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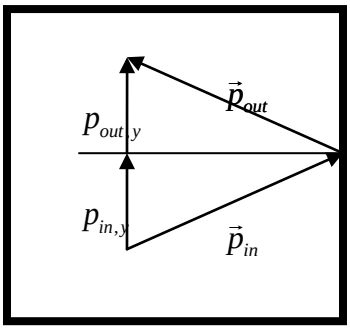
21.1 Calculate the Pressure Inside of a Gas Using the Microscopic Approach.
Assume we have N molecules of a gas inside of a container. We look at the molecules as point masses with no extension and no rotation. (This means that if we have two different gases with different molar masses, it is only the number of molecules which enters the ideal gas law. The total pressure inside of a container is the sum of the individual pressures of the gases.) The molecules have momentum and kinetic energy, they move at random velocities, their average velocity adds up to 0 in terms of vector addition. What matters is the average of the squared velocities. The interaction amongst themselves is negligible. We assume a cubic container of side-length L.



From our study of pressure we know that the pressure inside of the gas is the same as the pressure **on the walls** of the container.

(21.1) $P = \frac{F}{A}$; A is the area of a container wall.

F is the change of momentum of a molecule while bouncing off of the wall (elastic collision), divided by Δt.

Only the component perpendicular to the wall matters, because the other components cancel each other. This is already containted in the definition of pressure.

For an elastic collision momentum and kinetic energy are conserved.

$$\Delta\vec{p} = -\vec{i}p_{out,x} - p_{in,x}\vec{i} = -2p_x\vec{i}$$

(21.2) $$\vec{F} = \frac{\Delta\vec{p}}{\Delta t}; \Delta p = -2m\mathrm{v}_x$$

Δt is the average time between two bounces off of the same wall. During this time the molecule can travel the average distance 2L.
(Watch out for capital letters: P stands for pressure, p stands for momentum.)
Therefore:

(21.3) $$\mathrm{v}_x = \frac{2L}{\Delta t} \Rightarrow \Delta t = \frac{2L}{\mathrm{v}_x}$$

This gives us for the x-component of the average force $\bar{\vec{F}}$ of a single molecule or atom:

(21.4) $$\bar{F} = \frac{-2m\mathrm{v}_x}{\Delta t} = \frac{-2m\mathrm{v}_x}{2L/\mathrm{v}_x} = \frac{-m\mathrm{v}_x^2}{L}$$

This is the average force of the molecule. The force on the wall F_W is equal and opposite to the force on the molecule.

(21.5) $$\overline{F_w} = \frac{m\mathrm{v}_x^2}{\mathrm{L}}$$

To find the average pressure P_i on the wall exerted by one individual molecule we need to divide by the area of the wall which will give us the volume in the container V in the denominator of (21.5).

(21.6) $$P_i = \frac{mv_x^2}{LA} = \frac{mv_x^2}{V}$$

To get the average of all the molecules squared velocities we have to sum up all x-component contributions of all molecules hitting the walls perpendicular to the x direction:

(21.7) $$\overline{v_x^2} = \sum_{i=1}^{N} \frac{\overline{v_{ix}^2}}{N}$$

This average value is the same for each component x,y,z because of the huge number of molecules involved. So, rather than limiting ourselves to the velocities in one direction we take 1/3 of the average velocities in all three directions. We talk only about three principal directions because all velocities can be expressed in terms of the three x,y,z components. These are the three degrees of freedom for translational motion.

(21.8) $$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

(21.9) $$\overline{v_x^2} = \sum_{i=1}^{N} \frac{\overline{v_{ix}^2}}{N} = \frac{1}{3}\overline{v^2}$$

Therefore we get for the average pressure exerted by all molecules in the container with N molecules and volume V:

(21.10) $$P = \frac{1}{3}\frac{Nm\overline{v^2}}{V} = \frac{2}{3}\frac{N}{V}\underbrace{\left(\frac{1}{2}m\overline{v^2}\right)}_{\text{average kinetic energy of one molecule}}; PV = \frac{2}{3}N\underbrace{\underbrace{\left(\frac{1}{2}m\overline{v^2}\right)}_{\text{average kinetic energy of one molecule}}}_{\text{average kinetic energy of all N molecules}}$$

If we compare (21.10) with the ideal gas law PV=NkT we see some interesting facts:

(21.11) $$PV = \frac{2}{3}N\frac{1}{2}m\overline{v^2}$$

(21.12) $$PV = Nk_BT = \frac{2}{3}\underbrace{N\frac{1}{2}m\overline{v^2}}_{\text{average kinetic energy of the gas}}$$

21.1a Equipartition of Energy :

(21.13)

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT;$$

For each possible independent direction of movement the contribution of the average kinetic energy to the total internal energy U or E_{int} is $\frac{1}{2}k_BT$

We used this fact at the beginning of the class to define temperature. Note that a definition of temperature is therefore only possible for a very large number of randomly moving particles in thermal equilibrium. Each atom in translational motion contributes an average of $\frac{1}{2}k_BT$ to the internal energy of the gas for each translational degree of freedom. The total internal energy of such a gas is therefore:

(21.14) For N atoms: $U \equiv E_{\text{int}} = N\frac{3}{2}k_BT$

(21.15) For n moles: $\Delta U = \frac{3}{2}nR\Delta T$

Note that this result confirms our hypothesis that **the internal energy of an ideal gas is completely definable by its temperature**.

Each degree of freedom contributes $\frac{1}{2}k_BT$ to the internal energy of a molecule.

This statement can be generalized to include rotational kinetic energies for independent angles of rotation, and kinetic as well as potential energies of oscillation for possible directions of oscillations. These independent angles of rotation and possible independent directions of oscillations in a molecule together with the three independent directions of translational motion are called **degrees of freedom**.

When we talk about the velocity of a single molecule in a statistical, thermodynamic context we always mean the square-root of the average squared velocities or the **root-mean-square velocity**.

(21.16) $$v_{\text{rms}} \equiv \sqrt{\overline{v^2}} = \frac{1}{3}\sqrt{\frac{\sum_{i=1}^{i=N}\overline{v_{ix}^2}+\overline{v_{iy}^2}+\overline{v_{iz}^2}}{N}} = \frac{1}{3}\sqrt{\sum_{i=1}^{N}\frac{\overline{v_{ix}^2}}{N}} = \frac{1}{3}\overline{v^2}$$

We can therefore talk about the rms velocity in this sense, for example the rms speed of an oxygen atom at 20°C:

$$v_{\text{rms}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\cdot 8.314\cdot 293}{0.016}} = 676 m/s$$

(21.17) $m \triangleq$ *mass* of the individual molecule.

M $\triangleq$ mass of one mol of molecules

Note : the velocity we get in this way is the velocity between collisions among molecules. It is **not the drift velocity** v_d with which one molecule in one corner of a room drifts to another corner, in a random motion. We talk about drift velocity and random motion later.

3.2 Molar Specific Heat of an Ideal Gas.
We have earlier defined the specific heat c (small cap c) of a solid substance as the heat energy that is required to increase the temperature of the substance by 1 degree Celsius. According to the law:

(21.18) $$Q = cm\Delta T; c = \frac{Q}{m\Delta T}$$

As most solids are incompressible within the accuracies involved in these calculations, pressure and volume did not come into play. This is obviously different for a gas. When we increase the temperature of a gas both pressure and volume change dramatically. We therefore define two different processes, one at constant pressure, and another at constant volume. The obvious amount for which we measure and calculate the specific heat is one mol. We therefore need to determine the **molar specific heat C_P** (capital C) of a gas at constant pressure and at constant volume C_V.
Recall that we sometimes also use the term heat capacity instead of specific heat.

(21.19) $$Q_V = nC_V\Delta T \text{ heat transfer for n moles at constant volume}$$
$$Q_P = nC_P\Delta T \text{ heat transfer for n moles at constant pressure}$$

3.2a Heat transfer of a gas at constant volume (iso-volumetric process):
If the volume is constant, no work is being done. We use the first law of thermodynamics
$\Delta U = Q + W$ and the new formula (21.15) $\Delta U = \frac{3}{2}nR\Delta T$

(21.20) $$\Delta V = 0 \Rightarrow W = 0 \Rightarrow \Delta U = Q = nC_V\Delta T = \frac{3}{2}nR\Delta T \Rightarrow$$

(21.21) $$\boxed{C_V = \frac{3}{2}R = \frac{3}{2}\cdot 8.314 = 12.5\frac{J}{mol\cdot K}}$$

For a mono atomic gas the molar specific heat equals 1.5R=12.5 J/molK. This reveals that we can also write for the internal energy of an ideal gas with three degrees of freedom:

(21.22) $$\boxed{\Delta U = \frac{3}{2}nR\Delta T = nC_V\Delta T}$$

3.2b Heat transfer of a gas at constant pressure (iso-baric process):
We use the first law of thermodynamics and the definition of work done on a gas

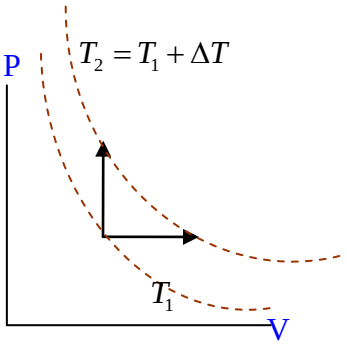
$$\Delta U = Q + W = C_P n\Delta T - \underbrace{P\Delta V}_{nR\Delta T}$$

(21.23) $$PV = nRT \Rightarrow \text{for constant pressure:} P\Delta V = nR\Delta T$$
$$\Delta U = C_P n\Delta T - nR\Delta T$$

(For non-constant pressure we would get through implicit differentiation of PV=nRT
$$PdV + VdP = nRdT \text{)}$$

Note that the internal energy U is the same along any isothermal line. ΔU is the same if we move from any starting point passing through T_i to any other isothermal line, like the one passing through the endpoint in the isobaric expansion under consideration. If we choose the vertical

path for isovolumetric expansion we can use (21.20); ΔU for a constant volume compression is given by $\Delta U = nC_V\Delta T = \frac{3}{2}nR\Delta T$.



This means that the change in **internal energy** is the same for a process at constant pressure (**horizontal line**) or at constant volume (**vertical line.**) At constant volume we had $\Delta U = Q = nC_V\Delta T$ Therefore from (21.23) we get:

(21.24)
$$\Delta U = C_P n\Delta T - nR\Delta T = nC_V\Delta T \Rightarrow$$
$$C_P n\Delta T - nC_V\Delta T = nR\Delta T$$

and finally

(21.25) $$\boxed{C_P - C_V = R \Rightarrow C_P = \frac{5}{2}R = 12.5\frac{J}{mol\bullet K}}$$

(We could also have used the simple fact that $\Delta U = \frac{3}{2}nRT$ for any gas with three degrees of freedom and we would have gotten the same result, namely that $C_P = \frac{5}{2}R$. Generally, the first approach is used because it establishes a **universal** relationship between C_P and C_V and is independent of the number of degrees of freedom of the gas. (The internal energy changes with a higher degree of freedom.)

The ratio of the molar specific heat often comes into play. It is called the adiabatic constant γ.

(21.26) $$\boxed{\frac{C_P}{C_V} = \frac{5}{3} \hat{=} \gamma = 1.67}$$

21.3 Adiabatic Processes for an Ideal Gas. (Proof that $PV^\gamma = \text{constant}$ for adiabatic processes.)

Adiabatic processes are processes occurring without heat exchange. This does not mean, however, that the temperature remains the same. (That would be an isothermal process for which dT=0). The change in internal energy during any adiabatic process is given by:

For adiabatic processes:

(21.27) $$\Delta U = \cancel{Q} + W \Rightarrow dU = dW = -PdV$$

We know from (21.22) that

(21.28) $$dU = \frac{3}{2}nRdT = nC_V dT$$

Therefore we can equate:

$$nC_V dT = -PdV$$

(21.29) $$ndT = \frac{-PdV}{C_V}$$

There are three dependent variables. To solve this we need to use another equation in order to eliminate one variable:

We **always** have for any ideal gas:

$$PV = nRT$$

(21.30) we get through implicit differentiation:

$$PdV + VdP = nRdT$$

We use this result to eliminate n·dT in equation (21.29).

(21.31)
$$PdV + VdP = \frac{-RPdV}{C_V}$$

We now have a differential equation in V and P, which we solve by separating the variables:

$$PdV + VdP = \frac{-RPdV}{C_V} \text{ divide by PV}$$

(21.32)
$$\frac{dV}{V} + \frac{dP}{P} = -\frac{RdV}{VC_V}$$

$$\left(1 + \frac{\mathrm{R}}{C_V}\right)\frac{dV}{V} = -\frac{dP}{P}$$

(21.33)
$$1 + \frac{R}{C_V} = \frac{C_V + R}{C_V} = \frac{C_P}{C_V} = \gamma$$

(21.34)
$$\gamma\frac{dV}{V} + \frac{dP}{P} = 0 \Rightarrow \text{integration } \gamma \ln V + \ln P = \text{constant} \Rightarrow$$
$$\ln\left(V^{\gamma}P\right) = \text{constant}$$

For all adiabatic processes of ideal gases we therefore get the important result that :

(21.35)
$$\boxed{\begin{aligned} PV^{\gamma} &= \text{constant} \\ P_iV_i^{\gamma} &= P_fV_f{}^{\gamma} \end{aligned}}$$

By using the ideal gas law we can substitute the pressure in this:

(21.36)
$$P = \frac{nRT}{V} = nRTV^{-1}$$

(21.37)
$$\boxed{T_iV_i^{\gamma-1} = T_fV_f{}^{\gamma-1}}$$

We can also replace V in (21.35) to get:

$$P_i\left(\frac{nRT_i}{P_i}\right)^{\gamma} = P_f\left(\frac{nRT_f}{P_f}\right)^{\gamma};V = \frac{nRT}{P}$$

(21.38)
$$P_i^{1-\gamma}T_i^{\gamma} = P_f{}^{1-\gamma}T_f{}^{\gamma} \Rightarrow \left(\frac{T_i}{T_f}\right)^{\gamma} = \frac{P_f{}^{1-\gamma}}{P_i^{1-\gamma}} = \underbrace{\left(\frac{P_f}{P_i}\right)^{1-\gamma} = \left(\frac{P_i}{P_f}\right)^{-(1-\gamma)}}_{\text{inverting the ratio}} = \left(\frac{P_i}{P_f}\right)^{\gamma-1}$$

and finally :

(21.39)
$$\boxed{\frac{T_i}{T_f}=\left(\frac{P_i}{P_f}\right)^{\frac{\gamma-1}{\gamma}}=\left(\frac{P_i}{P_f}\right)^{1-\frac{1}{\gamma}}}$$

21.4 The Equipartition of Energy.

We earlier defined the molar heat capacity C_V through $Q=nC_V\Delta T$ We now know that the internal energy of an ideal gas depends only on the temperature. Therefore, we can write for infinitesimal changes in the heat transfer:

(21.40)
$$\boxed{\begin{array}{l} dU=dQ=nC_V dT \text{ or for one mole n=1} \\ C_V=\dfrac{dU}{dT} \end{array}}$$

The internal energy of one mole of an ideal gas is equal to $\frac{1}{2}RT$ for every **degree of freedom**. (Or $\frac{1}{2}k_BT$ for each molecule) In the case of a mono-atomic gas, the atom can move linearly in three directions x,y,z and therefore has **three degrees of freedom**. In the case of a di-atomic molecule, we can consider the molecule as a bar-bell with the atoms sitting at the end of the bar. The rotational kinetic energy comes from the two rotations around axes perpendicular to the bar, thus we have **two more degrees of freedom** of rotation available.

Furthermore, there are often situations in which the gas atoms oscillate within their molecular structure. Oscillators have two kinds of energy, kinetic and potential, each account for additional possible **degrees of freedom of oscillation**.

The energies (in a gas) due to oscillation do not kick in unless the gas or other substance is heated to a high temperature. The reason for this lies in the fact that the energies in molecules are **quantized**, they do not continuously increase from 0 to higher values. In the case of oscillators, for example, the smallest possible energy is $\frac{1}{2}\hbar\omega$ where ω is the angular frequency of oscillation corresponding to the particular molecule. Each excited energy state adds an additional $\hbar\omega$. Thus, the Nth excited state has an energy of $N\hbar\omega$ above the **ground-state**. It is these energies of the excited states that contribute to the specific heat of the gas.

The specific heat of a gas at constant volume is therefore:

(21.41)
$$C_V=\frac{dU}{dT};U=d_f\cdot\left(\frac{1}{2}RT\right);d_f \triangleq \text{degree of freedom=3,5,7}$$
$$C_V=\frac{d_f\cdot R}{2}$$

The definition of the heat capacity at constant pressure is not affected and remains at

(21.42)
$$\boxed{C_P-C_V=R}$$

What changes is of course $\gamma=\frac{C_P}{C_V}$ And the value of γ can be checked relatively easily in experiments with adiabatic processes for which we have equation (21.35)

$$\boxed{PV^{\gamma} = \text{constant} \qquad P_i V_i^{\gamma} = P_f V_f^{\gamma}}$$

For a diatomic gas with 5 degrees of freedom, like for example a hydrogen molecule we get:

(21.43) $$C_V = \frac{5}{2}R;\ C_P = C_V + R = \frac{7}{2}R;\ \gamma = \frac{C_P}{C_V} = \frac{7}{5} = 1.40$$

memorize:

(21.44) $$\boxed{\gamma = \frac{C_P}{C_V} = \frac{7}{5} = 1.40 \text{ for diatomic gases } C_V = \frac{5}{2}R;\ C_P = \frac{7}{2}R \\ = \frac{5}{3} = 1.67 \text{ for monoatomic gases: } C_V = \frac{3}{2}R;\ C_P = \frac{5}{2}R}$$

Problem: The inverse of the bulkmodulus B is called compressibility :

(21.45) $$\Delta P = -B\frac{\Delta V}{V} \Rightarrow \frac{1}{dP} = -\kappa\frac{V}{dV} \Rightarrow \kappa = -\frac{1}{V}\frac{dV}{dP}$$

a) Show that if an ideal gas is compressed isothermally, its compressibility is given by $\kappa_{iso} = \frac{1}{P};\ B_{iso} = \frac{1}{\kappa_{iso}} = P$.

Well, for an ideal gas we have $PV = nRT = const. \Rightarrow PdV + VdP = 0 \Rightarrow \frac{dV}{dP} = -\frac{V}{P}$

For an adiabatic compression we also have to differentiate

$$PV^{\gamma} = const \Rightarrow V^{\gamma}dP + \gamma PV^{\gamma-1}dV = 0 \Rightarrow \frac{dV}{dP} = -\frac{1}{\gamma}\frac{V}{P}$$

$$-\frac{1}{V}\frac{dV}{dP} = \frac{1}{\gamma P} = \kappa_{adiab};\ B_{adiab} = \gamma P$$

Thus we obtain for the coefficient of adiabatic compression or the adiabatic bulk modulus:

(21.46) $$\kappa_{adiab} = \frac{1}{\gamma P} = \frac{1}{B_{adiab}};\ B_{adiab} = \gamma P$$

The speed of an adiabatic sound wave in a liquid is given by:

(21.47) $$v_s = \sqrt{\frac{B}{\rho}} = \sqrt{\frac{\gamma P}{\rho}}$$

If we treat air as an ideal gas, we can express its density in terms of the ideal gas law:

(21.48) $$PV = nRT = \frac{m}{M_m}RT;\ P = \frac{m}{V}\frac{RT}{M_m} = \rho\frac{RT}{M_m};$$

(21.49) $$\boxed{\rho = \frac{PM_m}{RT};\ \text{with } m\text{= mass of the gas, } M_m = molar\ mass}$$

Inserting this density into the formula for speed of sound (21.47) we get

(21.50) $$\boxed{v_s = \sqrt{\frac{\gamma RT}{M_m}}}$$

Air consists of 79% nitrogen and 21% oxygen molecules. The molar mass of air is therefore:

(21.51) $$M_{air} = \left(0.79 \cdot 28 + 0.21 \cdot 32\right) grams = 29 grams$$

We write the temperature in terms of 273Kelvin +x Kelvin, or

(21.52) $$T = 273\left(1 + \frac{T_{Celsius}}{273}\right) Kelvin$$

(21.53) $$v_s = \sqrt{\frac{\gamma RT}{M_m}} = \sqrt{\frac{273\gamma R}{M_m}} \cdot \sqrt{1 + \frac{T_{Celsius}}{273}} = 331\frac{m}{s}\sqrt{1 + \frac{T_{Celsius}}{273}}$$

21.5 The Molar Specific Heat of Solids.

It is an expermental observation that the molar specific heat of solids approaches the value of 3R, asymptotically with increasing temperature T. The value is approximately 25 J/mol·K. (Law by **DuLong-Petit**.)

This can be easily explained by the equipartition law. The atoms and molecules in a solid are not free to rotate or move linearly. What they can do however is oscillate in their cristal lattices. Each atom or molecule has a kinetic and potential energy associated with it for each of the three independent directions of oscillation, x, y, z. (6 degrees of freedom for oscillation).

(21.54) $$E = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right) + \frac{1}{2}\underbrace{k}_{\text{spring constant}}\left(x^2 + y^2 + z^2\right)$$

Therefore the total heat capacity at constant volume is $C_V = \frac{d_f}{2}R = \frac{6}{2}R = 3R$

This implies that atoms in a solid behave essentially as three-dimensional oscillators.

Let us calculate the specific heat of copper by using the result above. Its molar mass is 63.5 g/mol. The molar specific heat is 3R= $3 \cdot 8.314 = 24.9 J / mol \cdot K$. If we divide this by the mass per mole we get the specific heat per gram and Kelvin or 0.393 J/(g K) = 0.393kJ/(kg K)= 0.0938 cal/(g K).

The tabulated measured specific heat for copper is 0.0923 cal/gK.

With few exception, all solid metals have molar heat capacities around **25 J/molK**.

21.6 The Boltzmann Distribution Law.

At the end of ch19 temperature ideal gas law.doc we derived a formula for the pressure change in the atmosphere with increasing height at constant temperature

(21.55) $$P = P_0 e^{-\frac{M_{molecule} g}{k_B T} y} = P_0 e^{-\frac{M_{mol}}{RT} y}$$

By means of the ideal gas law we can convert pressure into number of molecules per unit volume

$$PV = Nk_BT \Rightarrow P = \frac{N}{V} k_B T = nk_B T \text{ and}$$

or **number-density n**. $P_0 V_0 = Nk_B T_0 \Rightarrow P_0 = \frac{N}{V_0} k_B T = n_0 k_B T \Rightarrow$

$$\frac{P}{P_0} = \frac{n}{n_0}$$

The law (21.55) turns into a law showing how the number of molecules changes with increasing height, or with increasing potential energy mgy. This number declines exponentially with height.

(21.56) $n_V = n_0 e^{-\frac{mgy}{k_B T}}$, where n_0 is the number density for y=0

(Note, the above law is counter-acted by **diffusion** which is another physical phenomenon describing the **random tendency of all molecules to occupy the largest possible volume**. As the density of air decreases exponentially diffusion increases. We used the concept of diffusion when discussing the free adiabatic expansion of a gas.)

This law is merely a particular case of the much more general **Boltzmann distribution law**.

(21.57) $$\boxed{n_V(E) = n_0 e^{-\frac{E}{k_B T}}}$$

The function which is a form of a larger class of functions, called **probability distribution functions,** states that the probability of finding the molecules in a particular energy state (per unit volume) **decreases exponentially with the energy of the molecule** divided by $k_B T$.

Multiplying (21.57) by the differential dE we get the number of molecules per unit volume with energies between E and E+dE:

(21.58) $$\boxed{n_V dE = n_0 e^{-\frac{E}{k_B T}} dE}$$

Sometimes it is more convenient to divide equation (21.58) by the total number of molecules N to obtain a formula **normalized** to unity. We then get a formula giving us the **probability**, a number between 0 and 1, to find the molecules in an energy interval between E and E+dE.

(21.59) $$\frac{n_V dE}{N} = \frac{n_0}{N} e^{-\frac{E}{k_B T}} dE$$

This is all reminiscent of the Gaussian normal distribution function :

(21.60) $$f_G(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$$

By using the probability distributions such as (21.59) **we can find the <u>average value</u>** $\overline{f(E)}$ **of <u>any other physical quantity f(E)</u> which is a function of the energy**.

(21.61)

$$\overline{f(E)} = A\int_0^\infty f(E)e^{-\frac{E}{k_BT}}dE$$

A is the normalization constant: $A=\dfrac{1}{\int_0^\infty e^{-\frac{E}{k_BT}}dE}$

The probability to find a particle in any energy state between 0 and ∞ is equal to 1. 100% probability = certainty.

Example :Consider a gas at a temperature of 2.5E3 Kelvin, whose atoms occupy only two energy levels separated by 1.5 eV. Calculate the ratio of atoms occupying the two energy levels.

(21.62)
$$r = \frac{n_0 e^{-\frac{E_2}{k_BT}}}{n_0 e^{-\frac{E_1}{k_BT}}} = e^{-\frac{E_2-E_1}{k_BT}} = e^{-\frac{1.5eV}{k_BT}}$$

Let us calculate Boltzmann's constant in terms of eV:

(21.63)
$$k_B = 1.38\cdot 10^{-23}\,J/K = \frac{1.38\times 10^{-23}\,J/K}{1.6\times 10^{-19}\frac{J}{eV}} = 8.63\times 10^{-5}\frac{eV}{K}$$

(21.64)
$$r = e^{-6.95} = 9.6\times 10^{-4} \approx 0.1\%$$

The potential energy or the energy levels in atoms are some areas where we can use Boltzmann's law. But, in the context of theromodynamics the kinetic energy of molecules is much more interesting. We can calculate the rms speed of atoms and molecules, using $\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$ But at a given temperature what would be the percentage of molecules having this speed more or less. To answer such questions we have to reformulate **Boltzmann's law in terms of the velocities** of molecules and their kinetic energies.

In the Boltzmann distribution function we we need to replace the energy by the kinetic energy:

(21.65)
$$n_V(K) = n_0 e^{-\frac{mv^2}{2k_BT}}$$

The kinetic energy has contributions from all three degrees of freedom:

(21.66)
$$\frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)$$

The velocities in the various directions are not very instructive. We need to find the velocity distribution in terms of the radial velocity. Compare this situation to polar coordinates. There, we can find the values for dr in a spherical shell of thickness dr. In other words, **the infinitesimal volume element dV in spherical coordinates** is given by:

(21.67) $$4\pi r^2 dr$$

We use the same concept in **velocity space**, whose Cartesian coordinates are v_x, v_y, v_z. The infinitesimal volume element in velocity space, becomes:

(21.68) $$dv_x \cdot dv_y \cdot dv_z = 4\pi v^2 dv$$

Therefore, the probability to find a molecule in the spherical velocity shell between the velocities v and v+dv is given by.

(21.69) $$\boxed{f(v)dv = Ae^{-\frac{mv^2}{2k_BT}} 4\pi v^2 dv}$$

To determine the constant A we need to follow the procedure given in (21.61). So, we need to calculate the integral:

(21.70) $$\int_0^\infty f(v)dv = 1 \Rightarrow \frac{1}{A} = \int_0^\infty e^{-\frac{mv^2}{2k_BT}} 4\pi v^2 dv$$

21.6a Gaussian Integrals.

To evaluate this and other similar integrals a **few formulas** are useful:

(21.71) $$I_0 = \int_0^{+\infty} e^{-\alpha x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

Proof:

(21.72)
$$I_0 = \int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2}\int_{-\infty}^\infty e^{-\alpha x^2} dx = \frac{1}{2} I$$

$$I^2 = \int_{-\infty}^\infty e^{-\alpha x^2} dx \int_{-\infty}^\infty e^{-\alpha y^2} dy = \int_{-\infty}^\infty \int_{-\infty}^\infty e^{-\alpha\left(x^2+y^2\right)} dxdy = \text{(using polar coordinates)}$$

$$I^2 = \int_0^{2\pi} \int_0^\infty e^{-\alpha r^2} r dr d\theta \text{ with } x^2 + y^2 = r^2$$

$$and: dx \cdot dy = r dr d\theta. \text{ The integration over the angle gives us } 2\pi$$

$$I^2 = 2\pi \int_0^\infty e^{-\alpha r^2} r dr = \text{ and we use yet another common variable transformation:}$$

$$\alpha r^2 = z;\ dz = 2\alpha r dr$$

$$I^2 = \frac{\pi}{\alpha}\int_0^\infty e^{-z} dz = \frac{\pi}{\alpha}\left(-e^{-z}\right)_0^\infty = \frac{\pi}{\alpha}(-0+1) = \frac{\pi}{\alpha}$$

$$I^2 = 4I_0^2 = \frac{\pi}{\alpha} \Rightarrow I_0 = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

I_1 can be easily integrated:

(21.73) $$I_1 = \int_0^{+\infty} x e^{-\alpha x^2} dx = \frac{1}{2\alpha}$$

We can show that the subsequent integrals I_n, with n=2, 3,… can be easily calculated by differentiation under the integral sign according to :

(21.74) $$\boxed{\frac{d}{d\alpha}\int_a^b f(x,\alpha)dx = \int_a^b \frac{\partial}{\partial\alpha}\left[f(x,\alpha)\right]dx}$$

We get for the Gaussian integrals :

(21.75) $$\boxed{I_n = -\frac{dI_{n-2}}{d\alpha}}$$

(21.76) $$I_2 = \int_0^{+\infty} x^2 e^{-\alpha x^2} dx = -\frac{dI_0}{d\alpha} = \frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}}$$

(21.77) $$I_3 = \int_0^{+\infty} x^3 e^{-\alpha x^2} dx = -\frac{dI_1}{d\alpha} = \frac{1}{2\alpha^2}$$

(21.78) $$I_4 = \int_0^{+\infty} x^4 e^{-\alpha x^2} dx = \frac{d^2 I_0}{d\alpha^2} = \frac{3}{8}\sqrt{\frac{\pi}{\alpha^5}}$$

Using (21.76) in (21.70)we get for the normalization constant A :

(21.79)
$$\frac{1}{4\pi A} = \frac{1}{4}\sqrt{\frac{\pi}{\alpha^3}} \Rightarrow 4\pi A = 4\sqrt{\frac{\alpha^3}{\pi}} \Rightarrow A = \frac{1}{\pi}\sqrt{\frac{\alpha^3}{\pi}} = \sqrt{\frac{\alpha^3}{\pi^3}}$$
$$\alpha = \frac{m}{2k_B T} \Rightarrow A = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}}$$

With this constant the probability distribution becomes the Maxwell distribution formula (note the extra 4π from the spherical volume element $4\pi v^2 dv$);

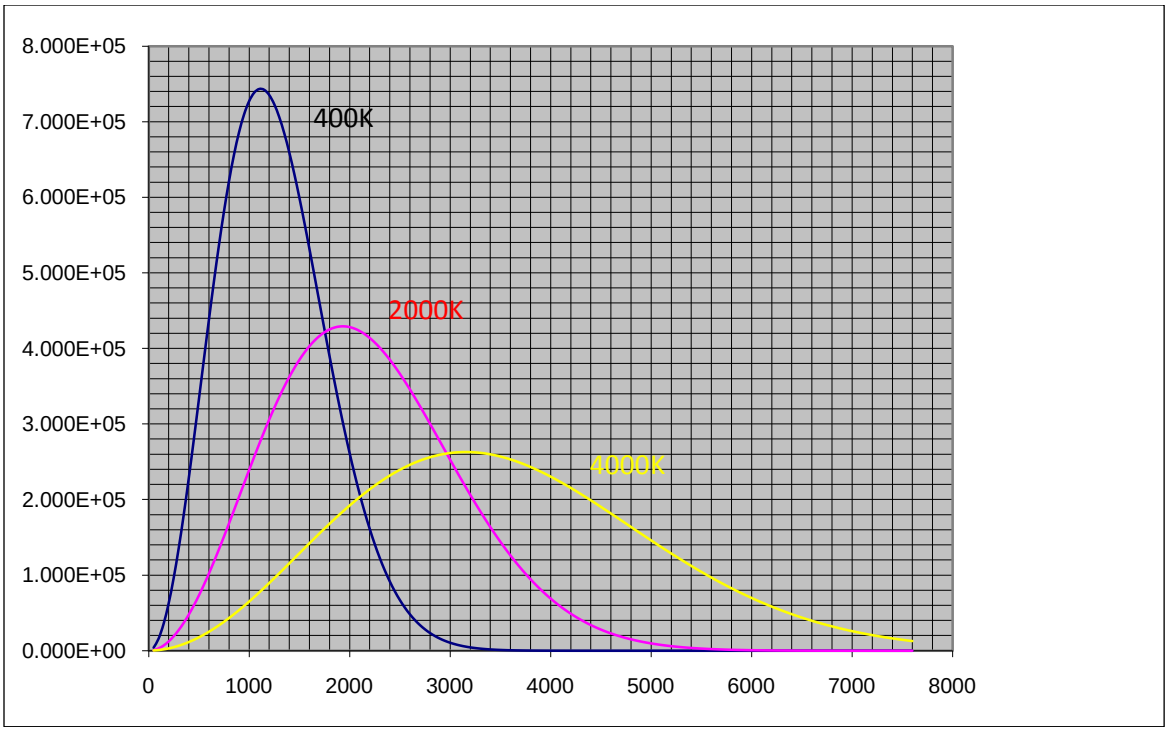
(21.80)
$$\boxed{\begin{aligned} f(v)dv &= Ae^{-\frac{mv^2}{2k_B T}} 4\pi v^2 dv = A' e^{-\frac{mv^2}{2k_B T}} v^2 dv \\ A' &= 4\pi A = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \end{aligned}}$$

It is sometimes useful to work with the Maxwell distribution formula in terms of the kinetic energy E, rather than speed: We get:

(21.81) $$f(E)dE = \frac{2}{\sqrt{\pi}}\left(k_B T\right)^{-\frac{3}{2}}\sqrt{E}\, e^{-\frac{E}{k_B T}} dE$$

21.6b The Maxwell distribution:

Note the v^2 term which is responsible for the **Maxwell tail**, i.e. the fact that the Maxwell distribution function goes to 0 much more slowly than a pure Gaussian function. Also note that the maximum of the function decreases with higher temperatures (the exponent increases), the whole function becomes more flat and the peak moves to the right.



For N particles, we just multiply the formula by N and obtain the number of particles N_v with velocities between v and v+dv.

For the **most probable speed** v_{mp} we take the derivative of f(v) with respect to v and, setting it equal to 0, we find:

(21.82)
$$\boxed{v_{mp}=\sqrt{\frac{2kT}{m}}=1.4\sqrt{\frac{kT}{m}}=1.4\sqrt{\frac{RT}{M}}}$$

We find the average velocity according to the formula (21.61)

(21.83)
$$\bar{v}=\int_0^\infty f(v)v\,dv=4\pi A\int_0^\infty v e^{-\frac{mv^2}{2k_BT}}v^2dv=4\pi AI_3=4\pi A\frac{1}{2\alpha^2}$$

We evaluate this integral by using formula (21.77):

We get

(21.84)
$$\boxed{\bar{v}=4\pi\left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}}\frac{1}{2\alpha^2}=2(\alpha\pi)^{-\frac{1}{2}}=2\sqrt{\frac{2k_BT}{\pi m}}=\sqrt{\frac{8k_BT}{\pi m}}=1.6\sqrt{\frac{k_BT}{m}}}$$

The rms speed is obtained from

(21.85)
$$\boxed{\frac{1}{2}m\overline{v^2}=\frac{3}{2}k_BT\Rightarrow v_{rms}=\sqrt{\frac{3k_BT}{m}}=1.73\sqrt{\frac{k_BT}{m}}}$$

This is the same result we get by using :

(21.86)
$$\overline{v^2} = \int_0^{+\infty} A' e^{-\frac{mv^2}{2k_BT}} v^2 \cdot v^2 dv = 4\pi A I_4 = 4\pi \left(\frac{\alpha}{\pi}\right)^{\frac{3}{2}} \frac{3}{8} \alpha^{-\frac{5}{2}} \pi^{\frac{1}{2}} =$$
$$\frac{3}{2} \alpha^{-1} \pi^{1-\frac{3}{2}+\frac{1}{2}} = \frac{3}{2\alpha} \pi^0 = \frac{3 \cdot 2k_BT}{2m} = \frac{3k_BT}{m}$$

21.6c Estimating temperatures for chemical and nuclear reactions :
a) Using the Equipartition of energy to calculate the temperature necessary to permit a atomic or nuclear process.

We find in the kinematic theory of atoms that for every degree of freedom in the motion of a particle an average energy of kT/2 is required. k_b is the **Boltzmann constant with a value of: *1.380650x10^{-23} J/Kelvin***

$\frac{1}{2} m\overline{\left(v_x^{\,2} + v_y^{\,2} + v_z^{\,2}\right)} = \frac{3}{2} kT$ for three degrees of freedom x,y,z $k = 1.38 \times 10^{-23} \frac{J}{K^\circ}$

Hydrogen Atom : This relationship between energy and temperature is often a good way to estimate the temperature involved in maintaining or creating the particular energy form. For example, the groundstate energy of a hydrogen atom is
-13.6 eV. Therefore, to break up a **hydrogen atom**, or to put it together, a temperature is required in the neighborhood of

$13.6eV \approx kT \Rightarrow T \approx \frac{13.6eV}{k} = \frac{13.6 \times 1.6 \times 10^{-19} J}{1.38 \times 10^{-23} JK^{-1}} = 9.86 \times 10^4 K$ So, we can expect that at temperatures around 10^5 Kelvin hydrogen atoms can be formed out of electrons and protons.

:
The **space shuttle** uses the energy of hydrogen gas being burnt with oxygen to deliver its propulsion :

(21.87) $$2H_2 + O_2 \rightarrow 2H_2O + energy(286kJ / mole)$$

The speed of the ejected water molecules is given by

(21.88) $$v_0 = \sqrt{\frac{3RT}{M_{mol}}}$$

This means that the hotter the gas in the combustion chamber and the lighter the gas, the faster the ejected gas will be. The endspeed v of a rocket is given by :

Seen from the reference system of the rocket, the initial momentum is 0.

$-v_{eject} dm = mdv \Rightarrow v_{eject} \frac{dm}{m} = -dv$ integrating gives

$v_{eject} \ln \frac{m_f}{m_i} = -\left(v_f - v_i\right) \Rightarrow$ inverting the fraction takes care of the minus sign:

$v_{eject} \ln \frac{m_i}{m_f} = v_f - v_i$

(21.89) $$v_f - v_i = +v_{eject} \ln \frac{m_i}{m_f} \approx v_{eject} \ln 6$$

The maximum amount of fuel is about 6 times the mass of the empty rocket. We see that the speed is limited by the available temperatures for the combustion chamber. (It should not melt !)

If we assume 2000K we get a speed of only 1.7km/s for the increase of v_{eject} and therefore roughly 1.7·2km/s for the final speed of the rocket. We need three times that speed just to put a rocket into orbit. Hence the reason for several stages of a rocket.

Nuclear Fusion in the Sun :
The **exterior of the sun** has an approximate temperature of 6000 K, the interior of 10^7K.
A hydrogen nucleus with 1 proton and 1 neutron is called a deuteron, a hydrogen nucleus with 1 proton and 2 neutrons is called a triton. They are isotopes which are being created during the fusion process of four hydrogen atom nuclei to one helium nucleus. A summary of these processes can be written as follows :

Nuclear fusion inside of the sun:

$$^2H + {}^3H \rightarrow {}^4He + n + 17.6MeV$$

deuteron + triton $\rightarrow$ Helium4 + a neutron + 17.6 MeV

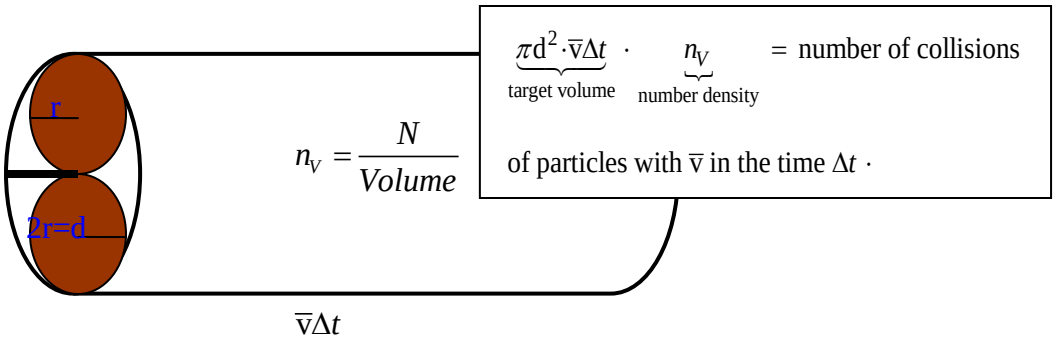
Following the reasoning above this would require a median thermal energy corresponding to temperatures of approximatly 1 million times the energy required in the formation of an H atom, namely about 10^{11}K. This temperature does not exist even in the interior of the sun with a temperature around 10 million K. However, because of the Maxwell distribution of speeds there will be some particles available which can tunnel through the Coulomb wall. (p 827 Gerthsen)
This gamma radiation consists of photons, which travel to the surface of the sun, all the while losing energy to the point where the photons are mostly of an energy corresponding to the sun-light spectrum. The random motion is caused by collisions with proton-sized nuclei. As the photons decrease in energy they increase in wavelength, thus causing more collisions.

21.7 Mean Free Path.

The mean free path of particles is the average distance λ of any particle between collisions. If two particles of spherical shape approach each other to within the distance of their combined radius they will collide. If we assume that they have the same radius, that distance is d=2r. The same result is obtained if we assume that one of the particles has a radius of 2r and the other is a dimensionless point. The target area is that of a circle with area $\pi d^2 = \mathbf{4\pi r^2}$.

The number of collisions in the time Δt is equal to the **number of such particles per unit volume n_V=N/V** (particle density) times the volume of a cylinder with the above target area as base and length $v\cdot\Delta t$.
We proceed as follows:

- Find the number of collisions in the time Δt, which is the number of particles contained in a cylinder of base πd^2 muliplied by the average length travelled by a molecule in the time Δt, which is $v\Delta t$. The velocity can be v_{rms}, v_{mp}, or $\bar{v}$. This volume multiplied by the number density n_v gives us an estimate for the **number of collisions n_{coll} in the time Δt**.
- Dividing by Δt gives us the **mean frequency** for collisions: $f = n_{coll}/\Delta t$
- The inverse of frequency is the time between collisions (**mean free time**) τ.
- The **mean free length λ** is given by $v\cdot\tau$



(21.90) number of collisions is $n_{coll} = \pi d^2 n_V \bar{v}\Delta t$

The number of collisions per time interval Δt is the frequency at which collisions occur f_{coll}:

(21.91) $$f_{coll} = \frac{\text{number of collisions}}{\text{unit time}} = \frac{\pi d^2 n_v \bar{v}\Delta t}{\Delta t} = \pi d^2 n_v \bar{v}$$

Think of the mean free path as the wavelength, then we have $\bar{v} = f \cdot \lambda$

The inverse of frequency is period $T_{coll} = \tau$, which is the mean free time:

(21.92) $$f_{coll} = \frac{\text{number of collisions}}{\text{unit time}} = \frac{\pi d^2 n_v \bar{v}\Delta t}{\Delta t} =$$
$$\text{mean free time} = T_{coll} = \tau = \frac{1}{f_{coll}} = \frac{1}{\pi d^2 n_V \bar{v}}$$

A particle travels an average distance of $\bar{v} \cdot \tau$. Its mean free path l is the distance between collisions, therefore:

(21.93) $$\text{mean free path } \lambda = \bar{v} \cdot \tau = \frac{1}{\pi d^2 n_V} = (\text{target area} \times \text{number density})^{-1}$$

In a more quantitatively accurate calculation we must include the fact that particles in the considered volume are not stationary. This analysis leads to an additional $\sqrt{2}$ factor in front of the π. Everything else remains correct. Thus we have as our final results:

(21.94)
$$\text{mean free path } \lambda = \frac{\text{average distance}}{\text{number of collisions}} = \frac{1}{\sqrt{2}\pi d^2 n_V}$$
$d = 2r = diameter$ of target cylinder; $n_V = \frac{N}{V}$ = number-density
number of collisions $= \sqrt{2}\pi d^2 n_V \bar{v}\Delta t$

Example: Find the mean free path and time for atoms at standard conditions:
Let us assume the diameter of an atom to be 5·10E-10 m. At **atmospheric pressure and room temperature** we get

(21.95)
$$n_v = \frac{P}{k_B T} \left(\text{from PV=N}k_B T\right)$$
$$= \frac{10^5}{k_B T} = 2.5\cdot 10^{25} \text{ atoms per m}^3 = n_V$$

We get therefore a mean free path of 3.6E-8 m. 100 atomic diameters.

For the mean collision frequency and mean free time (period) we get similarly the corrected values :

(21.96)
$$f_{coll} = \frac{\text{number of collisions}}{\text{unit time}} = \sqrt{2}\pi d^2 n_V \bar{v}$$
$$\text{mean free time} = T_{coll} = \tau = \frac{1}{f_{coll}} = \frac{1}{\sqrt{2}\pi d^2 n_V \bar{v}}$$

Obviously,

(21.97)
$$\bar{v} = \lambda \cdot f = \frac{\lambda}{\tau}$$
$$f = \sqrt{2} \cdot \underbrace{\text{volume of target-cylinder}}_{\pi d^2 \bar{v}} \cdot \underbrace{\text{density of particles}}_{n_V = N/V}$$

Problem : In deep space we have roughly three particles per m^3. Assume that we are dealing with hydrogen atoms of diameter 0.1 nm. We have an average temperature of 3K. What is the mean free path of a particle, and what is the time interval between collisions?

(21.98)
$$\lambda = \left(\sqrt{2}\pi d^2 n_v\right)^{-1} = \left(1.4\cdot 3\cdot 10^{-20}\cdot 3\right)^{-1} = 7.9\cdot 10^{15} km$$
(about 1 million times the distance between Pluto and the sun.)

If we take the rms speed as our average speed, we get

(21.99)
$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3\cdot 1.38E-23\cdot 3}{1.67E-27}} = 270\frac{m}{s}$$

(21.100)
$$v = \frac{\lambda}{T} \Rightarrow T = \frac{\lambda}{v} = \frac{7.9E18}{270} = 2.9E16 s = 920 \text{million years}$$

Let us also calculate the pressure :

(21.101)
$$P = \frac{NkT}{V} = n_V kT = 3\cdot 1.38E-23\cdot 3 = 1.2\cdot 10^{-22} Pa$$