and is called Entropy

$$\boxed{dS = \frac{dQ_R}{T}}$$

$$S_f - S_i = \Delta S = \int_{i}^{f} \frac{dQ_R}{T}$$

While the state function, S has a unique value for a particular equilibrium state it should
be noted that the above defines only entropy difference

Example. Ideal gas

First Law states $\qquad\qquad dU = dQ_R - PdV$

It follows that

$$dS = \frac{dQ_R}{T} = \frac{dU}{T} + \frac{P}{T}dV$$

We already have an equation of state

$$U = \frac{3}{2}PV \qquad\qquad PV = nRT \qquad\qquad \frac{P}{T} = \frac{nR}{V}$$

$$dS = \frac{3}{2}nR\frac{dT}{T} + nR\frac{dV}{V} = a(V,T)dT + b(V,T)dV$$

with

$$a = \frac{3nR}{2T} \qquad\qquad\qquad b = \frac{nR}{V}$$

We see that V and T are the natural variables of S and we can test to find if S is a perfect differential,

$$\frac{\partial a}{\partial V} = \frac{\partial}{\partial V}\left(\frac{3nR}{2T}\right) = 0 \qquad\qquad \frac{\partial b}{\partial T} = \frac{\partial}{\partial T}\left(\frac{nR}{V}\right) = 0$$

therefore

$$\frac{\partial a}{\partial V} = \frac{\partial b}{\partial T}$$

and dS is therefore a perfect differential.

Because V and T are the natural variables of S we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{3}{2}\frac{nR}{T}dT + \frac{nR}{V}dV$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2}\frac{nR}{T} \qquad\qquad \Rightarrow \qquad\qquad S = \frac{3}{2}nR\ln T + f(V)$$

and

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{nR}{V} \qquad\qquad \Rightarrow \qquad\qquad S = nR\ln V + g(T)$$

Both of these together give

$$\boxed{S(V,T) = \frac{3}{2}nR\ln T + nR\ln V + const}$$

Examples of entropy change

i)   Water at temperature T left in garden (ie heat reservoir) to warm up to ambient temperature, T_a

$$S_f - S_i = \Delta S = \int_i^f \frac{dQ_R}{T}$$

The final temperature is T_a and in between T and T_a the temperature in the integral changes continuously. Also we know that $dQ_R = +c_P m_{H_2O}dT$

$$\Delta S = c_P m_{H_2O}\int_T^{T_a}\frac{dT}{T} = c_P m_{H_2O}\log_e\frac{T_a}{T}$$

ii)   Water at temperature T placed in a freezer to cool down to $-T_F$

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$$\Delta S = \int_{i}^{f} \frac{dQ_R}{T}$$

Needs to be done in three parts first water cooling to 0 C followed by ice formation and finally ice cooling to $-T_F$

$$\Delta S = c_P^{H_2O} m_{H_2O} \int_{T}^{273.15} \frac{dT}{T} + \frac{l_{H_2O \to Ice} m_{H_2O}}{273.15} + c_P^{Ice} m_{H_2O} \int_{273.15}^{T_F} \frac{dT}{T}$$

$$\Delta S = c_P^{H_2O} m_{H_2O} \log_e \frac{273.15}{T} + \frac{l_{H_2O \to Ice} m_{H_2O}}{273.15} + c_P^{Ice} m_{H_2O} \log_e \frac{T_F}{273.15}$$

iii)   We may be asked to find the entropy change of the garden (universe) in pt i)

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

Where $\Delta Q = -c_P^{H_2O} m(T_a - T)$

$$\Delta S = -\frac{c_P^{H_2O} m(T_a - T)}{T_a}$$

Note the signs for ΔQ where it is positive for heat absorbed and negative for heat given up. In parts i) and iii) whethere the heat is absorbed by the water or the ambient depends on whether $T < T_a$ and the way the calculation is set up incorporates this with the correct sign for ΔQ.

Note also that there is no reason why $\Delta S_{Garden} = \Delta S_{H_2O}$ as entropy is not a conserved quantity but it will either be conserved or increased in an isolated system undergoing thermodynamic processes where it is conserved in the case of reversible processes. In other words; $\Delta S_{Net} = \Delta S_{Garden} + \Delta S_{H_2O} \geq 0$ in all processes. This is another way of stating the Second Law of Thermodynamics.

iv)   Water with mass m_1 at T_1 is mixed with water of mass m_2 at T_2 and the mixing takes place adiabatically. Calculate the entropy change
We need to begin by calculating the final temperature, T_f and this we do by recognising that in adiabatic mixing there is no net heat flow

$$\Delta Q_1 + \Delta Q_2 = m_1 c_P (T_f - T_1) + m_2 c_P (T_f - T_2) = 0$$

$$\Delta Q_1 + \Delta Q_2 = m_1 c_P (T_f - T_1) + m_2 c_P (T_f - T_2) = 0$$
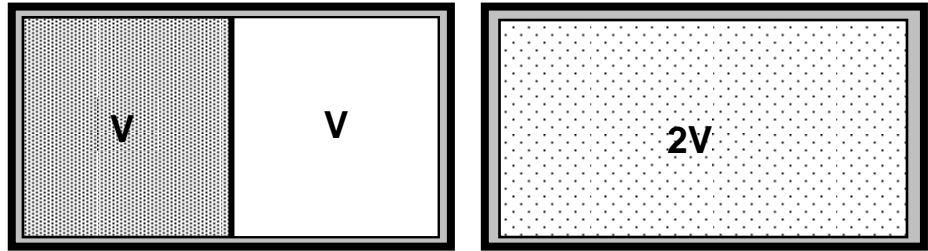
$$T_f = \frac{(m_1 T_1 + m_2 T_2)}{m_1 + m_2}$$

Now we find ΔS as the sum of two entropy changes ΔS_1 plus ΔS_2 calculated as previously

$$\Delta S = c_P \left(m_1 \int_{T_1}^{T_f} \frac{dT}{T} + m_2 \int_{T_2}^{T_f} \frac{dT}{T} \right) = c_P \left(m_1 \log_e \frac{T_f}{T_1} + m_2 \log_e \frac{T_f}{T_2} \right)$$

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This is an example of entropy of mixing. Note in the above example that if $T_1 = T_2$ then both equal T_f and then $\Delta S = 0$

      v)   Joule free expansion

Previously we had

$$S(V,T) = \frac{3}{2} nR \ln T + nR \ln V + const$$

And therefore

$$\Delta S = S_f - S_i = \frac{3}{2} R \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}$$

There is no heat flow and no work done (walls are adiabatic and rigid) and therefore no change in internal energy or temperature.

$$\Delta S = R \ln \frac{2V}{V} = R \ln 2 > 0$$

The entropy has increased with no heat flow.

There are many examples of calculating entropy changes in the lecture notes and in the coursework/solutions on the website. In every example for an isolated system we find

$$\Delta S_{Net} \geq 0$$

Where the equality only holds for reversible changes.

This is another statement of the Second Law.

i) Clausius Inequality and Second Law
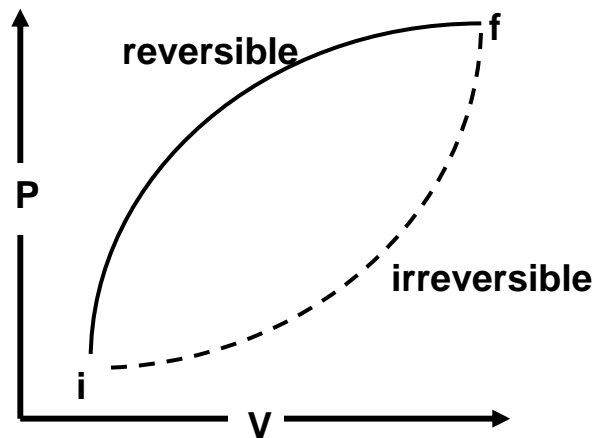
We consider a cycle with an irreversible path from an initial state, i, to a final state, f, followed by an reversible path back from f to i

The Clausius inequality states

$$\oint \frac{dQ}{T_{ext}} = \int_i^f \frac{dQ}{T_{ext}} + \int_f^i \frac{dQ_R}{T} \leq 0$$

NB. When we use the Clausius inequality we distinguish between reversible and irreversible processes and the temperature used in the inequality. If the process is irreversible then the temperature is that of the external source supplying the heat to the system, T_{ext} , whereas in the case of a reversible process $T_{ext} = T_{Sys} = T$ and no distinction is made. Recall that in the definition of dS based around this it is reversible heat flows that are the basis of the definition!

It follows from the above that

$$\int_i^f \frac{dQ}{T_{ext}} \leq -\int_f^i \frac{dQ_R}{T} = \int_i^f \frac{dQ_R}{T} = S_f - S_i = \Delta S$$

Whence for any change between equilibrium states i and f

$$\Delta S \geq \int_i^f \frac{dQ}{T_{ext}} \quad , \qquad dS \geq \frac{dQ}{T_{ext}} \qquad \text{(Irreversible change)}$$

$$\Delta S = \int_i^f \frac{dQ_R}{T} \qquad dS = \frac{dQ_R}{T} \qquad \text{(Reversible change)}$$

If we consider a thermally isolated system with $dQ = 0$ then clearly from the above inequality it follows that

$$\Delta S \geq 0 \qquad dS \geq 0 \qquad \text{(Thermally isolated system)}$$

and for a reversible change

$$\Delta S = 0 \qquad dS = 0 \qquad \text{(Reversible change in thermally isolated system)}$$

Again the statement; for a system taken in isolation (the universe), **the sum** of the entropy changes of all the parts is such that $\Delta S \geq 0$. This is an equivalent statement to the Clausius inequality.

In summary;

1) **The entropy of a thermally isolated system can only increase or remain constant.**
2) **Spontaneous changes in isolated systems lead to an increase in entropy.**
3) **In a thermally isolated system, S will tend to the maximum value possible**
4) **In a totally isolated system, S will tend to the maximum possible value at fixed U ie. U will remain constant.**

These are all;
  ENTROPY STATEMENTS OF
  THE SECOND LAW OF THERMODYNAMICS

$$\Delta S_{Universe} \geq 0$$

This expression of the second law is related (of course) to the two statements by Clausius and by Kelvin and Planck.

a) **Kelvin's statement** was that heat could not be converted into work with 100% efficiency, or equivalently that some heat must always be ejected as waste from the engine into a cold reservoir.
We can relate this to the form of the second law given by the inequality by asking what happens to entropy if we can convert heat to work with no waste heat being rejected to a cold reservoir. The heat has come **from** a hot body and therefore involves a **decrease**

$$\Delta S = -\frac{\int dQ}{T_1} = -\frac{Q_1}{T_1} < 0$$

in the entropy of that body. The work performed of itself has no effect on the entropy of the system or universe and the second law as an inequality is violated, entropy has been reduced. The Kelvin-Planck is therefore equivalent to the inequality.

b) **Clausius' statement** that heat could not flow spontaneously from a colder to a hotter body can be related to the new entropic second law by imagining the scenario, breaking Clausius' statement, where a glass of water is placed in a warm oven and ice forms spontaneously as the colder body, the water , loses heat to the warmer body, the oven. The water as it cools loses heat and will see a decrease in its entropy

$$\Delta S_{H_2O} = -\frac{\int dQ}{T_{H_2O}} = -\frac{\Delta Q}{T_{H_2O}}$$

whilst the warmer oven receiving the heat will see an increase in its entropy of

$$\Delta S_{Oven} = +\frac{\int dQ}{T_{Oven}} = +\frac{\Delta Q}{T_{Oven}}.$$

We see immediately that the occurrence of the temperature in the denominator of these expressions means that the same amount of heat has transferred from the water and to the oven and yet the change in entropy is much larger for the colder water than it is for the warmer oven and

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$$\Delta S_{Universe} = \frac{\Delta Q}{T_{Oven}} - \frac{\Delta Q}{T_{H_2O}} = \Delta Q \left(\frac{T_{H_2O} - T_{Oven}}{T_{H_2O} T_{Oven}} \right) < 0$$

The second law in its entropic form is again violated. Heat cannot therefore leave a colder body and flow to a hotter body as this will inevitable lead to a decrease in entropy in contravention of the entropic forms of the second law.

c)   Engines and the waste heat.

We can see now that the "waste" heat rejected into the cold reservoir in any real engine is absolutely necessary as it raised that body's entropy by an amount $\Delta S = \frac{\int dQ}{T_2} = \frac{Q_2}{T_2}$ such that

$$\Delta S_{univese} = -\frac{Q_1}{T_1} + \frac{Q_2}{T_2} > 0$$

Ie the entropy is increased and because **the heat came from a hot body** and was **rejected to a colder body**, from our measure of entropy where the temperature of the body appears in the denominator, this allows a smaller amount of heat $Q_2 < Q_1$ to be rejected to the colder body but still for there to be a greater entropy increase to allow full compliance with the second law and yet leave some energy, $Q_1 - Q_2$ from the hot body to be available to perform useful work, W.

The Thermodynamic Identity.

With the definition of entropy

$$dS = \frac{dQ_R}{T}$$

We recognise that we can write dQ in a form ***involving only state functions***

$$dQ = TdS$$

This allows the First Law to be written in terms of state functions only. For example we have for a gas

$$dU = TdS - PdV$$
This is known as the **Thermodynamic Identity**.

All differentials in this identity are now perfect differentials, independent of path!

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

This tells us that U can be described using only the variables S and V ie. $U = U(S, V)$ with S and V being a pair of natural variables that specify the behaviour of the internal energy. Furthermore we can from the previous equation that

$$\left(\frac{\partial U}{\partial S} \right)_V = T \qquad \left(\frac{\partial U}{\partial V} \right)_S = -P$$

Or alternatively

$$dS = \frac{1}{T}dU + \frac{P}{T}dV = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$

Implying that S can be specified completely through the variables U and V ie. $S = S(U, V)$
This allows us to write;

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \qquad\qquad \left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

There are many examples of using the p-artial differential of some thermodynamic function with respect to its natural variables to obtain expressions for other thermodynamic functions a practice that is frequently very useful.

Using the entropic version of heat flow we can obtain equations for the heat capacities at constant volume or pressure

$$C_V = \lim_{\Delta T \to 0}\left(\frac{\Delta Q_R}{\Delta T}\right)_V = \lim_{\Delta T \to 0}\left(\frac{T\Delta S}{\Delta T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial \ln T}\right)_V$$

and

$$C_P = \lim_{\Delta T \to 0}\left(\frac{\Delta Q_R}{\Delta T}\right)_P = \lim_{\Delta T \to 0}\left(\frac{T\Delta S}{\Delta T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial \ln T}\right)_P$$

By measuring either C_V or C_P we may determine S by integration.

Microscopic Interpretation of Entropy

Ludwig Boltzmann was the first to give a microscopic explanation of entropy as follows;
Entropy is a measure of the MICROSCOPIC probability of finding the system under study in a given MACROSCOPIC equilibrium state.
By probability we mean here a number that is proportional to the number of distinct ways a system can arrange itself microscopically to achieve a particular macroscopic equilibrium state.

$$\boxed{S(U,V)=k_{\mathrm{B}}\ln\Omega(U,V)}$$

Ω is the number of microscopic arrangements that will give the macroscopic arrangement that it is specified for and for a gas

$$\Omega_{Position} = \left(\frac{V}{(\Delta X)^3}\right)^N \qquad\qquad \Omega_{Momentumn} = \left(\frac{p_{rms}^3}{(\Delta p)^3}\right)^N$$
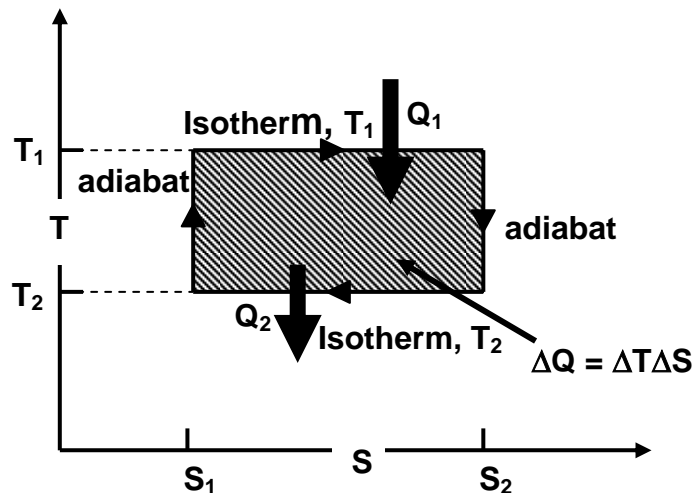
S is an extensive variable and we can add entropies to find an overall entropy eg.

$$S_{Net} = S_{Position} + S_{Momentum}$$

$$S_{Net} = k_B\left(\ln\Omega_{Position} + \ln\Omega_{Momentum}\right) = k_B \ln\Omega_{Position}\Omega_{Momentum}$$

This property of the extensivity of S can be applied in many ways eg when mixing two substances we may find the entropy of each and add to find the overall entropy.

The Carnot Cycle on a T-S diagram

We may represent the Carnot cycle (or any other) on a T-S diagram as shown above where the isotherms are horizontal lines and the adiabats where no heat is absorbed must be vertical lines of constant entropy or isentropes.

The area inside the rectangle representing the Carnot cycle on a $T - S$ diagram is

$$T_1 \int_{S_1}^{S_2} dS + T_2 \int_{S_2}^{S_1} dS = Q_1 - Q_2 = \Delta T \Delta S$$

By application of the first law and the fact that over a cycle $\Delta U = 0$ the area is also the net work done ie. it is the total heat absorbed..

Consideration of the T-S diagram for a Carnot engine also allows us to obtain the Carnot form of the efficiency straight away by simple calculation of areas

$$\eta_E = \frac{W}{Q_1} = \frac{\Delta T \Delta S}{T_1 \Delta S} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

6.   Photons & Paramagnets

Photon gas and equation of state. Planck radiation distribution, Stefans law and Wiens law. Paramagnets and work. Curies law.

Thermodynamics of Photons

The following equations all apply to photons

$$p = \frac{h}{\lambda} = \hbar k \quad \text{(de Broglie)} \qquad\qquad E = h\nu \qquad \text{(Planck)}$$

$$E = pc \qquad \text{(Einstein)} \qquad\qquad |\vec{v}| = c \qquad \text{(Einstein)}$$

Using these we can find

$$\vec{p} \bullet \vec{v} = \left(\frac{E}{c}\right) c = E$$

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For an ideal monatomic gas the equation of state can be written in the form

$$PV = \frac{N}{3}\langle \vec{p} \bullet \vec{v} \rangle = \frac{2}{3}U \qquad \textbf{(Ideal Gas)}$$

All photons have the same momentum (if the radiation is monopchromatic) and the average is no longer necessary. Thus for photons this equation of state, using what we have so far derived becomes

$$\boxed{PV = \frac{N}{3}E = \frac{1}{3}U} \qquad \textbf{(Photon Gas)}$$

Or we can define an energy density, $u = U/V$ and have for the pressure,

$$P = \frac{1}{3}u \qquad \textbf{(Photon Gas)}$$

We are interested in the radiation field in a cavity that is in thermal equilibrium at ba temperature T. Generally the radiation in a cavity is spread across all wavelengths and thus

$$u = \int_0^\infty u_\lambda d\lambda$$

In **equilibrium** u_λ must be **isotropic** (equal numbers of photons at any given wavelength travelling in any given direction) just as in a material gas where the molecules will have an isotropic distribution due to many random collisions with the walls. This means that it is also the case that u_λ must be **independent of the wall material.** *(See coursenotes)* The only property of a cavity that u_λ can depend on is the temperature, T

$$u_\lambda = u_\lambda(T).$$

And therefore from this it follows that

$$u = \int_0^\infty u_\lambda d\lambda = u(T)$$

According to an argument by Boltzmann the cavity radiation can be treated like a *P-V-T* system and therefore **the thermodynamic identity** may be used;

$$dU = TdS - PdV$$

$$U(T) = u(T)V \qquad \Rightarrow \qquad dU = d(u(T)V) = TdS - PdV$$

We can use the equation of state $P = \frac{1}{3}u$

$$d(u(T)V) = TdS - \frac{1}{3}u(T)dV$$

Rearranging

$$TdS = \left(udV + u'VdT \right) + \frac{1}{3}udV \qquad \left(u' = \frac{du}{dT} \right)$$

$$dS = \left(\frac{u'}{T}V \right)dT + \left(\frac{4}{3}\frac{u}{T} \right)dV$$

T and V are the natural variables of S as found previously for a gas and the above equation is in the form;

$$dS = a(V,T)dT + b(V,T)dV$$

dS is a perfect differential, therefore, $\dfrac{\partial a}{\partial V} = \dfrac{\partial b}{\partial T}$, 　　　　ie. $\left(\dfrac{\partial^2 S}{\partial V \partial T} = \dfrac{\partial^2 S}{\partial T \partial V} \right)$

$$\frac{\partial}{\partial V}\left(\frac{u'}{T} V \right) = \frac{u'}{T} = \frac{\partial}{\partial T}\left(\frac{4}{3}\frac{u}{T} \right) = \frac{4}{3}\left[\frac{u'(T)}{T} - \frac{u}{T^2} \right]$$

$$\frac{u'}{T} = \frac{4}{3}\frac{u'}{T} - \frac{4}{3}\frac{u}{T^2}$$

$$\frac{1}{3}\frac{u'}{T} = \frac{4}{3}\frac{u}{T^2} \qquad \Rightarrow \qquad u' = 4\frac{u}{T} = \frac{du}{dT}$$

$$\frac{du}{u} = 4\frac{dT}{T}$$

Integrating

$$\ln u = 4 \ln T + \text{const} = \ln(T^4) + \text{const}$$

$$\boxed{\; u(T) = AT^4 = \frac{U}{V} \;}$$

$$dS = \left(\frac{u'(T)}{T} V \right) dT + \left(\frac{4}{3}\frac{u(T)}{T} \right) dV = 4AT^2 V dT + \frac{4}{3}AT^3 dV$$

Again using T and V as natural variables of S we may write

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\left(\frac{\partial S}{\partial T} \right)_V = 4AT^2 V \qquad \textbf{integrate wrt } \textbf{\textit{T}} \qquad \Rightarrow \qquad S = \frac{4}{3}AT^3 V + f(V)$$

And

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{4}{3}AT^3 \qquad \textbf{integrate wrt } \textbf{\textit{V}} \qquad \Rightarrow \qquad S = \frac{4}{3}AT^3 V + g(T)$$

The only consistent solution to these two forms of S is

$$S = \frac{4}{3}AT^3 V + const$$

If we require that at $T = 0$, $S = 0$ then we require that const $= 0$.

$$\boxed{\; S = \frac{4}{3}AT^3 V \qquad\qquad s = \frac{S}{V} \propto T^3 \;}$$

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Defining some properties of the walls of the cavity as follows;

(i) α_λ is the spectral absorptivity of the surface of the wall at temperature T

(ii) $\alpha_\lambda d\lambda$ the fraction of incident energy that is absorbed by the surface between λ and $\lambda + d\lambda$..

(iii) ε_λ is the spectral emissivity of the surface at temperature T

(iv) $\varepsilon_\lambda d\lambda$ is the energy emitted per unit area per second by the surface between λ and $\lambda + d\lambda$.

The number of particles in a gas of **density** n striking unit area of the wall in unit time is given by

$$\frac{1}{4} n \langle v \rangle$$

where for photons the mean speed $\langle v \rangle = c$

The energy absorbed per unit area per second in the wavelength interval $(\lambda, \lambda + d\lambda)$ is therefore

$$E_{abs}(\lambda) = \alpha_\lambda \left(\frac{c}{4} n_\lambda E_\lambda d\lambda \right) \qquad E_{abs}(\lambda) = \alpha_\lambda \frac{c}{4} u_\lambda d\lambda$$

In equilibrium the energy absorbed is equal to the energy emitted and thus

$$\alpha_\lambda \frac{c}{4} u_\lambda d\lambda = \varepsilon_\lambda d\lambda$$

$$\frac{\varepsilon_\lambda}{\alpha_\lambda} = \frac{c}{4} u_\lambda(T)$$

The quotient on the left hand side, $\dfrac{\varepsilon_\lambda}{\alpha_\lambda}$ is a universal function of λ and T irrespective of the material of the surface. This is known as **Kirchoff's Law.**

A **black body** is one where all of the radiation falling on it is absorbed, $\alpha_\lambda^{Blackbody} = 1$

$$\varepsilon_\lambda^{blackbody} = \frac{c}{4} u_\lambda(T)$$

$$\int_0^\infty \varepsilon_\lambda^{blackbody} d\lambda = \frac{c}{4} \int_0^\infty u_\lambda(T) d\lambda = \frac{c}{4} u(T) = \frac{cA}{4} T^4$$

Total energy emitted is

$$\boxed{\varepsilon_{Tot} = \sigma T^4 \qquad \qquad \textbf{The Stefan Boltzmann law}}$$

$$\sigma = \frac{cA}{4} = 5.67 \times 10^{-8} Wm^{-2} K^{-4} \qquad \text{is } \textbf{the Stefan constant}$$

It also follows that

$$\boxed{\begin{array}{l} u(T) = AT^4 = \dfrac{4\sigma}{c} T^4 \\[2mm] \text{and} \\[2mm] S = \dfrac{4}{3} AT^3 V = \dfrac{16\sigma}{3c} T^3 V \end{array}}$$

$$u_\lambda(T) = \frac{8\pi hc}{\lambda^5} \frac{1}{exp\left(\frac{hc}{\lambda k_B T}\right) - 1} \quad \Rightarrow \quad u_\lambda(T) = \left(\frac{8\pi}{\lambda^4}\right) \times \left(\frac{1}{exp\left(\frac{h\nu}{k_B T}\right) - 1}\right) \times (h\nu)$$

The first bracket is the density of states, the second bracket is the Bose Einstein distribution function describing the probability of occupation of a bosonoc state at energy $E = h\nu$ and the third bracketb is the energy of a single photon

Stefan's constant is given by

$$\sigma = \frac{2\pi^5 k_B^4}{15 h^3 c^2}$$

Thermodynamics of Paramagnets
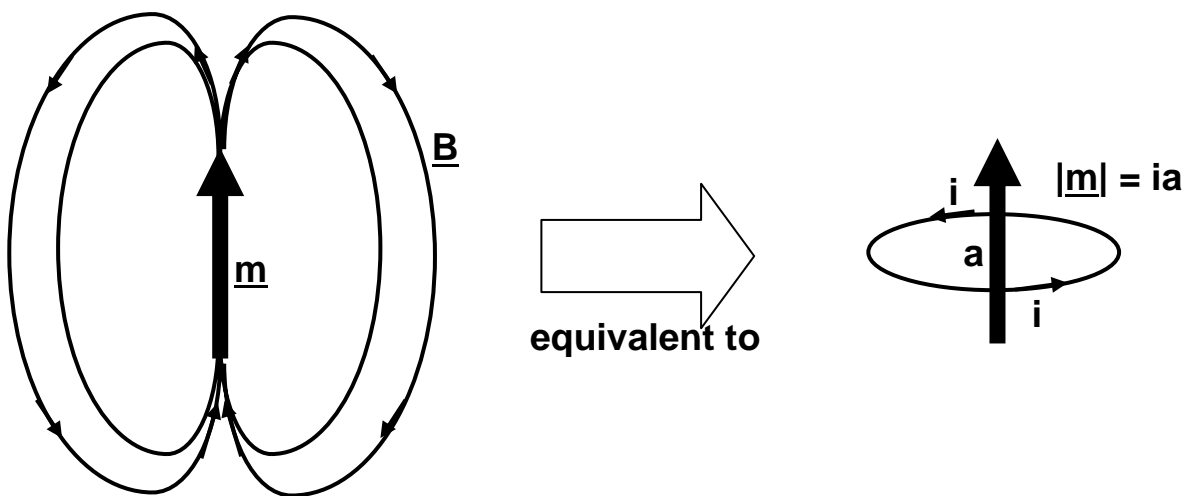
An electron with its intrinsic spin is considered as a small magnet with dipole moment

$$\vec{m}_e = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} \, Am^2$$

Thermodynamics is concerned with a body containing many of these dipoles and their alignment in an applied magnetic field $\vec{B}_0$

In the applied field the dipole acquires an energy

$$u = -\vec{m}_e \bullet \vec{B}_0$$

Giving a sample containing many of theses small dipoles an overall magnetic moment, $\mathcal{M}$, described by

$$B_m = \mu_0 \frac{\mathcal{M}}{V} = \mu_0 M$$

And thus a total field exists

$$B = B_0 + B_m = B_0 + \mu_0 M$$

Here M is the magnetic moment per unit volume.

The work done on the paramagnetic system by the external applied field can be shown to be

$$dW = +B_0 d\mathcal{M}$$

Note the sign

Using this we may write down the first law for a paramagnet with a fixed volume if we compare for a gas where we had the thermodynamic identity

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$$

For the paramagnet in comparison we have;

$$\mathrm{d}U = T\mathrm{d}S + B_0\mathrm{d}\mathcal{M}$$

Curies Law and Equation of State

M is is proportional to the applied field at low applied fields and

$$B_\mathrm{m} = \mu_0 M = \chi_\mathrm{m} B_0$$

Where the quantity χ_m is the magnetic susceptibility. Experimentally down to low temperatures

$$\chi_m = \frac{\mathcal{C}}{T}$$

Known as **Curie's Law**

where C is Curie's constant specific to a given material.
We can then write

$$\mu_0 \mathrm{M} = \frac{\mathcal{C}}{T} B_0 \qquad\qquad B_0 = \left(\frac{\mu_0 T}{\mathcal{C}V} \right) \mathcal{M}$$

Where the latter is the equation of state of a paramagnetic system at low temperatures. Specific heat capacities may be defined for a paramagnet

$$C_{B_0} \equiv \left.\frac{dQ_R}{dT}\right|_{B_0=const} = \left.T\frac{dS}{dT}\right|_{B_0=const} = T\left(\frac{\partial S}{\partial T}\right)_{B_0}$$
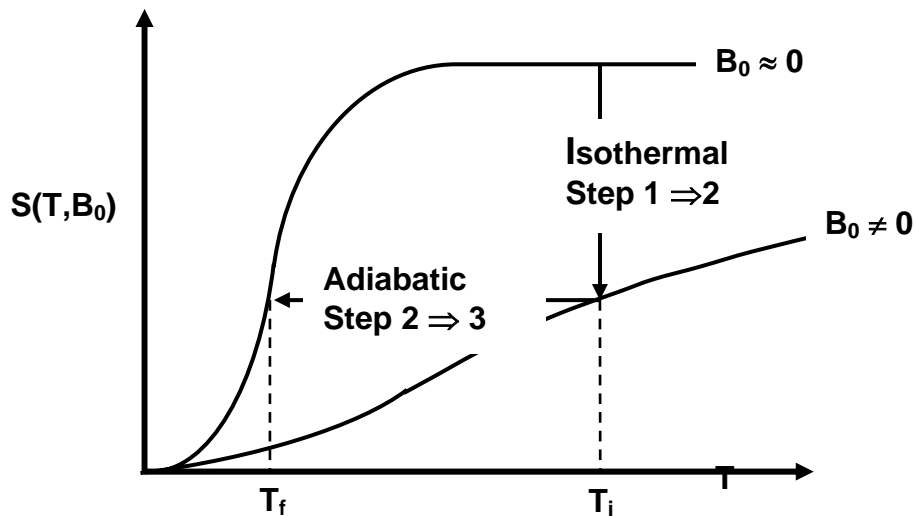
$$C_M \equiv \left.\frac{dQ_R}{dT}\right|_{\mathcal{M}=const} = \left.T\frac{dS}{dT}\right|_{\mathcal{M}=const} = T\left(\frac{\partial S}{\partial T}\right)_{\mathcal{M}}$$

How these heat capacities depend on T and V take a simple form as the applied field, B_0, tends to zero.

$$C_{B_0}(T,B_0)\big|_{B_0=0} = C_{B_0}(T,0) = \frac{Vb}{T^2}$$

This is **Schottky's Law**

Paramagnetic Cooling

The basic principles of adiabatic cooling can be shown on a S-T diagram. It can be shown that $S(T)$ has the form indicated. The entropy of a paramagnet is determined by the degree of randomness of the spins. At low temperatures in a small magnetic field the spins align with the field and the entropy decreases. As temperature is raised the spins become disaligned and the entropy saturates when the spins are completely random. At a higher applied magnetic field the same arguments hold except that it requires a higher temperature to randomise the spins.

6.   Maxwell Relations, Phase Changes & Third Law.

How to find the natural variables of a function of state. How to obtain new relationships amongst thermodynamic variables. New state variables, G, F and H. Clausius Clapeyron equation. The Third Law of Thermodynamics.

State Functions, Natural Variables and Maxwell Relations
There are two more state functions that need to be introduced, in introducing them the idea of natural variables is reenforced and the properties of perfect differentials used to obtain Thermodynamic relations known as Maxwell Relations illustrated.

The Gibbs Free Energy
The Gibbs function or Gibbs free energy for a fluid is

$$G = U - TS + PV$$

The incremental of G is

$$dG = dU - TdS - SdT + PdV + VdP$$

But from the First Law in the form of the Thermodynamic Identity we have

$$dU - TdS = -PdV$$

so

$$dG = -SdT + VdP$$

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Any change in *G* depends only on changes in *T* and *P* which are ***the natural variables*** of *G*

$$G = G(T,P)$$

Using the natural variables of *G* to write the incremental d*G* as

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

By comparing again the coefficients of the increments of the natural variables in the two equations

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad\qquad V = \left(\frac{\partial G}{\partial P}\right)_T$$

These are expressions for the thermodynamic parameters, S and V in terms of partial differentials of the Gibbs function wrt one of its natural variables!

By making use of the properties of perfect differentials we may write,

$$\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T} \qquad \Rightarrow \qquad \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)$$

Using the expressions for S and V found previously we are able to write

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

This is known as a Maxwell Relation

Six simple steps to get from the definition of a Thermodynamic state function to a Maxwell relation via thew Thermodynamic Identity.

The significance of the Gibbs Free Energy lies in situations where pressure and temperature are held constant. In such a circumstance in a closed system

$$dG = -SdT + VdP = 0$$

The equilibrium condition for a system held at constant <u>pressure</u> and <u>temperature</u> is that the Gibbs free energy should be a minimum.
Equivalently any changes in the system will be such as to reduce *G* or to leave it unchanged.

The Helmholtz Free Energy
**i)	Definition.**
The Helmholtz free energy for a fluid is

$$F = U - TS$$

**ii)	<u>The incremental</u>** of *F* is

$$dF = dU - TdS - SdT$$

iii) <u>**From Thermodynamic Identity**</u> we have

$$dU - TdS = -PdV$$

so

$$dF = -SdT - PdV$$

iv) <u>**Natural Variables of F**</u>

Any change in F depends only on changes in T and V which are ***the natural variables*** of F

$$F = F(T,V)$$

Using the natural variables of G to write the incremental dG as

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

v) <u>**Comparing incrementals**</u>

By comparing again the coefficients of the increments of the natural variables in the two equations

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad\qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

These are expressions for the thermodynamic parameters, S and P in terms of partial differentials of the Helmholtz free energy wrt one of its natural variables!

vi) <u>**Finding the Maxwell Relation**</u>

By making use of the properties of perfect differentials we may write,

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T} \qquad \Rightarrow \qquad \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right) = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)$$

Using the expressions for S and V found previously we are able to write

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

This is another Maxwell Relation

The significance of the Helmholtz Free Energy lies in situations where volume and temperature are held constant. In such a circumstance in a closed system

$$dF = -SdT - PdV = 0$$

The equilibrium condition for a system held at constant <u>volume</u> and <u>temperature</u> is that the Helmholtz free energy should be a minimum.
Equivalently any changes in the system will be such as to reduce F or to leave it unchanged.

Enthalpy

We can also remind ourselves at this stage of an earlier state function, Enthalpy, H and go through the same procedures to obtain expressions for thermodynamic quantities and another Maxwell relation.

  i)   **Definition.**

  ii)

$$H = U - PV$$

ii)   **Incremental**

$$dH = dU + PdV + VdP$$

iii)   **From the Thermodynamic Identity** $dU - PdV = TdS$

$$dH = TdS + VdP$$

iv)   **The Enthalpy H has natural variables S and P and therefore**

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

v)   **Comparing with the incremental**

$$T = \left(\frac{\partial H}{\partial S}\right)_P \qquad V = \left(\frac{\partial H}{\partial P}\right)_S$$

vi)   **And the Maxwell relation**

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

Gibbs Free Energy, Phase Changes and Clausius Clapeyron equation.

A substance eg. the fluid in our PVT system paradigm will exisit in phases other than that of a gas where at low temperatures and high pressures the intermolecular interactions may cause the fluid to change from gas to liquid or gas/liquid to solid. Such phase changes are described on PVT diagrams with phase boundaries and the changes that occur in crossing the phase boundary. Consider that the substance has a total mass M and it co-exists in two phases eg. vapour phase and liquid phase. As we change phase (by altering P, V or T) conservbation of mass requires;

$$M = M^{V} + M^{L} = cons\,tant$$

If g^V and g^L be the Gibbs functions per unit mass or specific Gibbs function for each phase

$$G = M^{V} g^{V} + M^{L} g^{L}$$

The condition for equilibrium at fixed P and T is that the Gibbs function must be minimized ie. $dG = 0$

$$dG = d(M^{V} g^{V} + M^{L} g^{L})$$

$$dG = g^{\mathcal{V}}(T,P)dM^{\mathcal{V}} + g^{\mathcal{L}}(T,P)dM^{\mathcal{L}}$$

Conservation of mass requires

$$dM = dM^{\mathcal{V}} + dM^{\mathcal{L}} = 0 \qquad \Rightarrow \qquad dM^{\mathcal{V}} = -dM^{\mathcal{L}}$$

Giving

$$dG = \left(g^{\mathcal{V}} - g^{\mathcal{L}}\right)dM^{\mathcal{V}} = 0 \quad \text{for any } dM^{V}$$

We then have the equilibrium condition for the co-existence of the phases that

$$g^{\mathcal{V}}(T,P) = g^{\mathcal{L}}(T,P)$$

along the liquid/vapour co-existence line in the *P-V* diagram and similarly

$$g^{\mathcal{L}}(T,P) = g^{\mathcal{S}}(T,P)$$

and

$$g^{\mathcal{V}}(T,P) = g^{\mathcal{S}}(T,P)$$

Along the other phase coexistence lines.

The $g(T,P)$ are three different functions and the above condition is only true along the co-existence lines and furthermore at the triple point;

$$g^{\mathcal{V}}(T,P) = g^{\mathcal{L}}(T,P) = g^{\mathcal{S}}(T,P)$$

For first order phase changes eg. the liquid-vapour transition, the liquid-solid transition, the transition is accompanied by a change in density and also in a latent heat. Sticking with the Liquid-Vapour transition

$$g^{\mathcal{L}}(T+dT, P+dP) = g^{\mathcal{V}}(T+dT, P+dP)$$

Using Taylor's theorem

$$g^{\mathcal{L}}(T,P) + \left(\frac{\partial g^{\mathcal{L}}}{\partial T}\right)_P dT + \left(\frac{\partial g^{\mathcal{L}}}{\partial P}\right)_T dP + ... = g^{\mathcal{V}}(T,P) + \left(\frac{\partial g^{\mathcal{V}}}{\partial T}\right)_P dT + \left(\frac{\partial g^{\mathcal{V}}}{\partial P}\right)_T dP + ...$$

$$dT\left\{\left(\frac{\partial g^{\mathcal{L}}}{\partial T}\right)_P - \left(\frac{\partial g^{\mathcal{V}}}{\partial T}\right)_P\right\} = dP\left\{-\left(\frac{\partial g^{\mathcal{L}}}{\partial P}\right)_T + \left(\frac{\partial g^{\mathcal{V}}}{\partial P}\right)_T\right\}$$

Using the thermodynamic relations;

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \qquad\qquad s = -\left(\frac{\partial g}{\partial T}\right)_P$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T \qquad\qquad v = \left(\frac{\partial g}{\partial P}\right)_T$$

$$dT\left(s^{\mathcal{V}} - s^{\mathcal{L}}\right) = dP\left(v^{\mathcal{V}} - v^{\mathcal{L}}\right)$$

$$\frac{dP}{dT} = \frac{s^{\mathcal{V}} - s^{\mathcal{L}}}{v^{\mathcal{V}} - v^{\mathcal{L}}}$$

Taking a fixed quantity of matter from the vapour state to the liquid state in a phase transition will involve an increase in order with an accompanying decrease in entropy.

$$\Delta Q_R = T\Delta S = -Latent\ \ Heat\ \ \text{-}\ \mathcal{L}_{\mathcal{V} \to \mathcal{L}}$$

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$$\Delta Q_R = T\Delta s = -\ell_{V \to L}$$

Where ℓ_{VL} is the latent heat of condensation (vapour to liquid) per unit mass and the minus sign ensures that the change in entropy is negative as required.

NB. Latent heats are usually given as positive quantities and thought needs to be given as to what sign is needed.

$$s^{L} - s^{V} = -\frac{\ell_{V \to L}}{T}$$

Therefore

$$\boxed{\frac{dP}{dT} = \frac{\ell_{V \to L}}{T(v^{V} - v^{L})}}$$

This is the **Clausius Clapeyron equation.**

For changes from liquid to vapour or from solid to vapour the following simplification is possible;
$v^{V} \gg v^{L}$ and it is a good approximation to treat the vapour as an ideal gas. Consider 1 mole and let $l_{V \to L}$ and v^{V} be the latent heat and volume per mole.

$$v^{V} = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\ell_{V \to L}}{RT^2/P} = \frac{\ell_{V \to L}P}{RT^2}$$

$l_{V \to L}$ can be taken as a constant over a small temperature/pressure range

$$\frac{dP}{P} = \ell_{V \to L}\frac{dT}{RT^2}$$

Integrating

$$\ln P = -\ell_{V \to L}\frac{1}{RT} + const$$

which becomes

$$\ln\frac{P}{P_0} = -\ell_{V \to L}\frac{1}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)$$

Where $const = \ln P_0 + \dfrac{\ell_{V \to L}}{T_0}$

Where P_0 and T_0 are any known pressure, temperature pair along the liquid-vapor curve. The same approximations can be used for the solid-vapour transition.
The equation can be re-written

$$\boxed{P = P_0\, exp-\left(\frac{\ell_{V \to L}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right)}$$

Describing the co-existence curve

At the triple point;

$$\ln P_{TP} = -\ell_{V \to L}\frac{1}{RT_{TP}} + C_1 = -\ell_{V \to S}\frac{1}{RT_{TP}} + C_2$$

The Third Law of Thermodynamics

The third law of thermodynamics attempts (among other things) to give information about the entropy at absolute zero, $S(0)$.

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial \ln T}\right)_V \qquad\qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial \ln T}\right)_P$$

$$S(T) = \int \frac{C_V}{T} dT \qquad\qquad\qquad S(T) = \int \frac{C_P}{T} dT$$

S might be found by making the integral into a definite integral

$$S(T) - S(T_0) = \int_{T_0}^{T} \frac{C_V}{T} dT \quad\Rightarrow\quad S(T) = S(T_0) + \int_{T_0}^{T} \frac{C_V}{T} dT$$

In other words $S(T)$ can be obtained to some arbitrary constant $S(T_0)$ and we could make the reference temperature T_0 absolute zero.

There are at least 4 statements that describe the Third Law;

   (i)   Macroscopic Statement.
It is impossible to reduce the temperature of a macroscopic system to absolute zero in a finite number of steps or processes.

   (ii)   Nernst Statement or Nernst heat theorem (1906)
The entropy difference between two distinct equilibrium states of a substance tends to zero at absolute zero.

   (iii)   Planck Statement (1911)
The entropy of all perfect crystals is the same at absolute zero and may be taken as zero.

   (iv)   Simon Statement.
The entropy component from each aspect of a system which is in internal thermodynamic equilibrium tends separately, to zero at absolute zero.

The third law carries with it a number of consequences;

a)   Specific Heat Capacity tends to zero as $T \to 0$.
$\Delta \ln T \to -\infty$ as $T \to 0$ so it is essential that $C_V \to 0$ in order that $\Delta S \to 0$.

b)   Thermal expansion goes to zero at low temperatures.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad\qquad \text{therefore} \qquad \beta = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T$$

Where the Maxwell relation $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$ was used

However the Nernst formulation tells us that entropy change $\Delta S \to 0$ as $T \to 0$ therefore implying that $\beta \to 0$ as $T \to 0$.

c)   Curies Law breaks down at low temperature.
The Curie law states

$$\chi = \frac{C}{T}$$

The third law carries the implication that $\left(\dfrac{\partial S}{\partial B_0}\right)_T \to 0$ at low temperatures. This is incompatible with the Curie law

d)   Ideal gases are a fiction at T = 0

The ideal monatomic gas has been used over and over to act as the paradigm system allowing very useful results to be obtained. One of those results has already been destroyed by the third law at absolute zero namely the finding that $C_P - C_V = R$ for 1 mole of gas. We have seen that both heat capacities go to zero negating this result. Further problems arise for the ideal gas when we consider the entropy of an ideal gas

$$S = C_V \ln T + R \ln V + const$$

As $T \to 0$, using this equation, we find $S = -\infty$ clearly in contradiction to the third law.

e)   First order phase changes

The Clausius Clapeyron equation for the coexistence line of two phases is

$$\frac{dP}{dT} = \frac{s^V - s^L}{v^V - v^L} = \frac{\Delta s}{\Delta v}$$

As $T \to 0$, according to the Nernst statement, $\Delta s \to 0$. This implies that as $T \to 0$, $\dfrac{dP}{dT} \to 0$ ie. for a coexistence curve that extends to $T = 0$ the slope must vanish at $T = 0$.

7.   Kinetic Theory

Maxwell Boltzmann velocity distribution, speed distribution, Mean speed, root mean square speed and most probable speed. Diffusion, effusion, mean free path.

The Kinetic part of the course was concerned with the motions of collections of large numbers of molecules, their statistical nature and their effects in terms of macroscopic observables.

Our first example of this was the the relationship between pressure, volume and internal energy for a monatomic gas, $U = \dfrac{3}{2}PV$ using simple concepts from kinetic theory, that is by considering the collision and consequent momentum change of a gas molecule with the wall of its container as the source of the pressure of the gas.

This was followed by showing that the internal energy which is the sum of the kinetic energies of the constituent atoms is given by

$$U = \sum_{n=0}^{N} \frac{1}{2}mv_n^2 \quad \Rightarrow \quad U = N\frac{1}{2}\left\langle mv^2 \right\rangle \quad \Rightarrow \quad U = N\frac{3}{2}k_B T$$

This is a resuklt of the equipartition theorem where there is on average $\dfrac{1}{2}k_B T$ per degree of freedom with three translational degrees of freedom for a monatomic gas.

This was used with the equation of state $U = \dfrac{3}{2}PV$ to obtain a further equation of state

$$PV = Nk_B T = nRT$$

N is the total number of molecules, $n = \dfrac{N}{N_A}$ is the number of moles of the gas and $R = N_A k_B$ is the molar gas constant.

Maxwell Boltzmann Velocity and Speed Distributions.

An elegant argument given in full in the course and coursenotes gives the probability that a particular molecule/atom has a velocity **v** as

$$f(v) = A\,exp\left[-\frac{b}{2}mv^2\right] = \left(\frac{m}{2\pi k_B T}\right)^{3/2} exp\left[-\frac{mv^2}{2k_B T}\right]$$

The Maxwell-Boltzmann Velocity Distribution

We obtained this velocity distribution by using the following physics;

(i)   A simple application of detailed balance

(ii)   The conservation laws, specifically conservation of energy

(iii)   Time reversal and rotational symmetry of Newton's laws.

$\frac{1}{2}mv^2 = E$ and we may see the Maxwell-Boltzmann distribution in terms of the probability that a molecule has an energy, E

$$P(E) \propto exp\left(-\frac{E}{k_B T}\right)$$

The exponential factor is known as the **Boltzmann factor or the Boltzmann-Gibbs factor**

Maxwell Boltzmann Velocity Distribution at T, 2T and 4T
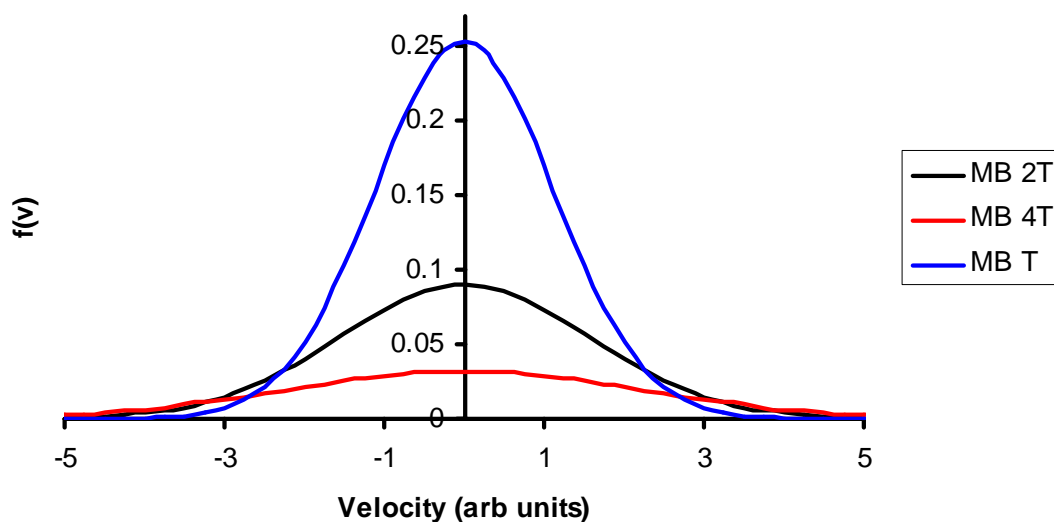
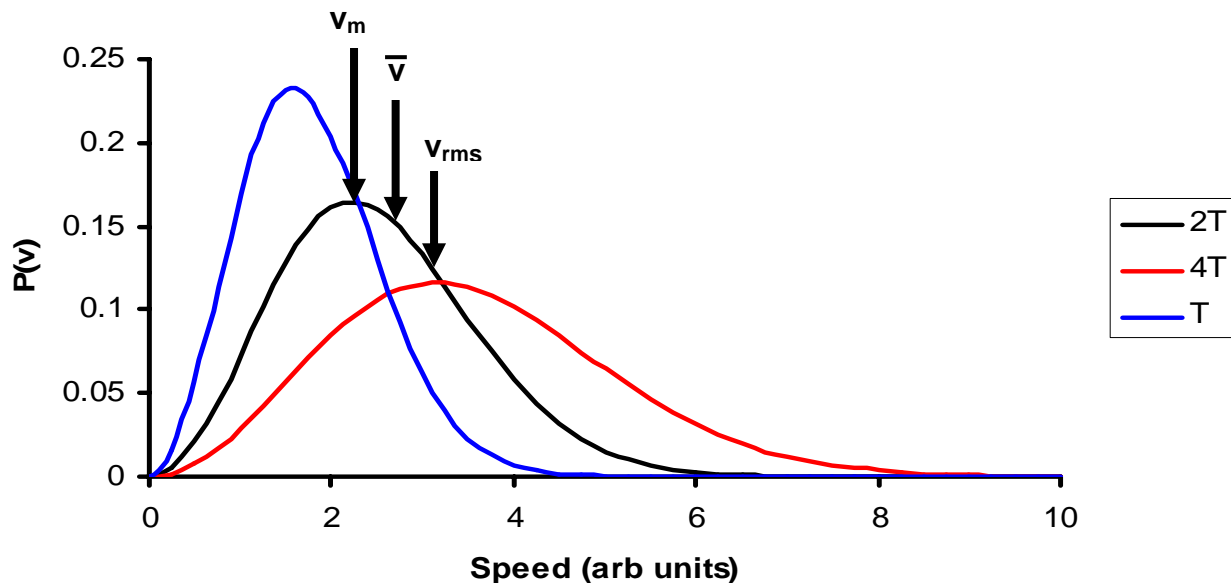The Maxwell-Boltzmann velocity distribution is a Gaussian function of the type $y = A\,exp\left(-\dfrac{(x-x_0)^2}{\sigma^2}\right)$ as shown above.

We may want to know the speed distribution which doesn't concern itself with direction and which can be derived from the velocity distribution as

$$P(v) = 4\pi v^2 f(v) = 4\pi\left[\frac{m}{2\pi k_B T}\right]^{3/2} v^2 \, exp\left(-\frac{mv^2}{2k_B T}\right)$$

The Speed Distribution.

Normalised Speed Distribution at T, 2T and 4T

The question "what is the velocity of a typical gas molecule in a gas at a particular temperature" may be answered in sseveral possible ways as follows;

    (i)   The _**root mean square velocity**_ might be given, v_{rms}. This we have seen previously when obtaining the relation between temperature, kinetic energy and internal energy.

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}} = 1.73\sqrt{\frac{k_B T}{m}}$$

    (ii)   We might also give the _**mean speed**_ $\bar{v}$ defined as

$$\bar{v} = \int_0^\infty vP(v)\,dv = \sqrt{\frac{8k_B T}{\pi m}} = 1.59\sqrt{\frac{k_B T}{m}}$$

    (iii)   Finally we could offer _**the most probable speed**_, v_m , which is the value of v at which $P(v)$ has its maximum.

$$v_m = \sqrt{\frac{2k_BT}{m}} = 1.4\sqrt{\frac{k_BT}{m}}$$

Particle flux colliding with wall

The flux or number of particles hitting unit area in unit time is given by

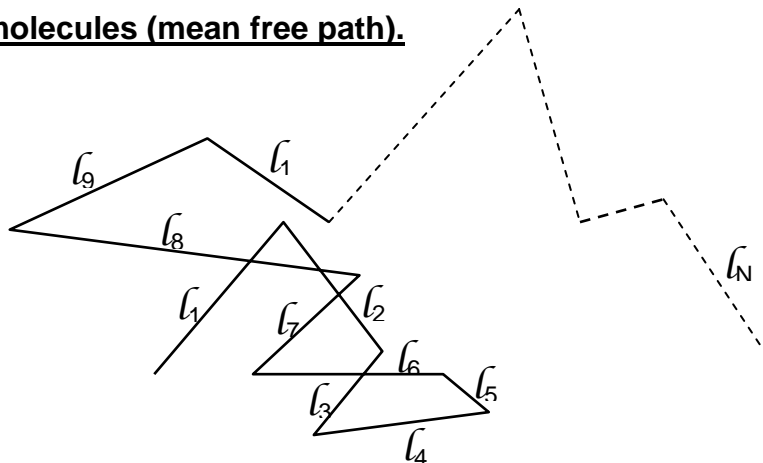$$\Phi = \frac{1}{4}n\bar{v} = \frac{1}{4}n\sqrt{\frac{8k_BT}{\pi m}}$$

where n is the number density.

If the gas is an ideal gas with the usual equation of state, $PV = Nk_BT$ ($nR = Nk_B$) then

$$n = \frac{N}{V} = \frac{P}{k_BT}$$

$$\Phi = \frac{1}{4}n\sqrt{\frac{8k_BT}{\pi m}} = \frac{P}{\sqrt{2\pi m k_BT}}$$

Colliding with other molecules (mean free path).

The trajectory of a particular molecule in a dilute gas is made up of a series of straight line segments interrupted after some length, l, by collision, resulting in change of direction. The actual distance traveled, $\mathcal{L} = \sum_i l$ is considerably greater than the actual distance traversed in real space.

An average distance traveled between collisions, λ, called the mean free path is defined as

$$\lambda = \frac{\sum\limits_{i}^{N} l_i}{N}$$

where N is the number of segments and l_i is the length of free flight on segment i. λ depends on the size of the molecules or on the range of the forces between them, ie they present an area to other molecules within which, if the other molecule trespasses it can be deemed to have collided (felt the influence) of the other molecule. The molecule sweeps out a cylinder with a geometric cross section area,

$$\sigma_G = \pi a^2.$$

The tube length in a time t will be approximately $\bar{v}t$ giving a total volume

$$V = \sigma_G \bar{v}t$$

The molecule will encounter nV other molecules where n is the number density of molecules giving a number of collisions

$$N_C = n\sigma_G \bar{v} t$$

The number of collisions per distance traveled is then

$$\frac{N_C}{\bar{v} t} = n\sigma_G$$

The distance traveled between collisions is the mean free path, λ, and is equal to the inverse of this

$$\boxed{\lambda = \frac{1}{n\sigma_G}}$$

More accurately use the velocity distribution function to take some account of the motion of the target spheres then the mean free path is given by;

$$\lambda = \frac{1}{\sqrt{2}n\sigma_G}$$

An alternative description of the collision process defines the collision frequency, v_C, where v_C is the number of collisions suffered per second

$$v_C = \frac{\bar{v}}{\lambda} = \sqrt{2}n\sigma_C \bar{v}$$

or a scattering time τ_S where

$$\tau_S = \frac{1}{v_C} = \frac{\lambda}{\bar{v}} = \frac{1}{\sqrt{2}n\sigma_C \bar{v}}$$

Molecular Effusion

The concept of mean free path may break down in circumstances where the gas is restricted to movement in structures whose characteristic dimensions are smaller than the mean free path. eg. a narrow pipe. It is necessary in such circumstances to drop the concept of mean behaviours such as the mean free path and develop other microscopic models. Such a regime is called the **Knudsen regime** and may occur in certain common circumstances where it is the mean free path that is unusually large rather than a structure that is particularly small eg.

(i) λ increases as the molecular number density decreases and therefore a high vacuum system will always go through a Knudsen regime when the vacuum is good enough.

(ii)   The mean free path will also become very large as mean velocity is greatly reduced as is the case at low temperatures and systems such as those involving liquid Helium and its vapour will pass through a Knudsen regime.
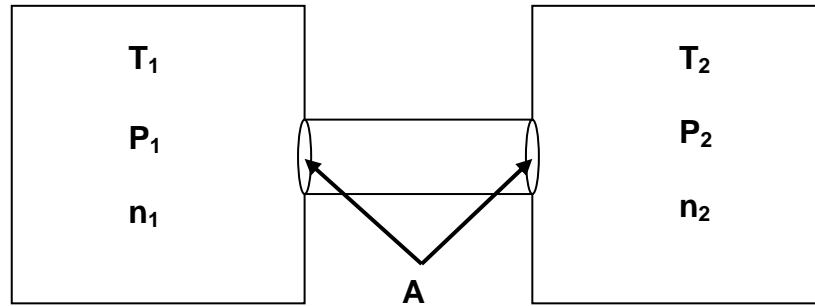
Molecular effusion occurs where two chambers are connected by a narrow pipe as shown above. The thermodynamic criteria for thermal equilibrium between the two chambers is that temperatures and pressures must be equal, $T_1 = T_2$ and $P_1 = P_2$. If there were a pressure difference between the two chambers the gas in the pipe would undergo molecular collisions more frequently from the high pressure side than the low pressure side and a resultant force would exist on the gas in the pipe leading to a pressure driven flow from high to low pressure tending to equalize the pressures. Equilibrium will be determined by the equality of molecular flux onto either end of the pipe and we may use our expressions for the flux to find

$$\frac{1}{4} n_1 \bar{v}_1 A = \frac{1}{4} n_2 \bar{v}_2 A$$

$$\frac{n_1}{n_2} = \frac{\bar{v}_2}{\bar{v}_1} = \sqrt{\frac{T_2}{T_1}}$$

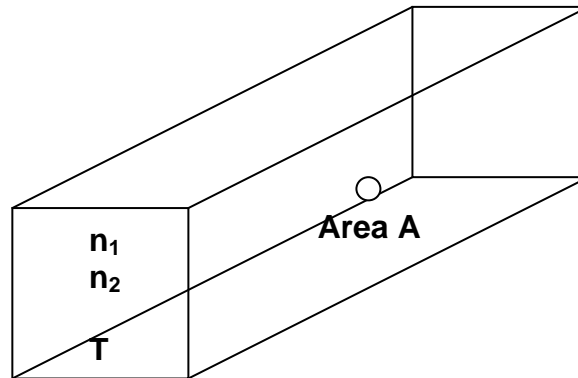Or use $P = \dfrac{N k_B T}{V} = n k_B T$ to rewrite

$$\frac{n_1 T_1}{n_2 T_2} = \frac{P_1}{P_2}$$

And thus

$$\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}}$$

We can write an expression for the number of molecules of species i that impinge on the hole from inside the box and escape through the hole in a time, t using our previously derived expression

$$N_i^e = \Phi_i \times A \times t = \frac{1}{4} n_i \bar{v}_i t A$$

Consider two molecular species in a box with a small hole in it of dimensions smaller than the mean free path.

The expression for the mean speed, $\bar{v} = \sqrt{\dfrac{8k_BT}{\pi m}}$ may be used to find the ratio of two types of molecule that have escaped in time t as

$$\frac{N_1^e}{N_2^e} = \frac{n_1}{n_2}\sqrt{\frac{m_2}{m_1}}$$

The fraction of each species that have escaped is

$$\frac{N_1^e}{n_1} = f_1 = \frac{N_2^e}{n_2}\sqrt{\frac{m_2}{m_1}} = f_2\sqrt{\frac{m_2}{m_1}}$$

And

$$f_1\Big/f_2 = \sqrt{\frac{m_2}{m_1}}$$

Negligible depletion of the molecular densities inside the chamber has been assumed ie. n_i does not change substantially with time.
If molecular species 1 is lighter than molecular species 2 then clearly

$$\frac{f_1}{f_2} > 1$$

and vice versa.
Lord Rayleigh and Ramsay used this effect in 1895 to isolate Argon from the atmosphere for whose discovery they shared the Nobel prize. The most well known use of effusion separation was to separate the light fissionable isotope of Uranium, U_{235} from the more common and heavier isotope, U_{238}

Free path distributions

There is the **mean** free path but the **distribution** of free paths may also be useful. By making some simple assumptions the number of free paths of length l may be found $N(l)$

(i) $N(l) - N(l + dl)$ is proportional to the distance dl.

(ii) $N(l) - N(l + dl)$ is proportional to $N(l)$, the number of particles that started in the interval $(l, l + dl)$.

We may express these two assumptions mathematically as

$$N(l) - N(l + dl) = CN(l)dl \qquad\qquad C = \text{constant}$$

$$\frac{N(l + dl) - N(l)}{dl} = \frac{dN(l)}{dl} = -CN(l)$$

$$\frac{dN(l)}{N(l)} = -Cdl$$

With boundary condition $N(l) = N_0$ at $l = 0$ this has a simple solution

$$N(l) = N_0 \, exp(-Cl)$$

$N(l)/N_0$ is the fraction of particles which have a free path greater than or equal to l .

alternatively $N(l)/N_0 = exp(-Cl)$ is **the probability that a particle which has just undergone a collision will survive a free flight of at least distance l.**

identifying $P(l)dl$ as the proportion of sample particles starting at $l = 0$ which suffer their first collision between l and $l + dl$.

$$P(l)dl = \frac{N(l) - N(l + dl)}{N_0} = C\frac{N(l)dl}{N_0}$$

Hence the probability distribution is simply

$$P(l) = Ce^{-Cl}$$

To determine the constant C note that the mean free path, λ, is the average free path and therefore by definition of $P(l)$
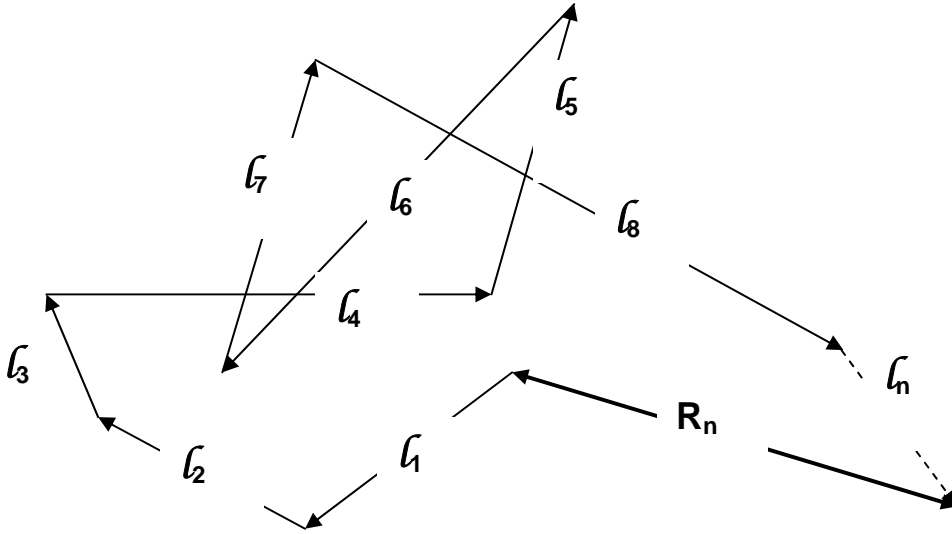
$$\lambda = \int_0^\infty lP(l) = C\int_0^\infty l\, e^{-Cl}\, dl$$

$$C = = \frac{1}{\lambda}$$

$$\boxed{P(l) = \frac{1}{\lambda}e^{-l/\lambda}}$$

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Mean Square Displacement & Diffusion Coefficient

A particle colliding with other particles as it moves under the effects of a potential (eg. gravitational, electrostatic) will travel a distance in real space far less than the actual distance it has travelled.

The above shows a particle undergoing a random walk in n segments i of length ℓ_i . After n steps/collisions it has moved a distance R_n in real space from its starting position.
Using vector notation explicitly

$$\vec{R}_n = \vec{\ell}_1 + \vec{\ell}_2 + \vec{\ell}_3 + \vec{\ell}_4 + \ldots\ldots + \vec{\ell}_n$$

To evaluate the vector sum we find the mean square displacement $\left\langle |R_n|^2 \right\rangle$

$$\left\langle |R_n|^2 \right\rangle = \left\langle R_n \cdot R_n \right\rangle = \left\langle \left(\ell_1 + \ell_2 + \ell_3 \ldots + \ell_n\right) \cdot \left(\ell_1 + \ell_2 + \ell_3 \ldots + \ell_n\right) \right\rangle$$

$$\left\langle |R_n|^2 \right\rangle = \left\langle |\ell_1|^2 \right\rangle + \left\langle |\ell_2|^2 \right\rangle + \ldots\ldots + \left\langle |\ell_n|^2 \right\rangle + 2\left\langle \ell_1 \cdot \ell_2 \right\rangle + 2\left\langle \ell_1 \cdot \ell_3 \right\rangle + \ldots\ldots + 2\left\langle \ell_{n-1} \cdot \ell_n \right\rangle$$

Using

$$\left. \begin{array}{l} \left\langle \ell_i \cdot \ell_j \right\rangle = \left\langle \ell_i \ell_j \cos\theta \right\rangle = 0 \\[2mm] \left\langle \ell_i \cdot \ell_i \right\rangle = \left| l_i^2 \right| \end{array} \right\}$$

$\left\langle |R_n|^2 \right\rangle$ simplifies to

$$\left\langle |R_n|^2 \right\rangle = \left\langle |\ell_1|^2 + |\ell_2|^2 + |\ell_3|^2 + \ldots + |\ell_n|^2 \right\rangle = n\left\langle |\ell|^2 \right\rangle$$

$$\left\langle |\ell|^2 \right\rangle = \left\langle \ell^2 \right\rangle = \int_0^\infty \ell^2 P(\ell)d\ell = \frac{1}{\lambda}\int \ell^2 e^{-\ell/\lambda}d\ell$$

$$\left\langle |\ell|^2 \right\rangle = \left\langle \ell^2 \right\rangle = \int_0^\infty \ell^2 P(\ell)d\ell = 2\lambda^2$$

The **mean square displacement** is then

$$\left\langle |R_n|^2 \right\rangle = 2n\lambda^2$$

We can convert the number of collisions, n, to the more useful parameter, the time elapsed, t,

$$n \approx \frac{t}{\tau_S}$$

with $\tau_S = \dfrac{\lambda}{\bar{v}}$, the **scattering time** being the time between collisions.

$$\boxed{\left\langle |R_n|^2 \right\rangle = 2n\lambda^2 = 2\bar{v}\lambda t = 6Dt}$$

where the **diffusion coefficient** D is defined as

$$\boxed{D = \frac{1}{3}\bar{v}\lambda}$$

The Diffusion equation (Fick's Law)

Diffusion is a process whereby particles (or energy as heat etc.) move from a high concentration region to that of lower concentration due to an imbalance in the flux at an interface from two opposite directions. The flux impinging on a surface is

$$J = \frac{1}{4}n\bar{v}$$

With the crossing surface at $z = 0$

$$\text{Flux from right } = \frac{1}{4}n(\lambda)\bar{v} = \frac{1}{4}\left(n(0) + \frac{\partial n}{\partial z}\bigg|_{z=0}\lambda\right)\bar{v}$$

$$\text{Flux from left } = \frac{1}{4}n(-\lambda)\bar{v} = \frac{1}{4}\left(n(0) - \frac{\partial n}{\partial z}\bigg|_{z=0}\lambda\right)\bar{v}$$

The net flux in the positive z direction is the difference between the second and the first of these

$$J_z = -\left(\frac{1}{2}\bar{v}\lambda\right)\frac{\partial n}{\partial z}\bigg|_{z=0} = -D\frac{\partial n}{\partial z}$$

This is known as **Fick's law.**

Here $D = \dfrac{1}{2}\bar{v}\lambda$ whereas previously $D = \dfrac{1}{3}\bar{v}\lambda$

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NB. <u>The earlier form is the correct one</u>

The rate of change of particle density is

$$\frac{\partial n}{\partial t} = -\frac{\partial J_z}{\partial z}$$

And using Fick's law

$$\frac{\partial n(z,t)}{\partial t} = D\frac{\partial^2 n(z,t)}{\partial z^2}$$

This is **<u>the Diffusion equation in 1 dimension</u>**

This may be generalised to 3D

$$\frac{\partial n(x,y,z,t)}{\partial t} = -\nabla \cdot J = D\nabla^2 n(x,y,z,t)$$

This is **<u>the Diffusion equation in 3 dimensions</u>**

Heat Conduction and Fouriers Equation
Diffusion of energy (heat) may be treated in the same way

$$J_z(z,t) = -\kappa\frac{\partial T(z,t)}{\partial z}$$

Is Fouriers Law

$$\kappa = \frac{1}{3}n\bar{v}\lambda\left(\frac{3}{2}k_B\right) = \frac{1}{2}n\lambda\sqrt{\frac{8k_BT}{\pi m}}k_B = n\lambda\sqrt{\frac{2T}{\pi m}}k_B^{3/2}$$

Is the thermal conductivity

$$\frac{\kappa}{D} = \frac{3}{2}nk_B \qquad\qquad \frac{5}{2}nk_B \ or \ \frac{7}{2}nk_B \ \text{for diatomic gases.}$$

$$\frac{\partial T(z,t)}{\partial t} = D^h\frac{\partial^2 T(z,t)}{\partial z^2}$$

Is the heat equation

with

$$D^h = \frac{\kappa}{\rho c_p}$$