

Combustion of fuels

Dr Owen Williams – University of Wales TSD:



Complete combustion

Fuels are substances that react with oxygen to release useful energy. Most of the energy is released as heat, but light energy is also released.

About 21 per cent of air is oxygen. When a fuel burns in plenty of air, it receives enough oxygen for **complete combustion**.

Complete combustion needs a plentiful supply of air so that the elements in the fuel react fully with oxygen.

Fuels such as natural gas and petrol contain **hydrocarbons**. These are compounds of hydrogen and carbon only. When they burn completely:

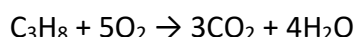
- the carbon oxidises to carbon dioxide
- the hydrogen oxidises to water (remember that water, H₂O, is an oxide of hydrogen)

In general, for complete combustion:

hydrocarbon + oxygen → carbon dioxide + water

Here are the equations for the **complete combustion of propane**, used in bottled gas:

propane + oxygen → carbon dioxide + water



Incomplete combustion

Incomplete combustion occurs when the supply of air or oxygen is poor. Water is still produced, but carbon monoxide and carbon are produced instead of carbon dioxide.

In general, for incomplete combustion:

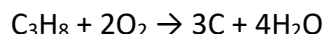
hydrocarbon + oxygen → carbon monoxide + carbon + water

The carbon is released as soot. Carbon monoxide is a poisonous gas, which is one reason why complete combustion is preferred to incomplete combustion. Gas fires and boilers must be serviced regularly to ensure they do not produce carbon monoxide.

Carbon monoxide is absorbed in the lungs and binds with the haemoglobin in our red blood cells. This reduces the capacity of the blood to carry oxygen.

Here are the equations for the **incomplete combustion of propane**, where carbon is produced rather than carbon monoxide:

propane + oxygen → carbon + water

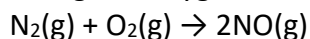


Nitrogen oxides

When fuels are burned in vehicle engines, high temperatures are reached. At these high temperatures, nitrogen and oxygen from the air combine to produce **nitrogen monoxide**.



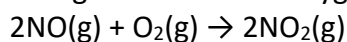
nitrogen + oxygen → nitrogen monoxide



When this nitrogen monoxide is released from vehicle exhaust systems, it combines with oxygen in the air to form **nitrogen dioxide**.



nitrogen monoxide + oxygen → nitrogen dioxide

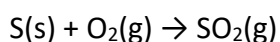


Nitrogen dioxide is a cause of acid rain.

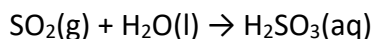
Nitrogen monoxide and nitrogen dioxide are jointly referred to as NO_x .

Sulfur dioxide and acid rain

Many fossil fuels contain sulfur impurities. When these fuels are burned, the sulfur is oxidised to form **sulfur dioxide**.



This sulfur dioxide then dissolves in droplets of rainwater to form **sulfurous acid**.



Effects of acid rain

Acid rain reacts with metals and rocks such as limestone. Buildings and statues are damaged as a result.

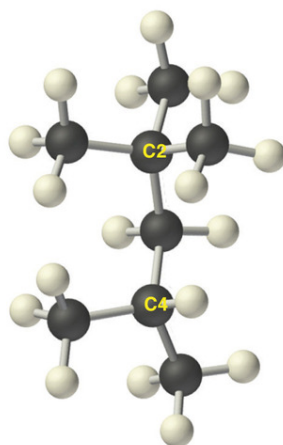
Acid rain damages the waxy layer on the leaves of trees and makes it more difficult for trees to absorb the minerals they need for healthy growth. They may die as a result.

Acid rain also makes rivers and lakes too acidic for some aquatic life to survive.

Combustion of Gasoline (Octane)

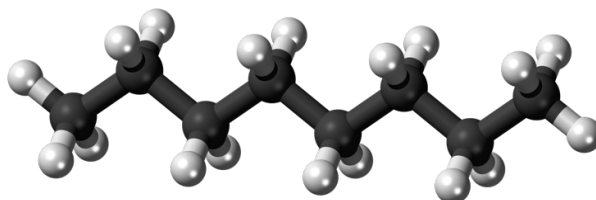
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Octane is a hydrocarbon and an alkane with the chemical formula C_8H_{18} , and the condensed structural formula $CH_3(CH_2)_6CH_3$. Octane has many structural isomers that differ by the amount and location of branching in the carbon chain. One of these isomers, 2,2,4-trimethylpentane (isooctane) is used as one of the standard values in the octane rating scale.

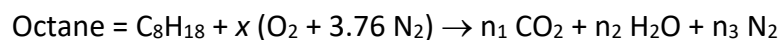


Isooctane (2,2,4-trimethylpentane)

Iso-Octane is harder to break up because its molecular structure is shorter. The shorter the molecule that the isomer of octane has, the harder it is to break up and hence the higher it's 'Octane rating'. As with all low-molecular-weight hydrocarbons, octane is volatile and luckily for us, very flammable.



Stoichiometric burning:



Since C = 8 on the left, C must be 8 on the right! So, $n_1 = 8$

H = 18 on the left, so we know that $18 = 2 \cdot n_2$

Therefore, $n_2 = 9$

Lastly, O = $2x$ on the left, so we know:

$$2x = 2n_1 + n_2$$

$$2x = 2(8) + 9$$

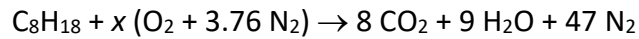
$$2x = 25$$

$$x = 12.5$$

So, n_3 must now be 3.76×12.5

$$n_3 = 47$$

So we get:



This is the 'Stoichiometric Equation'

Calculating the Stoichiometric Air Fuel Ratio:

The Air/Fuel Ratio (AFR) by mass is the ratio of the air mass to the fuel mass...

$$AFR \text{ by mass} = \frac{\text{Air Mass}}{\text{Fuel Mass}}$$

$$AFR \text{ by mass} = \frac{12.5(2 \times 16 + 3.76 \times 2 \times 14)}{8 \times 12 + 18 \times 1}$$

$$AFR \text{ by mass} = 15.05$$

Excel Stoichiometric Calculator:

All of this can of course be determined for any fuel composition and put in Excel for ease of manipulation.

Stoichiometry				
O2	21.00%	20.95	Atmospheric	Ratio
N2	79.00%	78.09	Composition	3.76
HC Fuel Balance $\text{C}_x\text{H}_y + a(\text{O}_2 + 3.76\text{N}_2) \rightarrow x\text{CO}_2 + (y/2)\text{H}_2\text{O} + 3.76a\text{N}_2$				
where...	$a = x + (y/4)$			
			a	12.5
Carbon (x)	8		CO2	8
Hydrogen (y)	18		H2O	9
			N2	47.00
m(air)	1717.3			
m(fuel)	114.232		Molecular Weight	
			Air	137.4
Stoich Ratio	15.0		Carbon	12.0
			Hydrogen	1.0
Equ Ratio	1.1		Oxygen	16.0
Fuel Ratio	16.5		Nitrogen	14.0

Stoichiometric air-to-fuel ratios of common fuels

In the combustion reaction, oxygen reacts with the fuel, and the point where exactly all oxygen is consumed, and all fuel burned is defined as the stoichiometric point. With more oxygen (over-stoichiometric combustion), some of it stays unreacted. Likewise, if the combustion is incomplete due to lack of sufficient oxygen, fuel remains unreacted. (Unreacted fuel may also remain because of slow combustion or insufficient mixing of fuel and oxygen – this is not due to stoichiometry). Different hydrocarbon fuels have different contents of carbon, hydrogen and other elements, thus their stoichiometry varies.

Fuel	Ratio by mass ^[6]	Ratio by volume ^[7]	Percent fuel by mass	Main Reaction
Gasoline	14.7 : 1	—	6.8%	$2 \text{ C}_8\text{H}_{18} + 25 \text{ O}_2 \rightarrow 16 \text{ CO}_2 + 18 \text{ H}_2\text{O}$
Natural gas	17.2 : 1	9.7 : 1	5.8%	$\text{CH}_4 + 2 \text{ O}_2 \rightarrow \text{CO}_2 + 2 \text{ H}_2\text{O}$
Propane (LP)	15.67 : 1	23.9 : 1	6.45%	$\text{C}_3\text{H}_8 + 5 \text{ O}_2 \rightarrow 3 \text{ CO}_2 + 4 \text{ H}_2\text{O}$
Ethanol	9 : 1	—	11.1%	$\text{C}_2\text{H}_6\text{O} + 3 \text{ O}_2 \rightarrow 2 \text{ CO}_2 + 3 \text{ H}_2\text{O}$
Methanol	6.47 : 1	—	15.6%	$2 \text{ CH}_4\text{O} + 3 \text{ O}_2 \rightarrow 2 \text{ CO}_2 + 4 \text{ H}_2\text{O}$
n-Butanol	11.2 : 1	—	8.2%	$\text{C}_4\text{H}_{10}\text{O} + 6 \text{ O}_2 \rightarrow 4 \text{ CO}_2 + 5 \text{ H}_2\text{O}$
Hydrogen	34.3 : 1	2.39 : 1	2.9%	$2 \text{ H}_2 + \text{O}_2 \rightarrow 2 \text{ H}_2\text{O}$
Diesel	14.5 : 1	—	6.8%	$2 \text{ C}_{12}\text{H}_{26} + 37 \text{ O}_2 \rightarrow 24 \text{ CO}_2 + 26 \text{ H}_2\text{O}$
Methane	17.19 : 1	9.52 : 1	5.5%	$\text{CH}_4 + 2 \text{ O}_2 \rightarrow \text{CO}_2 + 2 \text{ H}_2\text{O}$
Acetylene	13.26 : 1	11.92 : 1	7.0%	$2 \text{ C}_2\text{H}_2 + 5 \text{ O}_2 \rightarrow 4 \text{ CO}_2 + 2 \text{ H}_2\text{O}$
Ethane	16.07 : 1	16.68 : 1	5.9%	$2 \text{ C}_2\text{H}_6 + 7 \text{ O}_2 \rightarrow 4 \text{ CO}_2 + 6 \text{ H}_2\text{O}$
Butane	15.44 : 1	30.98 : 1	6.1%	$2 \text{ C}_4\text{H}_{10} + 13 \text{ O}_2 \rightarrow 8 \text{ CO}_2 + 10 \text{ H}_2\text{O}$
Pentane	15.31 : 1	38.13 : 1	6.1%	$\text{C}_5\text{H}_{12} + 8 \text{ O}_2 \rightarrow 5 \text{ CO}_2 + 6 \text{ H}_2\text{O}$

The deviations in the calculations from the known values tend to be due to the average composition of air used for the calculations. Generally, this is 21% Oxygen to 79% Nitrogen, however this is not exact.

Air Composition and Mass:

	Atomic No	Atomic Weight
H	1	1
C	6	12
N	7	14
O	8	16



Avogadro's number is the number of atoms of hydrogen to give you 1 gram $\approx 6.022 \times 10^{23}$

6.022×10^{23} atoms of carbon has a mass of 12g

6.022×10^{23} atoms of nitrogen has a mass of 14g

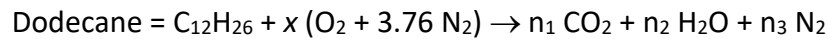
You need 6.022×10^{23} atoms of anything to get its weight in grams and then of course, 6.022×10^{26} atoms to get the atomic weight in kg (and we use both so be careful).

1 kmol of carbon = 12kg

What is a mole of moles? (for fun) <https://what-if.xkcd.com/4/>

Combustion of Diesel (Dodecane)

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$$n_1 = 12$$

$$2n_2 = 26 \therefore n_2 = 13$$

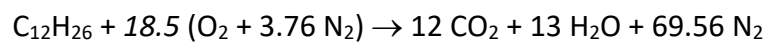
$$2n_1 + n_2 = 2x$$

$$24 + 13 = 2x$$

$$x = 37/2 = 18.5$$

$$n_3 = 18.5 \times 3.76 = 69.56$$

So, we have;



Calculating the Stoichiometric Air Fuel Ratio:

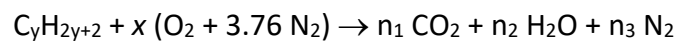
The Air/Fuel Ratio (AFR) by mass is the ratio of the air mass to the fuel mass...

$$AFR \text{ by mass} = \frac{\text{Air Mass}}{\text{Fuel Mass}}$$

$$AFR \text{ by mass} = \frac{18.5(32 + 3.76 \times 28)}{12 \times 12 + 26 \times 1}$$

$$AFR \text{ by mass} = 14.94$$

The generalised balance equation:



C	$n_1 = y$
H	$2n_2 = 2y + 2$
O	$2x = 2n_1 + n_2$
N	$n_3 = 3.76 \times (2n_1 + n_2)/2$

Masses of Fuels:

1 molecule of diesel $\rightarrow$ 12 molecules of CO_2

6×10^{26} molecules of diesel $\rightarrow 12 \times 6 \times 10^{26}$ molecules of CO_2

1 kmol diesel $\rightarrow$ 12 kmols CO_2

1 kmol diesel = $(12 \times 12 + 26) = 170$ kg

$\therefore$ You will make $12 \times (12 + 32)$ kg of $\text{CO}_2 \rightarrow 528$ Kg of CO_2

So basically, if you burn 1kg of diesel, you make $(528/170) \rightarrow 3.1$ kg of CO_2

Let's look at these numbers!

Assuming one tank is about 100 litres of diesel = (0.8 kg / litre)

So, this is 80 kg...

From this we get:

$3.1 \times 80 \text{ kg} \rightarrow 248 \text{ kg of } \text{CO}_2$

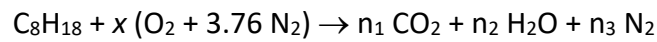
In one year $\rightarrow 50$ (once a week) $\times 248 \text{ kg}$

$= 12400 \text{ kg}$

$= 12.4 \text{ tons of } \text{CO}_2 \text{ a year!}$

Let's look an example for Gasoline:

Considering this fuel to be Iso-Octane:



C	$n_1 = 8$
H	$2n_2 = 18$
O	$2x = 16 + 9 = 25$
N	$n_3 = 3.76 \times 12.5$

Masses of Fuels:

1 molecule of gasoline $\rightarrow$ 8 molecules of CO_2

6×10^{26} molecules of gasoline $\rightarrow 8 \times 6 \times 10^{26}$ molecules of CO_2

1 kmol gasoline $\rightarrow$ 8 kmols CO_2

1 kmol gasoline = $(8 \times 12 + 18) = 114$ kg

$\therefore$ You will make $8 \times (12+32)$ kg of $\text{CO}_2 \rightarrow 352$ Kg of CO_2

So basically, if you burn 1kg of gasoline, you make $(352/114) \rightarrow 3.09$ kg of CO_2

Let's look at these numbers!

Assuming one tank is about 100 litres of gasoline = (0.75 kg / litre)

So, this is 75 kg...

From this we get:

$3.09 \times 75 \text{ kg} \rightarrow 231.75 \text{ kg of } \text{CO}_2$

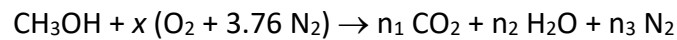
In one year $\rightarrow 50$ (once a week) $\times 231.75 \text{ kg}$

= 11587.5 kg

= 11.6 tons of CO_2 a year!

Combustion of Methanol

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C → 1	$n_1 = 1$
H → 4	$2n_2 = 4 \rightarrow n_2 = 2$
O → $2x + 1$	$2x + 1 = 2n_1 + n_2 = 2 + 2 = 4 \rightarrow x = 1.5$
N	$n_3 = 3.76 \times 1.5$

1 kmol methanol → 1 kmol CO₂

1 kmol methanol = (12 + 3x1 + 16 + 1) = 32 kg

∴ You will make 1 x (12+32) kg of CO₂ → 44 Kg of CO₂

So basically, if you burn 1kg of methanol, you make (44/32) → 1.375 kg of CO₂

Calculating the Stoichiometric Air Fuel Ratio:

The Air/Fuel Ratio (AFR) by mass is the ratio of the air mass to the fuel mass...

$$AFR \text{ by mass} = \frac{\text{Air Mass}}{\text{Fuel Mass}}$$

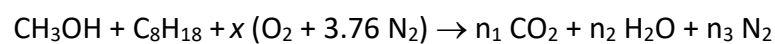
$$AFR \text{ by mass} = \frac{1.5(32 + 3.76 \times 28)}{12 + 3 + 16 + 1}$$

$$AFR \text{ by mass} = 6.435$$

The gasoline AFR was around 15 so the fuel ratio of methanol to gasoline is 15/6.44 = 2.33

The engine uses more methanol than gas so the effective CO₂ comparison with gasoline becomes → 1.38 x 22.33 which is 3.2 kg

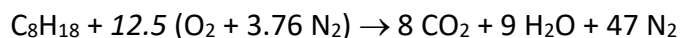
Blend of 50:50 Ethanol - Octane



So, what do you do with this?

Energy, Enthalpy and the laws of Thermodynamics

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Thermodynamics is defined as the branch of science that deals with the relationship between heat and other forms of energy, such as work. It is frequently summarized as three laws that describe restrictions on how different forms of energy can be interconverted.

Chemical thermodynamics is the portion of thermodynamics that pertains to chemical reactions.

The Laws of Thermodynamics:

First law: Energy is conserved; it can be neither created nor destroyed.

Second law: In an isolated system, natural processes are spontaneous when they lead to an increase in disorder, or entropy.

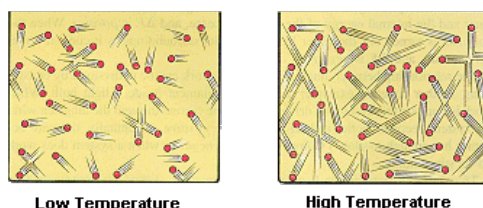
Third law: The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

There have been many attempts to build a device that violates the laws of thermodynamics. All have failed. Thermodynamics is one of the few areas of science in which there are no exceptions. No one EVER talk of these things!!!

Internal Energy

One of the thermodynamic properties of a system is its **internal energy**, E , which is the sum of the kinetic and potential energies of the particles that form the system. The internal energy of a system can be understood by examining the simplest possible system: an ideal gas. Because the particles in an ideal gas do not interact, this system has no potential energy. The internal energy of an ideal gas is therefore the sum of the kinetic energies of the particles in the gas.

The kinetic molecular theory assumes that the temperature of a gas is directly proportional to the average kinetic energy of its particles, as shown in the figure below.



The internal energy of an ideal gas is therefore directly proportional to the temperature of the gas.

Since it is the kinetic energy that is proportional to temperature, we know that heavier molecules move more slowly than lighter ones, but have the same kinetic energy.

Law of equipartition of energy

Law of equipartition of energy states that for a dynamical system in thermal equilibrium the total energy of the system is shared equally by all the degrees of freedom. The energy associated with each degree of freedom per molecule is $\frac{1}{2} kT$, where k is the Boltzmann's constant.

Let us consider one mole of a monoatomic gas in thermal equilibrium at temperature T . Each molecule has 3 degrees of freedom due to translatory motion. According to kinetic theory of gases, the mean kinetic energy of a molecule is $\frac{3}{2} kT$.

Given a thermodynamic system at an absolute temperature T , the average thermal energy carried by each microscopic degree of freedom in the system is $\frac{1}{2} kT$ (i.e., about 2.07×10^{-21} J, or 0.013 eV, at room temperature).

In classical statistical mechanics, this average is predicted to hold exactly for homogeneous ideal gases. Monatomic ideal gases (the six noble gases) possess three degrees of freedom per atom, corresponding to the three spatial directions, which means a thermal energy of $\frac{3}{2} kT$ per atom. This corresponds very well with experimental data.

$$E = \frac{3}{2} R_u T$$

Since $R_u = 6.022 \times 10^{26} \times 1.38 \times 10^{-23} \approx 8314 \text{ J/kmol.K}$ (or 8.314 J/mol.K)

(See last year's Powetrain and Control notes – Semester 2, Week 1)

The thermal energy can be used to calculate the root-mean-square speed of the atoms, which turns out to be inversely proportional to the square root of the atomic mass. The root mean square speeds found at room temperature accurately reflect this, ranging from 1370 m/s for helium, down to 240 m/s for xenon.

Handwritten calculation on a grid background:

$$\begin{aligned} \frac{1}{2} m v^2 &= \frac{3}{2} R_u T && \text{so} \\ v^2 &= \frac{3 R_u T}{m} \\ v^2 &= \frac{3 \times 8314 \times 298}{14} && \text{(Nitrogen gas)} \\ v &= 728 \text{ ms}^{-1} && \sim 1626 \text{ mph} \\ &&& \text{Nice!} \end{aligned}$$

Degrees of Freedom

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The number of degrees of freedom of a dynamical system is defined as the total number of co-ordinates or independent variables required to describe the position and configuration of the system.

For translatory motion

(a) A particle moving in a straight line along any one of the axes has one degree of freedom (e.g). Bob of an oscillating simple pendulum.

(b) A particle moving in a plane (X and Y axes) has two degrees of freedom. (e.g) An ant that moves on a floor.

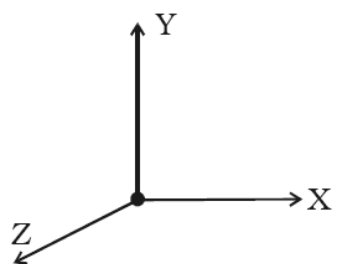
(c) A particle moving in space (X, Y and Z axes) has three degrees of freedom. (e.g) a bird that flies.

A point mass cannot undergo rotation, but only translatory motion. A rigid body with finite mass has both rotatory and translatory motion. The rotatory motion also can have three co-ordinates in space, like translatory motion. So, a rigid body will have six degrees of freedom - three due to translatory motion and three due to rotatory motion.

Monoatomic molecule

Since a monoatomic molecule consists of only a single atom of point mass it has three degrees of freedom of translatory motion along the three co-ordinate axes as shown in figure.

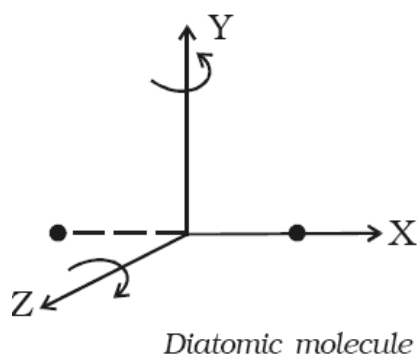
Examples: molecules of rare gases like helium, argon, etc.



Monoatomic molecule

Diatomic molecule

The diatomic molecule can rotate about any axis at right angles to its own axis. Hence it has two degrees of freedom of rotational motion in addition to three degrees of freedom of translational motion along the three axes. So, a diatomic molecule has five degrees of freedom as shown in figure. Examples: molecules of O_2 , N_2 , CO , Cl_2 , etc.



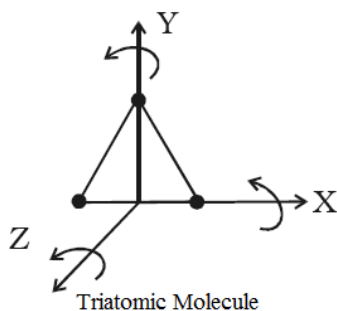
Triatomic molecule (Linear type)

In the case of triatomic molecule of linear type, the centre of mass lies at the central atom. It, therefore, behaves like a diatomic molecule with three degrees of freedom of translation and two degrees of freedom of rotation, totally it has five degrees of freedom as shown in figure. Examples: molecules of CO_2 , CS_2 , etc.



Triatomic molecule (Non-linear type)

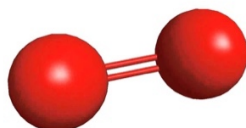
A triatomic non-linear molecule may rotate, about the three mutually perpendicular axes, as shown in figure. Therefore, it possesses three degrees of freedom of rotation in addition to three degrees of freedom of translation along the three co-ordinate axes. Hence it has six degrees of freedom. Examples: molecules of H_2O , SO_2 , etc.



In all the above cases, only the translatory and rotatory motion of the molecules have been considered. The vibratory motion of the molecules has not been taken into consideration.

<http://demonstrations.wolfram.com/TheSixDegreesOfFreedomOfADiatomcMolecule/>

So oxygen molecules can move in the 3 x, y, z axes, but can also rotate around these 3 axes, meaning we have 3 translational degrees of freedom and 3 rotational degrees of freedom. In terms of the rotation though, it only has significant moments of inertia in 2 of the rotational axes.



Thus, O_2 has 5 independent degrees of freedom in practice and the KE of each degree of freedom is $\frac{1}{2}k_B T$. Equipartition of energy (quantum mechanics) says that each degree of freedom has the same KE at a given temperature.

For non-linear molecules, all rotational motions can be described in terms of rotations around 3 axes, the rotational degree of freedom is 3 and the remaining $3n-6$ degrees of freedom constitute vibrational motion.

For a linear molecule however, rotation around its own axis is no rotation because it leaves the molecule unchanged. So there are only 2 rotational degrees of freedom for any linear molecule leaving $3N-5$ degrees of freedom for vibration.

The degrees of vibrational modes for **linear molecules** can be calculated using the formula:

$$3n-5$$

The degrees of freedom for **nonlinear molecules** can be calculated using the formula:

$$3n-6$$

n is equal to the number of atoms within the molecule of interest. The following procedure should be followed when trying to calculate the number of vibrational modes:

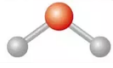
How many vibrational modes are there in the linear carbon dioxide (CO_2) molecule?

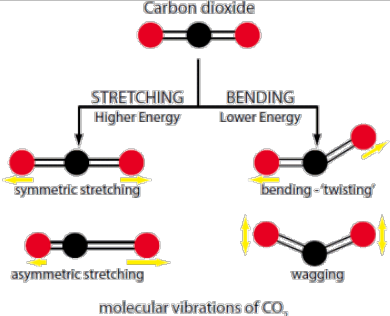
There are a total of 3 atoms in this molecule. It is a linear molecule so we use $3n-5$.

There are:

$$3(3) - 5 = 4$$

vibrational modes in CO_2 .

Type of molecule	N	Degrees of freedom	Modes
Monatomic, e.g. Ne 	1	3	3 translational 0 rotational 0 vibrational
Diatomic, e.g. HCl 	2	6	3 translational 2 rotational 1 vibrational
Triatomic linear, e.g. CO_2 	3	9	3 translational 2 rotational 4 vibrational
Triatomic non-linear, e.g. H_2O 	3	9	3 translational 3 rotational 3 vibrational

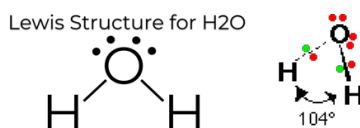


Would CO₂ and H₂O have a different number for degrees of vibrational freedom?



Following the procedure above, it is clear that CO₂ is a linear molecule while H₂O is nonlinear. H₂O contains 2 *lone pairs* which causes the molecule to be bent in shape, whereas, CO₂ has no lone pairs. It is key to have an understanding of how the molecule is shaped. Therefore, CO₂ has 4 vibrational modes and H₂O has 3 vibrational modes of freedom.

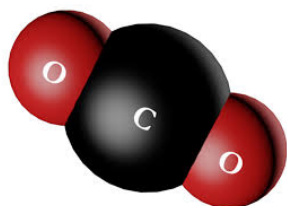
A lone pair is a concept used in valence shell electron pair repulsion theory (VSEPR theory) which explains the shapes of molecules.)



Oxygen has four pairs of electrons, two of which are lone pairs. These will take up a tetrahedral arrangement. The bond angle closes to 104°, because of the repulsion of the two lone pairs. The shape is not ‘described’ as tetrahedral, because we only "see" the oxygen and the hydrogens - not the lone pairs. Water is described as **bent or V-shaped**.

Anyway....

To make CO₂ hotter, you, by definition, have to make it move faster, but you must also feed in equal energy to its **rotation** and **vibration** degrees of freedom.



So the internal energy U = the sum of the : -

1. Transational KE
2. Rotational KE
3. Vibrational KE

$$\text{Enthalpy ... } H = U + PV$$