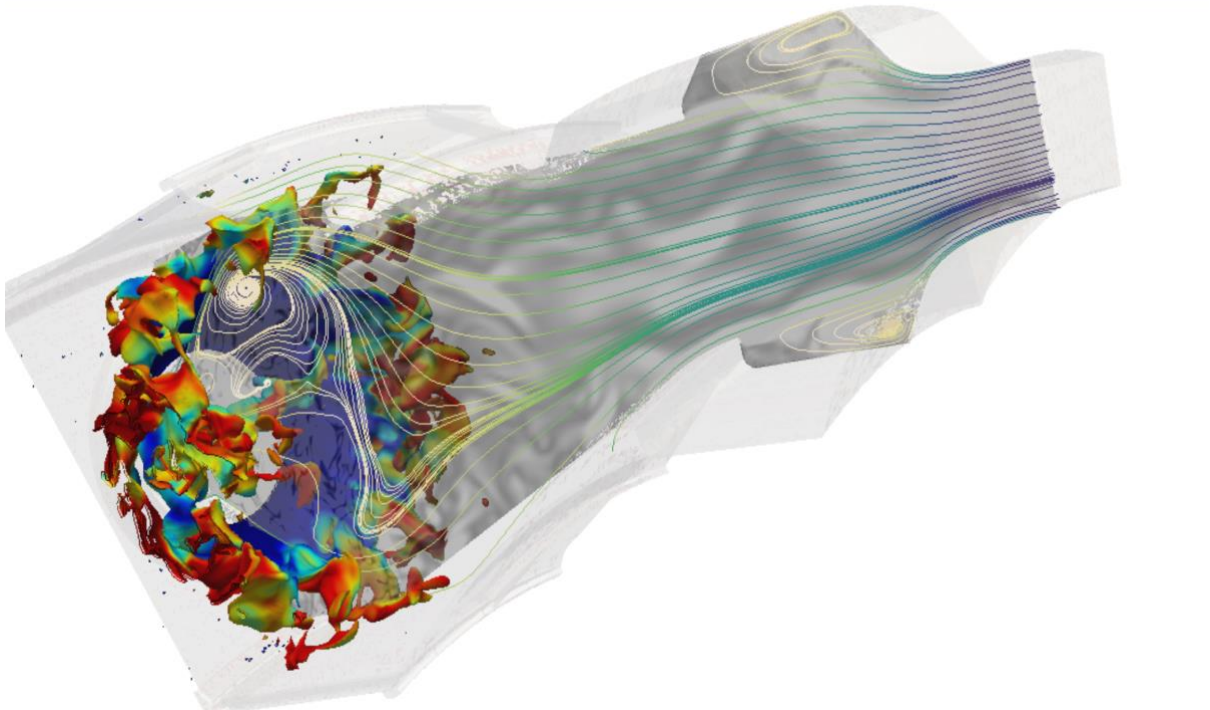


COMBUSTION FOR PROPULSION AND POWER

Lecture Notes for Lectures 1 & 2

Ivan Langella



Acknowledgement of contributions:

Gioele Ferrante

Alessandro Porcarelli

1. Introduction to combustion

In respect to isothermal and non-reacting flows, a lot of new complexity is introduced when treating a flow with chemical reactions. Instead of a single species, a multiplicity of species needs to be tracked. The number of species varies depending on fuel and oxidiser (air or oxygen in case of combustion) from 10 in case of hydrogen/oxygen combustion to more than 200 for heavy hydrocarbons such as those in the kerosene. Each species has its own heat coefficient, which in general depends on pressure and temperature. Moreover, species react with each other and the speed of these reactions has a strongly non-linear dependence on many parameters such as pressure, temperature and concentration of the species involved in the reaction themselves. In addition, transport coefficients (such as diffusion coefficients) also vary from species to species and further depend on temperature, implying that species diffuse, in general, differently from each other and these differences change with temperature. Since heat is released in the combustion process, the temperature of the fluid changes also in the process, affecting in turn the species transport coefficient and their reaction rates, which in turn affect the temperature and so on. All fluid dynamics variables are therefore coupled between each other, which is why combustion problems are very challenging. The use of liquid fuels such as those used in aviation further adds to this coupling as the evaporation process is endothermic, i.e. the evaporation of droplets of fluids subtracts heat from the combustion process, again affecting temperature, reaction rates etc.

A combustion process is different by other chemical reactions due to three main characteristics:

- Combustion consists of reactions of oxidation and reduction. This means that there is a species (the oxidising agent) that “steals” an electron from another species (the reducing agent). The species that has lost the electron is oxidised, while the species that has gained the electron is reduced.
- Most of the reactions are strongly exothermic, so at the end of the combustion process there is a net release of heat. Note that endothermic reactions still can occur, such as dissociations.
- The reactions in a combustion process require high activation energy in order to occur. This means that to have a release of energy, one first needs to provide energy to be able to break the bonds of the reactant molecules. This concept is illustrated in Fig. 1.1 for glucose/air combustion. The energy of the final products is lower than that of the reactants, meaning that the reactants have released the energy packed within their bonds (exothermic reaction). Sometimes catalysts can be used to reduce the activation energy. Nevertheless, the activation energy is given back at the end of the reaction and the net heat release only depends on the initial and final states. Note that an activation energy is required also for endothermic reactions, with the difference that the net energy balance would be negative in this case, i.e. the products have higher energy packed in their bonds than the reactants.

An important aspect is that the energy released by the exothermic reactions in the combustion process is generally sufficiently high to surpass the activation energy of nearby species and trigger further reactions. Therefore, once an initial energy is provided, the combustion process can self-sustain itself (provided there is enough fuel and oxidiser), which gives a significant advantage from an engineering point of view as compared to other types of chemical processes.

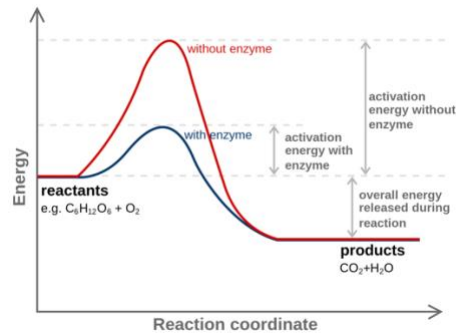


Figure 1.1[Wikipedia] – Reaction of glucose and air, with and without enzyme (catalyst).

What are at this point viable fuels from an engineering perspective? Most of the common fuels that are used to generate energy are of organic nature, meaning they are based on carbon and usually are of fossil origin. Except for the case of hydrogen (H_2), the chemical formula of these fuels has the form (C_nH_m) or $(C_nH_m - OH)$. In the second case (alcohols) the oxidiser is present in the fuel molecule within the OH group. We will see that combustion of alcohols releases because of this significantly less heat per kilogram than alkanes and aromatics, where oxygen is not present in the fuel. Carbon based fuels and hydrogen are, however, not the only options for combustion, as also metals (iron, aluminium, magnesium) or other elements (nitrogen, boron) can be burnt. Although some of these have interesting properties from an engineering point of view and in the energy gain, only hydrogen and hydrocarbons will be treated in this course. The main products of combustion in the case of hydrocarbons are always carbon dioxide (CO_2) and water vapour (H_2O), and they are thus unavoidable. There are, however, other minor species present at the end of the combustion, whose amount depends strongly on the efficiency of the combustion process. The combustion efficiency is defined as the actual amount of heat release over the ideal amount of heat release in case of complete reaction. In fact, reactions are never complete in reality for two reasons:

- A physical limitation, due to the fact that products absorb energy from the combustion itself and recombine into the reactants or dissociate. Even in the best possible conditions, the reaction at most will reach a state of equilibrium, where complete combustion is not achieved.
- An engineering limitation, due to the fact that either it is not possible to have the best possible conditions (for example there are heat losses in our system), or the time scales of our energy-generation device is not large enough for the combustion to even reach the equilibrium state.

The combustion efficiency in modern gas turbines (fuel/air combustion, subsonic) is acceptable for values of about 0.999 at least. This is not to be confused with the thermal efficiency in the combustor chamber, which is much lower. The combustor efficiency only relates to the combustion process. How can such high values be achieved, and why smaller values are not acceptable? The answer is to be found in the relation of combustion efficiency with emissions. First, these values are actually achievable in combustion for maximum temperatures (at the end of the combustion process) below about 2500 K, as long as residence times of reactants in the combustion chambers are high enough (order of 10 ms or above). In fact, the equilibrium point at these temperatures is strongly shifted towards the products. At higher temperatures (obtainable for example in rocket engines where oxyfuel combustion occurs) strong endothermic dissociations take place, acting as energy sinks. Unfortunately, even with high values of combustion efficiency, intermediate species are present, and among these some are

toxic such as carbon monoxide (CO), nitric oxides (NO, NO₂, etc., more generally indicated as NO_x), unburnt hydrocarbons (UHC) and soot. Since the number of elements (nitrogen, oxygen, hydrogen and carbon atoms) must be conserved, the presence of these intermediate species at the end of the combustion process implies that not all of the main products (CO₂ and H₂O) have been formed, and consequently not all of the energy has been released, which is why combustion efficiency and emissions are directly related. While having 0.999% of the theoretical amount of CO₂ is not a significant change (as compared to 100%), the level of CO or other unburnt hydrocarbons in that remaining 0.1% is a major concern, as even small amounts (hundreds of parts per million) are dangerous for the environment and our health. For efficiency values below 0.999 the amount of CO raises exponentially and to unacceptable levels. While CO and UHC are directly tied up with the combustion efficiency, the case of NO_x is slightly different as it is not composed by hydrogen or carbon from the fuel and thus it is not an essential species for the energy release process. The nitrogen (N₂) in the air needs very high activation energy to break its bonds, which is why its formation occurs prevalently towards the end of the combustion process, when a significant amount of energy has been released already and temperatures are high, implying higher chances of strong-enough collisions between two molecules of N₂. Once these bonds are broken, the atomic nitrogen recombines with available atomic oxygen, hydrogen and OH radicals in different ways before ending up in NO_x, and therefore the abundance of these intermediate species towards the end of the combustion process has a major role, and it is in this sense that NO_x formation is tied up with combustion efficiency. The process of NO_x formation is, however, relatively slow as compared to the main products of combustion (CO₂ and H₂O) and this poses important challenges for the design of a combustor chamber:

- While we aim to get as close as possible to complete combustion (higher efficiency), the reaction progress requires a certain amount of time. If this is too long (above 5-10 ms in a practical combustor), NO_x will increase too much, so while the resident times in a combustion chamber cannot be too small for efficiency purposes, one has to pay attention also to the opposite scenario due to the formation of toxic pollutants.
- Another issue is that NO_x forms prevalently at high power conditions (e.g. take-off), corresponding to higher temperatures, while CO and UHC form at low-power conditions (e.g. idle). As can be observed in Fig. 1.2a, there is only a narrow band of temperatures where both CO and NO_x are small, which can be achieved without loss of efficiency only at relatively high air-to-fuel ratios. Therefore, the reduction of toxic pollutants is always a compromise in case of hydrocarbon fuels.
- Close to the lean blow-out (LBO) limit the combustion process at practical conditions becomes unstable. Therefore, even in the case of hydrogen fuel where CO is not produced, having very high air-to-fuel ratios is very challenging.

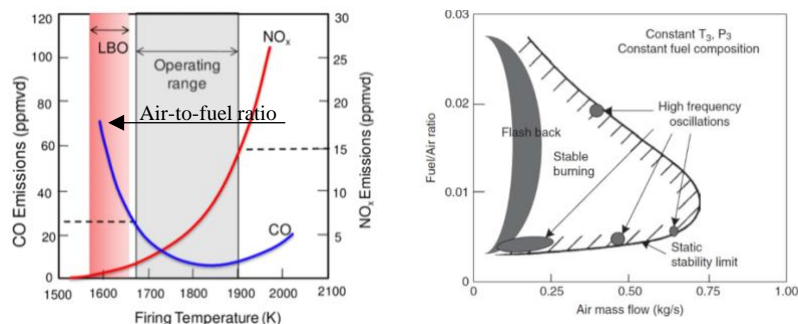


Figure 1.2. Variation of NO_x and CO with temperature (left) and a stability map (right).

To address these challenges in the design of a new-generation, environmentally friendly gas turbine, the interaction between combustion and the (turbulent) flow field has thus to be well understood not just in terms of emissions impact and efficiency, but also flame stability. In order to be able to do that, the thermodynamics of flames needs to be understood first. Note that, in general, we can categorise the combustion processes in

- **Autoignition and explosion.** This is the case for example of a perfectly or continuously stirred reactor, where the gas mixture is always homogeneous at any reaction stage, i.e. there are no gradients of velocity, pressure, temperature or species concentrations. Consequently, there are no convective and diffusive effects, and combustion can only evolve in time. We refer as explosion to the condition for which a sufficient number of radicals (species with a free bond) is present in the mixture so that a reactions chain is triggered, characterised by an exponential growth of radicals. This condition can be achieved by assisted ignition (e.g. with a spark) or, for certain operative conditions, is preceded by a phase called autoignition, where radicals are produced at a slower rate than in the explosion, until the threshold value for explosion is reached. We will return on this in Section 4. Also, do not confuse “explosion” with “detonation”.
- **Propagation.** The combustion properties in this case vary in space, allowing the presence of convective and/or diffusion processes, or more generally, transport processes. These in turn strongly interact with the combustion processes, so adding a new level of complexity. This is also the case where we can properly talk about “flame”. By definition, a flame is “a hot glowing body of ignited gas”, but this definition, associated to the presence of a fire in the public dictionary, is a bit ambiguous. For the purposes of this course, we will associate the flame to the presence of a “flame front”, i.e. the ignited gas also have a leading edge propagating through the reactant mixture.

In reality, the combustion is never only explosive or propagative. In a stirred reactor, some inhomogeneity is always present since neither combustion or diffusion processes (laminar or turbulent) are infinitely fast. Vice-versa, the mixture can auto-ignite in a propagative context or assist the propagation. However, at some conditions, we can say that combustion is dominated by autoignition or propagation processes. It is important also to note that transport processes compete with chemical processes in determining the local flame properties. If these are strong enough, a variation in some minor reaction may not produce any significant effect in the overall combustion process. Vice-versa, in explosions and auto-ignition processes sensitivity to chemical changes are much more relevant.

Deflagrations and detonations

A flame can be further categorised in premixed and non-premixed. In the first case fuel and oxidiser are mixed at a molecular level before combustion occurs, while in the second case they are not. Although this may look as an irrelevant difference, in reality the flame properties significantly change between the two cases. The main difference is that premixed flames have their own speed, i.e. the flame travels towards the premixed reactants, and is controlled by a delicate balance between reactions, diffusion and convection. In non-premixed flames combustion occur along the stoichiometric line and does not have a speed (but the flame can still move in space by the effect of the flow). In this case the flame is dominated by diffusive effects, which is why it is also referred to as “diffusion flame”. More on premixed and diffusion

flames will be discussed later in the course. Here we further categorise premixed flames into **deflagration** and **detonation**. By definition, we refer to deflagration when the flame speed is subsonic, and to detonation when it is supersonic (in this case there is a shock wave followed by the detonation wave). In reality, strong auto-ignitive processes are present in a detonation so the distinction as made before between propagation and explosion is less marked here. There is, however, another very important concept that distinguishes deflagration and detonation. To understand it, let's look at the $p - v$ diagram in Fig. 1.3, where $v = 1/\rho$ is the specific volume.

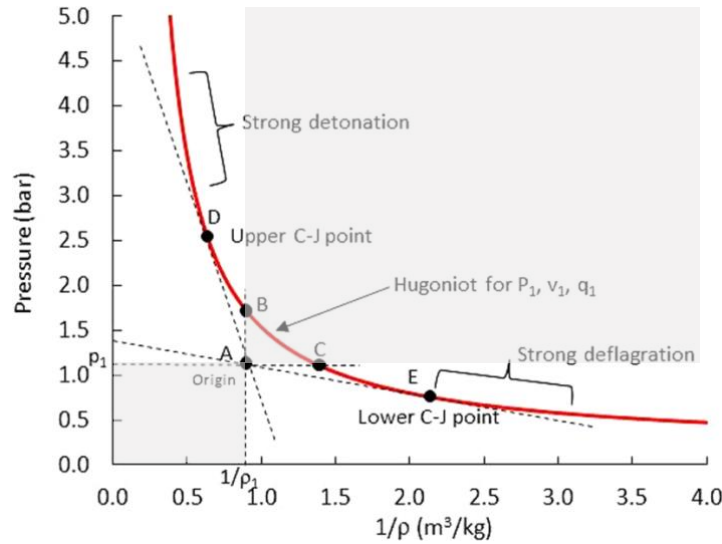


Figure 1.3. Hugoniot curve.

Let's suppose our reactant mixture has a certain density and pressure, indicated by point A in the figure. For simplicity, let's assume that our fluid can only move in direction x in a duct of constant section A (1D flow) and that the flow and the flame are steady (the flame does not move in respect to an Eulerian system of reference, which is possible if the speed of the reactants equals the flame speed). Let's also neglect diffusive processes for simplicity. For this reacting flow, mass and momentum conservation still apply, identically to the non-reacting flow case. By the continuity equation we know that the mass flow rate \dot{m} of our 1D flow is constant. Since the section area is also constant, then

$$\frac{\dot{m}}{A} = \rho u_x = \text{const}$$

where u_x is the flow velocity in direction x . From the momentum equation, instead:

$$p + \rho u_x^2 = \text{const}$$

By combining the two equations above and writing the equation for the points A and a generic point Y, we obtain:

$$p_Y - p_A = -\frac{\dot{m}^2}{A^2} \left(\frac{1}{\rho_Y} - \frac{1}{\rho_A} \right) \quad (1.1)$$

If we were to apply also the energy equation (not done here for simplicity), we would find that at the end of the combustion process, starting from point A, we can only end up on a point on the red curve, known as Hugoniot curve. Moreover, by looking at Eq. (1.1) we see that for a positive jump in specific volume, we can only have a negative jump of pressure and vice-versa (the term \dot{m}^2/A^2 is always positive). Therefore, there are directions in which we cannot move (the two regions in grey in the figure). Also, we can only move on straight lines, because if we differentiate Eq. (1.1) we obtain:

$$\frac{dp}{dv} = -\frac{\dot{m}^2}{A^2} = \text{const}$$

i.e. the slope of the curve from A to any point Y is constant. Now, if we move in the upper-left direction, we have a detonation, characterised by a strong jump in pressure and a milder jump in density. Therefore we could in first approximation assume that this process is isochoric. If we move from point A in the bottom-right direction, we have instead a deflagration, characterised by a strong jump in density. Moreover, only states between points C and E, named *weak deflagrations*, manifest in nature. The jump in pressure in this case is only of the order of 10 to 100 Pa (atmospheric pressure is 101325 Pa) and is therefore negligible in first approximation. Deflagrations can therefore be approximated as isobaric processes. This is a key point from an engineering point of view as will be seen in Section 3.

Incompressible and low-Mach flows

Deflagrations are characterised by low propagation speeds (order of cm/s to few m/s). One can then imagine that the Mach number in the corresponding flow is also relatively low, and in fact it is in general below 0.3 in modern gas turbines (except ramjets and scramjets). One can thus imagine to approximate the flow as incompressible. Nevertheless, even in the limit of $Ma \rightarrow 0$, the heat release from the combustion implies that density varies through the flame (the flow expands). So, is the flow incompressible or not at $Ma \rightarrow 0$ in a combusting flow? The answer is yes. This is because incompressibility means only that the density will not vary *as result of the pressure forces*, which compress the element of fluid. Density, in fact, does not vary because of pressure, but because of the thermal expansion of the flow (the temperature increases and pressure is almost constant, so the density decreases).

2. Review of thermodynamics

Let's revise the fundamental laws of thermodynamics and introduce the important elements that will be needed for investigating combustion phenomena and reacting flows later on. The first thing to do is to define a set of variables that we can use to build up relations for a system. For a general flow we usually define [in SI units]:

ρ	density [kg/m ³]
u_i	velocity (three components for each direction i) [m/s]
p	pressure [Pa or N/m ²]
T	temperature [K]
E	specific energy [m ² /s ² or J/kg]

These quantities are interpreted here in an Eulerian sense, meaning that they represent the condition of the fluid in a particular point in space. The thermodynamic quantities are related to each other by thermodynamic relations, and a minimum of two has to be chosen to characterise a problem. For example, in addition to the velocity, one can choose pressure and energy, while density and temperature can be found once the thermodynamic model (e.g. perfect gas) is known. The choice of the particular energy (enthalpy, internal energy, kinetic energy, etc.) is a matter of convenience and will become more obvious later on. What is needed at this point is some variable to track the different species. There are three possibilities:

$$\begin{aligned} Y_k &= \frac{\text{mass of species } k}{\text{total mass}} && \text{mass fraction} \\ X_k &= \frac{\text{moles of species } k}{\text{total moles}} = \frac{W}{W_k} Y_k && \text{mole fraction} \\ [X_k] &= \frac{\text{moles of species } k}{\text{volume}} = \rho \frac{Y_k}{W_k} && \text{molar concentration} \end{aligned}$$

where W_k is the molar mass of species k and W is the molar mass of the fluid defined as

$$\frac{1}{W} \equiv \sum_{k=1}^N \frac{Y_k}{W_k} \quad (2.1)$$

The reason of this definition will become clearer later. The three possibilities above are related between each other and whether to use one or another is a matter of convenience. In engineering problems mass and mole fractions are preferred due to mass conservation principles, while in chemistry concentrations are usually preferred.

We need now to make some assumption before we can establish relations among our variables. Let's take density for example. We want that density is a function of space and time, $\rho = \rho(\mathbf{x}, t)$; however, at the size of molecules this quantity would be discontinuous as one passes from one molecule to intermolecular space, and defining derivatives at these conditions is not possible. To treat a macroscopic system, we then assume **continuum**: the smallest element in our domain is assumed to be infinitely smaller than any size of interest (including for example small vortices), but still much larger than the size of molecules. We refer to this here as a particle of fluid, and as consequence each particle contains a large number of molecules. There

is of course the effect of the molecular movement we need to take into consideration, which is done in a statistical way by associating the particle of fluid to specific properties: viscosity, diffusion constants and temperature. These in fact are a measure of the effect of molecular movements, forces and collisions. At this point our variables defined earlier and their derivatives are always well defined at any location in space and time.

Next, we need a thermodynamic model. As we will only treat gases, we are going to use the **perfect gas** model. This model works well up about 5000 K, which is well above the temperature range of interest for aeronautical purposes. For rocket engines and oxyfuel combustion, temperature can get closer to this limit and one could instead argue whether the perfect gas assumption is valid. At this point, from the Dalton's law we know that the pressure p of the fluid within a certain volume of fluid is given by the sum of the partial pressures of all the N species present in the same vilume (at the same time):

$$p = \sum_{k=1}^N p_k \quad k = 1, 2, \dots, N \quad (2.2)$$

where the partial pressure of the single species, p_k , is the pressure that the species k would have if it were to occupy the entire volume. The single species has to obey the perfect gas law, therefore:

$$p_k = \rho_k \frac{R_0}{W_k} T \quad (2.3)$$

where R_0 is the universal gas constant and ρ_k is the partial density of species k defined as the ratio between the mass of species k in the volume and the volume itself, and it is easy to show that it is equal to:

$$\rho_k \equiv \frac{\text{mass of species } k}{\text{volume}} = \rho Y_k \quad (2.4)$$

By combining Eqs. (2.1) to (2.4) one gets an expression between temperature, density and pressure of a general mixture:

$$p = \sum_{k=1}^N p_k = R_0 T \sum_{k=1}^N \frac{\rho_k}{W_k} = \rho R_0 T \sum_{k=1}^N \frac{Y_k}{W_k} = \rho \frac{R_0}{W} T \quad (2.5)$$

This implies that we can use the same equation for perfect gas also in case of a mixture, as long as we define the molecular mass of the mixture as in Eq. (2.1).

We need now to define the work L . This is an important quantity in engineering because we aim to build a system that produce work so that we can exploit this work for any purpose. By definition, for a closed system (no exchange of mass) the infinitesimal increment of work is defined as:

$$\delta L = p dV \quad (2.6)$$

where V is the volume of our system (e.g. the cylinder in Fig. 2.1). Notice that a different symbol is used for the differential of V and L to distinguish the fact that the first is a function of state (its value only depends of the initial and final state and not on the particular transformation used to move from state to the other) and the second is not. This can be illustrated in the case of the moving piston in Fig. 2.1. Imagine we want to move from point 1

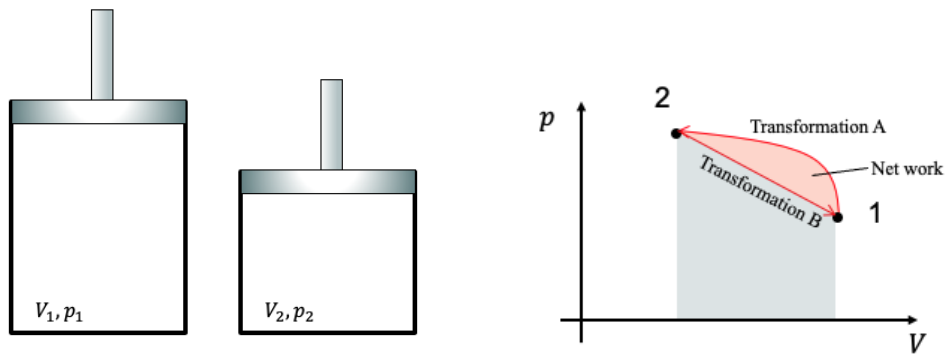


Figure 2.1. Representation of two states in a cylinder and two random transformations.

to point 2 in the $p - V$ diagram. To simplify the problem, we assume **quasi-static transformation**, i.e. the piston in the figure moves extremely slowly so that at each instant of time the new state is in equilibrium and there are no inhomogeneities in the fluid. In fact, if we were to compress fast, we would expect that convecting flows would appear in the piston and also conditions of pressure or other variables would not be the same at any point, making the problem more complicated. At quasi-static conditions, whatever way we compress, the final pressure or temperature would not be affected. However, the work done on the fluid, which is the area below the transformation curve in the $p - V$ diagram, would change depending on whether we compress in a way or another. This is of course of engineering relevance, because if we go back to state 1 with a different process than that used to move from 1 to 2, we have a net work done on or from the system. This is a direct consequence of the fact that L is not a state function. To be able to quantify the work in our quasi-static transformation at this point, we need to integrate Eq. (2.6), and to perform this integration the pressure relation $p = p(\rho, T)$ has to be known at any stage in the passage between state 1 to 2.

Exercise 1: Show that for an isotherm the work per unit mass between points 1 and 2 is given by $l_{12} = RT \ln (\rho_1/\rho_2)$. $R = R_0/W$ is the specific gas constant.

$$L = \int_{V_1}^{V_2} p dV =$$

First law of thermodynamics

We need to define at this point internal energy. The internal energy is the sum of all energies “packed” within the system (e.g. thorough the bonds of the molecules). The system can pack energy in different ways. Let’s consider again the piston of Fig. 2.1 and assume a quasi-static, adiabatic transformation: the system cannot exchange heat with the external environment. Then there must exist a function $U = U(\rho, T)$ such that

$$dU = -\delta L \quad (2.7)$$

What does this equation mean? The work we have applied to the system must have gone somewhere. Since the system is adiabatic, however, and the process is quasi-static, the only possibility is that the energy has been “packed” internally in the flow, in the way molecules are displaced for example or interact with each other. The variation of work done must then be equal to the variation of this function, which we define as internal energy. The negative sign comes from the convention used here that work is positive if done **by** the system. Since in the example of Fig. 2.1 work is done **on** the system, we need the negative sign, as internal energy is increasing (the system is packing energy). Now let’s remove the assumption of adiabaticity but fix the volume instead by blocking the movement of the piston (isochoric transformation). Instead, we provide heat to the system as shown in Fig. 2.2. As before, since the transformation is quasi-static (no convective effects possible and system always in thermodynamic equilibrium), the system must be packing the energy somehow, therefore with the same arguments we can say that internal energy is increasing and:

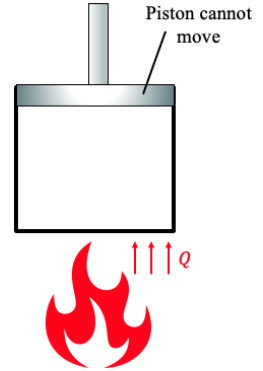


Figure 2.2. Isochoric transformation with heat addition

$$dU = \delta Q \quad (2.8)$$

note that in general the heat Q is not a state function, i.e. its variation depends on the process (an isochoric transformation in the current example). At this point we can remove the assumption of constant volume and combine Eqs. (2.7) and (2.8) for a general transformation, obtaining the first law of thermodynamic:

$$dU = \delta Q - \delta L \quad (2.9)$$

and remembering the expression (2.6) we write:

$$dU = \delta Q - p dV \quad (2.10)$$

It is interesting to notice that U is a function of state despite expression (2.9) indicates it is equal to a difference of two quantities which are not function of state. It can be demonstrated actually that, for a perfect gas, $U = f(T)$, i.e. the internal energy only depends on temperature (a general thermodynamic variable usually depends on two other thermodynamic variables).

Thermodynamic relations

To be able to build our thermodynamic relations, the last quantity we need to introduce is the heat capacity. Heat capacity is defined as the heat needed to increase the temperature in a system of 1 K:

$$C = \frac{\Delta Q}{T_2 - T_1}$$

Nevertheless, for the same heat variation ΔQ , the heat capacity would be different depending on the initial temperature of the system. In the limit of infinitesimal variation we can then write:

$$C = \frac{\delta Q}{dT} = C(T)$$

It is more convenient to work with intensive quantities, and therefore express the heat capacity either per unit of mass or per unit of moles. In the first case we define the specific heat capacity as:

$$c = \frac{1}{m} \frac{\delta Q}{dT} = \frac{\delta q}{dT} = c(T)$$

Since Q is not a function of state, the heat capacity as defined also is not a function of state. To be useful, we then define the heat capacity depending on the particular transformation. Most commonly we are interested in isobaric and isochoric transformation, for which we define:

$$\begin{aligned} c_p &= \left(\frac{\delta q}{dT} \right)_p && \text{heat capacity at constant pressure} \\ c_v &= \left(\frac{\delta q}{dT} \right)_v && \text{heat capacity at constant volume} \end{aligned} \quad (2.10)$$

Since the transformation is now univocally defined, the two quantities above only depend on the thermodynamic status at one point, i.e. they are function of state.

We can now build our relations. Let's use specific quantities (per unit mass), and use low-case letters to indicate them. The first law in Eq. (2.10) becomes:

$$du = \frac{1}{m} dU = \delta q - p dv \quad (2.11)$$

where $v = V/m = 1/\rho$ is the specific volume. We know that the internal energy is a function of state and thus, whatever transformation we consider between two states, its final value would not change. Therefore, we can assume the most convenient transformation to quantify it. If the process is isochoric in particular, the second term in the right-hand side of Eq. (2.11) vanishes. By combining this with the definition of c_v in Eq. (2.10) then we get:

$$(du)_v = (\delta q)_v = c_v dT \quad (2.12)$$

This expression is valid for a perfect gas **for any transformation** as u does not depend on volume. The use of an isochoric process was only convenient to us for finding its expression. Going back to a generic transformation, then we can write:

$$du = c_v dT = \delta q - p dv \Rightarrow \delta q = c_v dT + p dv \quad (2.13)$$

By differentiating the equation of state of perfect gases (for a single gas, so R is constant) we obtain

$$\begin{aligned} p &= \rho RT \Rightarrow pv = RT \\ p dv + v dp &= R dT \end{aligned} \quad (2.14)$$

$$p dv = R dT - v dp = R dT$$

Substituting into Eq. (2.13) one gets:

$$\delta q = c_v dT + R dT - v dp \quad (2.15)$$

Assuming now isobaric transformation, the last term in Eq. (2.15) vanishes, giving:

$$\delta q = (c_v + R) dT$$

and by dividing by dT (remembering we are at constant pressure):

$$\left(\frac{\delta q}{dT}\right)_p \equiv c_p = c_v + R \quad (2.16)$$

This expression is valid for any perfect gas. The actual variation of heat capacity with temperature is however not easy to find. In the strong assumption of constant heat capacity ($T \approx \text{const}$) and no vibrational modes (ok at ambient temperatures or below) the theoretical value of specific heat capacity at constant volume can be $c_v = 3R/2$ for a monoatomic gas and $c_v = 5R/2$ for a biatomic gas. For other cases the values have to be found experimentally. A graph is provided in Fig. 2.3, where the heat capacity at constant volume is shown per unit of moles rather than unit of mass. This graph helps to understand the meaning of heat capacity in

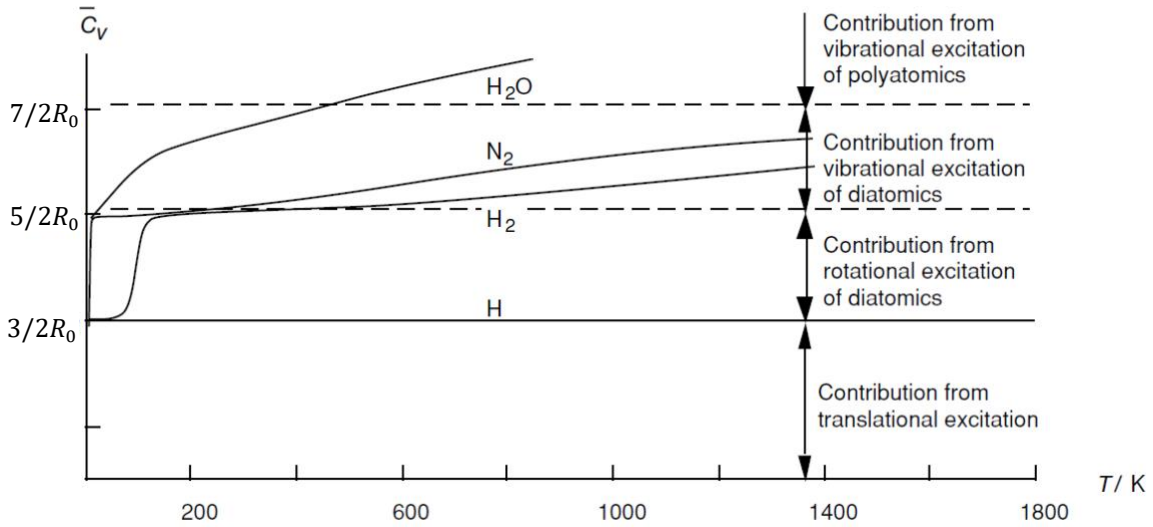


Figure 2.3. Temperature dependence of the molar heat capacity of various species.

in relation to how energy is packed into the system. In fact, from Eq. (2.12) we recall that, regardless of the actual transformation that our system is undergoing, the internal energy increase with temperature is proportional to the heat capacity at constant volume. In other words, the heat capacity at constant volume describes how internal energy varies with temperature and, recalling the definition of internal energy, how energy is packed in the system as temperature varies. At low temperatures, monoatomic species such as atomic hydrogen are stable and the measured value of $\bar{C}_v = Wc_v$ approaches the theoretical value $\bar{C}_v = 3R_0/2$ (equivalent to $c_v = 3R/2$). The only way energy can be packed in this case is in translational form, i.e. in the movement of the atom in space. As temperature is a measure of the (chaotic) translational motion of species, an increase of energy in form of heat directly corresponds to

an increase of temperature. As temperature increases, however, atomic hydrogen becomes unstable and recombines to form diatomic hydrogen. The energy packed into the system at this point goes only in part to the translational movement of the molecule, and in part also to its rotation, as shown in Fig. 2.3. Since only the first implies an increase of temperature, for the same heat δQ added to the system, temperature increases less as compared to the atomic species. Consistently, \bar{C}_v has to increase. As the temperature keeps increasing part of the energy is also used to excite the vibrational modes of the diatomic, therefore \bar{C}_v continues to increase, meaning that more and more heat is required to increase the temperature of the system of 1 K. Triatomic species have further modes of vibration that get excited at even larger temperatures. In respect to diatomic species, the various modes of vibration get excited at lower temperatures, implying that \bar{C}_v increases faster for triatomic as compared to diatomic and atomic species.

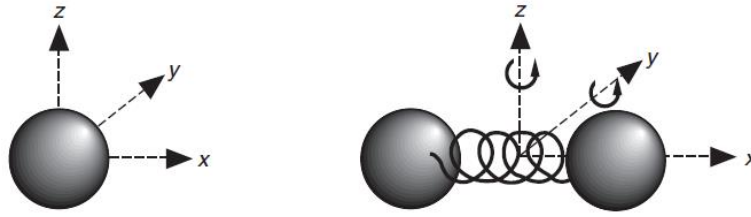


Figure 2.4. Translation of a monoatomic species (left); translation, rotation and vibration of a diatomic species (right).

To complete the picture, we need now to introduce the concept on **enthalpy**. We define the enthalpy of a system as the sum:

$$H \equiv U + pV \quad (2.17)$$

As all quantities on the RHS of Eq. (2.17) are functions of state, enthalpy is a function of state too, so its final value after a transformation from a state 1 to a state 2 does not depend on the type of transformation. But why are we interested in this quantity? Similarly to what we did for internal energy, let's differentiate Eq. (2.17). Expressing the quantities per unit mass then:

$$dh = du + p dv + v dp \quad (2.18)$$

From Eq. (2.11) $du = \delta q - p dv$ (first law of thermodynamic). Substituting in the above:

$$dh = \delta q - p dv + p dv + v dp \quad (2.19)$$

If we have now an isobaric process, the last term in Eq. (2.18) vanishes and we have $dh = \delta q$. This means that variation of heat at isobaric conditions correspond to variation of enthalpy, thus we can use the latter to quantify the heat in the system. Recalling also the definition of heat capacity at constant pressure (Eq. 2.10) we have:

$$c_p = \left(\frac{\delta q}{dT} \right)_p = \left(\frac{dh}{dT} \right)_p \Rightarrow dh = c_p dT \quad (2.20)$$

We have thus found two ways to express the heat variation in a system, respectively Eq. (2.13):

$$\begin{aligned}\delta q &= c_v dT + p dv & \text{and (combine Eqs. 2.19 and 2.20)} \\ \delta q &= c_p dT - v dp\end{aligned}\tag{2.21}$$

The two expressions are equivalent and valid for perfect gases. However, the second term on the RHS vanishes respectively for isochoric ($dv = 0$) and isobaric ($dp = 0$) processes, thus depending on the type of process it is more convenient to use one or the other.

Second law of thermodynamics

To explain the second law of thermodynamic let's first define entropy: it is the measure of the “disorder” of the system, or in more rigorous terms the number of all possible combination of microstates (disposition of molecules, orientation, etc.) for a fixed macrostate (same pressure, volume, temperature, etc) of a system. Now, let's suppose we want to extract energy from a system in the form of work, by adding heat, and let's suppose the process is isothermal.

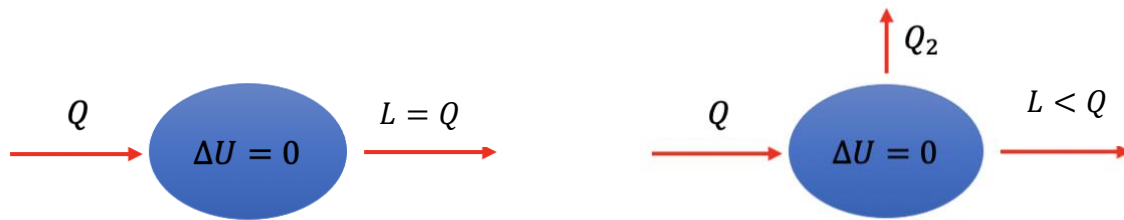


Figure 2.5. Two isothermal systems. The one on the left violates the second law.

Since the internal energy only depends on temperature in perfect gases, an isothermal system implies that $\Delta U = 0$. From the first law of thermodynamics there is nothing wrong in assuming that all of the heat is converted into work. However, this situation is not possible as it would violate the second law of thermodynamics, which studies transformations of heat into work and tells us that the entropy of the system plus the surrounding must increase in this case. The issue is that some transformation is not reversible. There must be then part of the energy that the system has to release to the surrounding in the form of heat. Not having this would be equivalent to having perpetual motion, which is impossible in nature at least for scales larger than the microscale. Clasius further found that, for a reversible process (indicated by the superscript ‘R’):

$$\oint \frac{\delta Q^R}{T} = 0$$

This is an important result because we know that heat is not a function of state, therefore its integral in a cycle is not zero in general. However, if the process is reversible, the variation of heat divided by temperature is a state function. It follows that the integral between two states 1 and 2 does not depend on the type of transformation, i.e.

$$\int_1^2 \frac{\delta Q^R}{T} = S_2 - S_1\tag{2.22}$$

and S is exactly the entropy of the system. By differentiating Eq. (2.22) one obtains, using quantities per unit of mass

$$\delta q = T ds \quad (2.23)$$

By replacing the above in the first law of thermodynamics, one obtains the Gibbs relation:

$$du = T ds - p dv \quad (2.24)$$

Gibbs further demonstrated that this equation is also valid when the process is irreversible, although the derivation is not shown here.

3. Thermodynamics of combustion

In this section we are going to see how to use thermodynamics to predict the behaviour of a combustion process. What is important to know from an engineering point of view is

- a) what the maximum temperature at the end of the combustion process is, so that we can predict the thermal stresses on the combustor walls and estimate the amount of cooling we need in both combustor and turbine stages;
- b) how much of the energy yielded by the combustion process can be exploited to produce work;
- c) the level of emissions at the end of the combustion process. Let's recall from Section 1 that the amount of intermediate species is strictly related to the combustion efficiency;
- d) how all of the above are affected by operative conditions such as initial temperature of the reactants, pressure, air-to-fuel ratio, etc.

One may believe that to answer all these questions it is unavoidable to explore in detail the chemical reactions occurring in the combustion process. Nevertheless, at many conditions the properties above are well approximated by simple thermodynamics relations. We are going to explore these here and understand their limitations. There are three levels of approximation we can make:

1. **Complete combustion and one-step chemistry.** We assume that fuel and oxidiser instantaneously react to form the main products (CO_2 and H_2O for hydrocarbons) and use only thermodynamic relations to figure out final temperature and how it is affected by operative conditions. The combustion efficiency is always 1 in this case and we cannot predict any minor species.
2. **Equilibrium combustion.** In this case we include a little bit more of chemistry by considering as many reactions as we want, but will assume that all them are at equilibrium, which implies that we can still work out final temperature only using thermodynamic relations. The combustion efficiency in this case is the maximum possible, but it is less than 1 as we will never reach complete combustion (although we can get very close for some conditions). We also can predict minor species. The limitation is that we still consider the reactions infinitely fast, so we do not take into account the time needed to reach equilibrium.
3. **Chemical kinetics.** We are now interested in the combustion time scales (for example because in our combustor the resident time of the reactants is comparable to the combustion scales). To figure out the combustion time scales we need to work out the reaction rates of the single reactions. The level of complexity lies, for a generic fuel, in being able to find the correct reactions and associated reaction rates.

For all of the approximations above we are going to consider a zero-dimensional system, i.e. we will always consider that our reactor is perfectly homogeneous at any reaction stage. This way we do not have to study (yet) how transport processes and convective forces affect the combustion process.

Let's sum up the key results from the thermodynamics overview of Section 2. We found two interesting processes, isochoric and isobaric, and in these specific cases the first law of thermodynamics can be written as:

$$\begin{aligned} du &= \delta q = c_v dT & (\text{constant volume}) \\ dh &= \delta Q = c_p dT & (\text{constant pressure}) \end{aligned} \quad (3.1)$$

These tells that if the process is isochoric (constant volume), the change of heat we have in a system can be quantified by the change of internal energy; and if it is isobaric, the change of heat can be quantified by a change of enthalpy. Both internal energy and enthalpy are state functions, so to quantify these changes we only need to know initial and final status. This is what ultimately allow us to obtain information on the combustion process without having to explore the chemical kinetics! Among the two processes above, however, the isobaric is of particular engineering interest for the following reason. Recalling the definition of enthalpy, from Eq. (2.18), in the case of isobaric process ($dp = 0$) we have:

$$\delta q = dh = du + p dv + \cancel{v dp}$$

So in an isobaric process the variation of enthalpy equals the variation of internal energy plus the term $p dv$. The latter is exactly the infinitesimal work (per unit mass), so this equation is telling us that, if the process is isobaric, unlike the isochoric case the heat is not only used to increase the internal energy of the system (i.e. is packed in the system at molecular level), but also to produce work. We have thus a chance to exploit this work for engineering applications! Whether or not, and how efficiently, we can exploit this work is another thing, and will be discussed later. The question at this point is: is there a process that is nearly isobaric? Yes there is, the **deflagration**, which is indeed a flame condition exploited in most of the combustion devices we use nowadays. The other flame condition is the detonation (sometimes also referred in more general terms as pressure-gain combustion), which occurs instead at almost isochoric conditions and, for the reasons above (only internal energy changes in isochoric processes), does not yield any work (or much less than for the isobaric case if not perfectly isochoric). Note that this does not imply that we cannot use the isochoric combustion within a cycle to extract work, but only that there is no work associated to the combustion process. In the [Humprey cycle](#) for example, which is representative of a pulse or rotating detonation engine (RDE), work can still be extracted by the expansion of the gas (by some turbomachinery for example) after the detonation process; but as one can expect the overall thermal efficiency is quite lower than with a Bryton cycle, where work also can be extracted by the deflagration process itself.

Now that we know the thermodynamic relations and have identified two engineering-relevant processes, we need to be able to quantify enthalpy (if isobaric process) and internal energy (if isochoric process). By integrating Eqs. (3.1) we get:

$$\begin{aligned} h &= h_{\text{int}} + \int_{T_0}^T c_p(T') dT' & (\text{isobaric}) & \quad \text{and} \\ u &= u_{\text{int}} + \int_{T_0}^T c_v(T') dT' & (\text{isochoric}) \end{aligned} \quad (3.2)$$

The values h_0 and u_0 are integration constants and we need some condition to find them. There is however no theoretical condition we can impose; therefore, we need to find the values experimentally. To do that, we need to first choose a convenient temperature T_0 . It is not convenient to set $T_0 = 0$ K (absolute zero) as performing any experiment at very low temperature would be hard. Instead, it is commonly accepted to use $T_0 = 298.15$ K. In this case the integration constant can be written as:

$$h_{\text{int}} = h_{T_0=0} + \int_{T=0\text{K}}^{T_0} c_p(T') dT' \quad (3.3)$$

As we can notice, we still have not resolved the issue, since we do not know what is the value of enthalpy at 0 K, $h_{T_0=0}$ and as said, it would be almost impossible to have a measure at that temperature. However, we can recognise that all we are really interested in the combustion process is how much heat we have added to the system. For this purpose, let's define the heat of reaction ΔQ_R :

The heat of reaction is the amount of heat that must be added or removed during a chemical reaction in order to keep all of the substances present at the same temperature. This is quantified by the jump in enthalpy in isobaric processes (jump in internal energy in isochoric processes). We will understand why the temperature has to be kept the same in this definition later.

With this in mind, we rewrite Eq. (3.3) as

$$h_{\text{int}} = h_{T_0=0} + \int_{T=0\text{K}}^{T_0} c_p(T') dT' = h_{\text{ref}} + \Delta h_f^0 \quad (3.4)$$

where h_{ref} is a reference state of our own choice and Δh_f^0 is the deviation from that state. In physical terms, we set without loss of generalities $h_{\text{ref}} = 0$ (as said, it does not matter as we are only interested in differences of enthalpies) and measure the deviation Δh_f^0 from a reference state. By convention this state, for any species k , is the state at which the constituent elements of that species in their most pure form at standard conditions (1 bar and 298.15 K). The variable Δh_f^0 is called standard enthalpy of formation (or heat of formation) and, from an engineering point of view can be defined as follows:

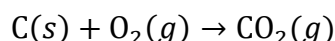
The enthalpy of formation of a compound is the change of enthalpy during the formation of 1 kg (if per unit mass) or 1 mole (if per unit of moles) of the substance from its constituent elements, with all substances in their standard states.

Eq. (3.2) can now be written as:

$$h = \Delta h_f^0 + \int_{298.15\text{ K}}^T c_p(T') dT' \quad (\text{isobaric}) \quad (3.5)$$

where the second term on the RHS is the sensible enthalpy of the gas and its sum to the enthalpy of formation is referred to as absolute enthalpy.

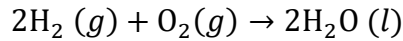
Let's give an example of enthalpy of formation. For the carbon dioxide (CO_2), the enthalpy of formation is the change of enthalpy during the following reaction:



This chemical equation shows how CO_2 , which is gaseous at standard conditions, is formed from graphite, which is solid at standard conditions, and oxygen, which is gaseous at standard conditions. Note that atomic oxygen is not stable at standard conditions, therefore it is molecular oxygen that has to be considered as elementary constituent. The enthalpy of

formation of the elementary constituents of any species is then always zero. Therefore, any diatomic gas which is stable at standard condition, has enthalpy of formation zero.

Let's see now the case of water:



Now, water is liquid at standard conditions. However, at the end of the combustion process we know that water will be in vapour form due to the high temperatures. Since the process of condensation is exothermic (by condensing, the water releases heat), in gaseous form there is still some heat that has not been released yet to the system (latent heat of vaporisation). Since in a combustion chamber there will be no time to wait for the condensation process, we are interested in quantify the heat of reaction with products in gaseous form. Therefore, we distinguish the heat of reaction between **high heating value** (HHV) and **low heating value** (LHV). The first is the heat of the process including the latent heat of vaporisation; the second does not include the latent heat and is therefore smaller than the HHV. But how do we compute the LHV for a generic reaction?

As first idea, we could think to directly compute the difference between the enthalpy of the products and the enthalpy of the reactants. To do this, we need to define the enthalpy of the gas mixture (Eq. 3.5 is valid in fact for a single species). The enthalpy of the mixture (per unit mass) is the sum of the enthalpies of the single species times their mass fraction:

$$h_{\text{mix}} \equiv \sum_{k=1}^N Y_k h_k = \sum_{k=1}^N Y_k \Delta h_{f,k}^0 + \int_{298}^T c_{p,\text{mix}}(T') dT' = \Delta h_{f,\text{mix}}^0 + \int_{298}^T c_{p,\text{mix}}(T') dT' \quad (3.6)$$

where we have defined the enthalpy of formation of the mixture and the heat capacity at constant pressure of the mixture as:

$$\Delta h_{f,\text{mix}}^0 = \sum_{k=1}^N Y_k \Delta h_{f,k}^0 \quad \text{and}$$

$$c_{p,\text{mix}} = \sum_{k=1}^N Y_k c_{p,k}$$

Note that, equivalently, we could define the enthalpy, enthalpy of formation and heat capacity of the mixture per unit of moles by substituting the mole fractions X_k to the mass fractions Y_k . At this point we could compute the jump of the mixture enthalpy between products and reactants as said. There is however an issue. If we were to differentiate Eq. (3.6), in fact, we would not obtain back the form of Eq. (3.1) for a combustion process, because the differential of the enthalpy of formation of the mixture would not be zero, since species mass fractions are changing. From a physical point of view, the issue is in the fact that variation of enthalpy represents in isobaric processes the heat **exchanged** with the external environment. Imaging an adiabatic system for simplicity, by energy conservation the enthalpy has to remain constant, so $\Delta H = 0$, which is true also in presence of chemical reactions. In other words, we cannot say that the variation of heat corresponds to the variation of absolute enthalpy **of the mixture**. To quantify the heat of reaction, we have thus to pretend to exchange this heat with the external environment, which is equivalent to decreasing the temperature of the products back to that of the reactants in an exothermic process. This is allowed because the algebraic sum of the heat evolved in separate stages is equal to the total amount of heat released when the reaction occurs directly (Hess' law), which in turn is a consequence of the fact that enthalpy is a state function.

This is also why we had to define the heat of reaction with a reduction of heat from the system by keeping the temperature constant. Using extensive quantities, the heat of reaction ΔQ_R for an isobaric process is thus:

$$(\Delta Q_R)_p = \Delta H_R = \Delta H_{f,\text{prod}}^0 + \int_{298.15\text{ K}}^{T_{\text{reac}}} C_{p,\text{prod}}(T')dT' - \Delta H_{f,\text{reac}}^0 - \int_{298.15\text{ K}}^{T_{\text{reac}}} C_{p,\text{reac}}(T')dT'$$

Note that in both integrals the upper extreme of integration is the reactant temperature. We can therefore put the above equation in more compact form as:

$$\begin{aligned} (\Delta Q_R)_p = \Delta H_R &= (\Delta H_{f,\text{prod}}^0 - \Delta H_{f,\text{reac}}^0) + \int_{298.15\text{ K}}^{T_{\text{reac}}} \Delta C_p(T')dT' \\ &= \Delta H_R^0 + \int_{298.15\text{ K}}^{T_{\text{reac}}} \Delta C_p(T')dT' \end{aligned} \quad (3.7)$$

In order to quantify the enthalpy of reaction univocally, we need to define a condition. Usually in tables standard conditions are used (1 bar and 298.15 K). In this case the last term in Eq. (3.7) vanishes and the heat of reaction can be computed from the standard enthalpies of formation of reactants and products. If the reactants are at higher (or lower) temperature than standard conditions, the heat of reaction will increase or decrease depending on the differences of heat capacity (Kirkhoff's law). This term signifies that energy is packed in the system differently at different temperatures and by different gases, and this affects the release of heat. Nevertheless, the last term in Eq. (3.7) between reactants and products is usually small and often neglected.

Eq. (3.7) is a great result as we can compute the heat of reaction from standard enthalpies of formation in an isobaric process, rather than having to define an experiment for any possible condition of temperature and pressure. Note that the enthalpy of formation of the products are lower than those of the reactants in exothermic reactions, signifying that heat has been liberated.

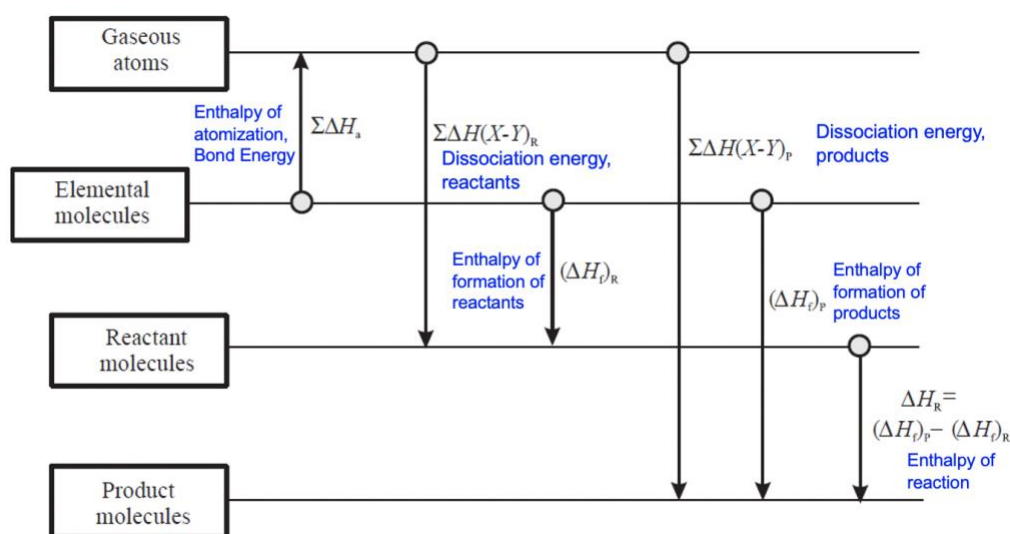


Figure 3.1. Relationships between enthalpy of formation and enthalpy of reaction. By Hess' law, the difference between enthalpy of formation of products and reactants is equal to the heat of reaction.

Similarly to what done for the enthalpy, one could define internal energies of formation for an isochoric process. Entropies are also standardised in tables as they are useful for equilibrium calculations as will be shown later. For a reversible process, the entropy variation is (Eq. 2.22):

$$ds = \frac{c_p}{T} dT \quad (\text{isobaric process}); \text{ and}$$

$$ds = \frac{c_v}{T} dT \quad (\text{isochoric process})$$

By integrating we obtain:

$$s = s_{298K}^0 + \int_{298K}^T \frac{c_p}{T'} dT' \quad (\text{isobaric})$$

$$s = s_{298K}^0 + \int_{298K}^T \frac{c_v}{T'} dT' \quad (\text{isochoric}) \quad (3.8)$$

Differently from the case of enthalpy and internal energy, we now know a condition for the entropy: it is zero at 0 K. Nevertheless, for consistency with the previous treatment, it is preferred to use the value of entropy at 298 K (and 1 bar). Standard entropies are found via experiments as for the standard enthalpies of formation, using for example a bomb calorimeter.

Exercise 2: In Fig. 3.2. some of the most common fuels used in combustion are shown. What do you notice?

Fuel	Chemical Formula	Molecular Weight (m_w) (integrals)	Enthalpy of Formation, Δh_f (kJ/kmol)	Higher Enthalpy of Reaction, Δh_R (MJ/kmol)	Lower Enthalpy of Reaction, Δh_R		Stoichiometric Air–Fuel Ratio, ϵ_{st}
					(kJ/kg)	(MJ/kmol)	
<i>Alkanes</i>	$C_n H_{2n+2}$						
Methane	CH ₄	16	−74,898	−891	−50,047	−802.9	17.16
Ethane	C ₂ H ₆	30	−84,724	−1561	−47,519	−1428.8	16.02
Propane	C ₃ H ₈	44	−103,916	−2221	−46,387	−2045.4	15.60
Butane	C ₄ H ₁₀	58	−124,817	−2880	−45,771	−2660.2	15.38
Pentane	C ₅ H ₁₂	72	−146,538	−3538	−45,384	−3274.3	15.25
Hexane	C ₆ H ₁₄	86	−167,305	−4197	−45,134	−3889.3	15.16
Heptane	C ₇ H ₁₆	100	−187,946	−4856	−44,955	−4504.4	15.10
Octane	C ₈ H ₁₈	114	−208,586	−5515	−44,820	−5119.5	15.05
Cetane	C ₁₆ H ₃₄	226	−455,5	−10,711	−44,000	−9963.4	14.88
<i>Aromatics</i>							
Benzene	C ₆ H ₆	78	+82,982	−3304	−40,605	−3172	13.20
Toluene	C ₇ H ₈	92	+50,032	−3950	−40,967	−3774	13.43
Xylene	C ₈ H ₁₀	106	+18,059	−4598	−41,276	−4378	13.60
Naphthalene	C ₁₀ H ₈	128	+150,934	−5233	−39,455	−5057	12.87
<i>Alcohols</i>	$C_n H_{2n+1} OH$	$C_n H_{2n+2} O$					
Methanol	CH ₃ OH	32	−201,301	−764	−21,114	−676	6.44
Ethanol	C ₂ H ₅ OH	46	−235,466	−1410	−27,742	−1278	8.85
Propanol	C ₃ H ₇ OH	60	−235,107	−2069	−31,504	−1893	10.30

Figure 3.2. Common fuels in combustion and their properties

Adiabatic flame temperature & equivalence ratio

The adiabatic flame temperature T_{ad} is the temperature of the combustion products when no heat losses occur during the combustion process, or equivalently when the combustion process is adiabatic. This is a very important quantity for engineering applications as we need an estimation of the highest temperatures in the combustor to properly size it. In order to find the adiabatic flame temperature, the most obvious thing to do is to use the conservation equations. In energetic terms, from the 1st law of thermodynamics we know that for an adiabatic system the heat exchanged with the surrounding is zero, thus:

$$du = \delta q - p dv = -p dv$$

By recalling the definition of enthalpy, $h = u + pv$, and differentiating, then:

$$dh = du + p dv + v dp$$

If we further assume the process is isobaric ($dp = 0$), combining the two equations above, we obtain:

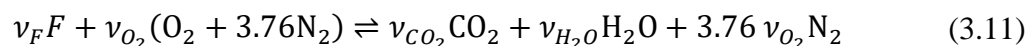
$$dh = -p dv + p dv = 0 \quad (3.9)$$

which tells that absolute enthalpy does not change during the combustion process at isobaric and adiabatic conditions. Note that if the mixture stays homogeneous through the reaction, the absolute enthalpy remains constant at any reaction progress – it can change otherwise, as for example in the case of differential diffusion (e.g. one species diffuses faster than the others). By integrating Eq. (3.9) between reactants and products, and recalling Eq. (3.5), we obtain:

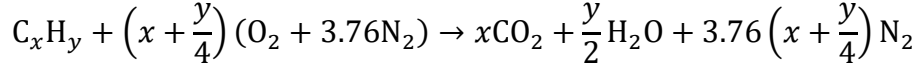
$$\Delta h_{f,prod}^0 + \int_{298\text{ K}}^{T_{prod}} c_{p,prod}(T')dT' = \Delta h_{f,react}^0 + \int_{298\text{ K}}^{T_{react}} c_{p,react}(T')dT' \quad (3.10)$$

If the combustion is adiabatic, $T_{prod} = T_{ad}$, and we need to solve Eq. (3.10) iteratively to find the value of temperature in the products. We know that the standard enthalpy of formation of any species can be found in tables. The functional form of the heat capacity with temperature for any species can be found using the [JANNAF](#) polynomials, which are 6th order polynomial fits to values found experimentally. However, to find enthalpies and heat capacity of the product mixture (the reactants composition is given), we need to know mass or mole fractions at the final state. These in turn depend on pressure, temperature and composition of the reactants, thus we need further conditions.

Let's assume a homogeneous mixture (no transport processes involved). For a generic hydrocarbon fuel, the chemical equation at stoichiometry is:



where ν_{O_2} and ν_F are the stoichiometric coefficients. Nitrogen was considered inert for simplicity. For a hydrocarbon fuel the balanced equation at stoichiometry can be written, in case of complete combustion, as:



This expression includes hydrogen fuel (carbon number $x = 0$) but not alcohols, due to the presence of oxygen in the fuel in the latter case. The 3.76 in front of the nitrogen molecule is due to the fact that oxygen and nitrogen have a ratio in volume of $N_2/O_2 \approx 79/21 (\approx 3.76)$ in air. Therefore, if we assume complete combustion and the reaction is stoichiometric, we can find the composition of the products easily. The mass fraction of species k in the products (for example H_2O), is:

$$Y_k = X_k \frac{W_k}{W}$$

where the mole fraction $X_k = (X_k)_{st}$ can be easily found at stoichiometry as:

$$(X_k)_{st} = \frac{v_k}{\sum_k v_k} = \frac{v_k}{v_{H_2O} + v_{CO_2} + 3.76v_{O_2}}$$

And the molecular mass of the products mixture is

$$W = \left(\sum_k \frac{Y_k}{W_k} \right)^{-1} = \sum_k X_k W_k \quad (3.12)$$

If the combustion is not complete, or not in stoichiometric proportions, the mole fraction of the product species X_k has to be found from the actual coefficients n_k , which are unknown:

$$X_k = \frac{n_k}{\sum_k n_k} \quad (3.13)$$

where $n_k = v_k$ only at stoichiometric condition in our notation. Let's discuss for now the case where the air-to-fuel ratio is not in stoichiometric proportions. In this case we have an excess of fuel (rich mixture) or air (lean mixture) which does not react. However, the excess fuel or air absorbs heat, implying not only that temperature in the system is reduced, but also that the reactions themselves may be affected, as they are progressing at lower temperatures than in the stoichiometric case. Consequently, the final composition is also affected. In order to distinguish between various conditions, instead of the fuel-to-air ratio $FAR = \dot{m}_{fuel}/\dot{m}_{air}$, it is more convenient to introduce the **equivalence ratio** ϕ , defined as the ratio between fuel and oxidiser mass, divided by the same ratio at stoichiometric conditions:

$$\phi \equiv \frac{Y_F/Y_{Ox}}{(Y_F/Y_{Ox})_{st}} = \frac{X_F/X_{Ox}}{(X_F/X_{Ox})_{st}} = \frac{\dot{m}_F/\dot{m}_{Ox}}{(\dot{m}_F/\dot{m}_{Ox})_{st}} \quad (3.14)$$

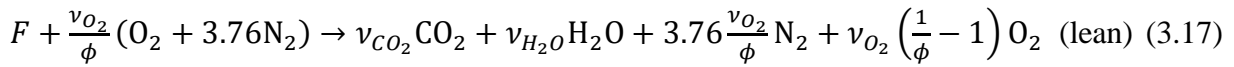
Note that in presence of convective fluxes, the equivalence ratio could also be expressed in terms of mass flow rates. With the given definition, when $\phi < 1$ the combustion is lean (excess of oxidiser), and when $\phi > 1$ the combustion is rich (excess of fuel). By introducing the stoichiometric mass ratio:

$$s = \left(\frac{Y_{Ox}}{Y_F} \right)_{st} = \frac{\nu_{Ox} W_{Ox}}{\nu_F W_F} \quad (3.15)$$

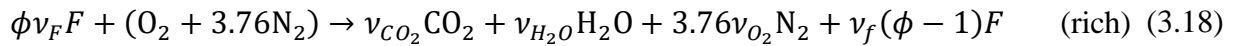
Eq. (3.14) can be further expressed as

$$\phi = s \frac{Y_F}{Y_{Ox}} = \frac{\nu_{Ox}}{\nu_F} \frac{X_F}{X_{Ox}} = \frac{\nu_{Ox}}{\nu_F} \frac{n_F}{n_{Ox}} \quad (3.16)$$

Eq. (3.16) tells us how to balance the generic equation (3.11) at any equivalence ratio. For example, assuming to burn 1 mole of fuel at lean conditions, then from Eq. (3.11) $\nu_F = n_F = 1$, thus from Eq. (3.16) $n_F = \nu_{Ox}/\phi$. Eq. (3.11) then becomes (assume complete combustion and inert nitrogen to balance the products for now):



Similarly for rich conditions, to burn 1 mole of oxidiser (which is now the limiting factor) we have $\nu_{Ox} = n_{Ox} = 1$ and $n_F = \phi \nu_F$. Eq. (3.11) becomes:



The mole fractions in the products can thus be found at this point using Eq. (3.13).

Exercise 3. Find that the mass fraction of the fuel at a given equivalence ratio is:

$$Y_F = \frac{1}{1+s/\phi} \quad \text{for oxyfuel combustion (no nitrogen); and} \quad (3.19)$$

$$Y_F = \frac{1}{1+\frac{s}{\phi} \left(1+3.76 \frac{W_{O_2}}{W_{N_2}} \right)} \quad \text{for fuel/air combustion} \quad (3.20)$$

Hint: By conservation of mass, $\sum_k X_k = \sum_k Y_k = 1$. This applies at any reaction stage. Remember also that $X_{N_2} = 3.76 X_{O_2}$ independently of ϕ .

3.1. Complete combustion

As hinted already in the previous section, we can work out combustion products temperature and composition relatively easily at any equivalence ratio in case of complete combustion. Let's then use this assumption for the time being, to understand how accurately we can predict the combustion properties. First of all, let's find an expression for the adiabatic flame temperature. To sum up, we are assuming:

- Infinitely fast reactions (reactants are converted into products instantaneously);
- Isobaric and adiabatic process;
- Complete combustion (the reaction is irreversible);

- 1-step chemistry (intermediate species are not taken into account. This is a direct consequence of complete combustion).

Regardless of the equivalence ratio, we can recognise that an additional mole of fuel added to the reaction, assuming there is enough oxygen, must yield an increased amount of products **in stoichiometric proportions**. In other words, while the number of moles of fuel and oxygen are, for $\phi \neq 1$, not in stoichiometric proportions, i.e. $n_{Ox}/n_F \neq \nu_{Ox}/\nu_F$, their variation Δn_k must be. Therefore, we can write:

$$\frac{\Delta n_F}{\Delta \nu_F} = \frac{\Delta n_k}{\Delta \nu_k} \Rightarrow \frac{\Delta Y_F}{W_F \Delta \nu_F} = \frac{\Delta Y_k}{W_k \Delta \nu_k} \quad (\text{lean combustion}) \quad (3.21)$$

and

$$\frac{\Delta n_{Ox}}{\Delta \nu_{Ox}} = \frac{\Delta n_k}{\Delta \nu_k} \Rightarrow \frac{\Delta Y_{Ox}}{W_{Ox} \Delta \nu_{Ox}} = \frac{\Delta Y_k}{W_k \nu_k} \quad (\text{rich combustion}) \quad (3.22)$$

where $\Delta \nu_k$ is the net stoichiometric coefficient of species k (difference of products and reactants). The reason we distinguish between lean and rich combustion is due to the fact that oxygen or the fuel may be limiting the reaction in one or the other case. Also, this way $\Delta \nu_k$ always equals $\pm \nu_k$ and the sign is positive if k is a product, and negative if it is a reactant. From Eq. (3.10) we have:

$$\sum_k^{\text{prod}} Y_k \Delta h_{f,k}^0 + \int_{298\text{ K}}^{T_{\text{prod}}} c_{p,\text{prod}}(T') dT' = \sum_k^{\text{reac}} Y_k \Delta h_{f,k}^0 + \int_{298\text{ K}}^{T_{\text{reac}}} c_{p,\text{reac}}(T') dT'$$

The above equation can be rearranged as (note the sum is now over all species):

$$\sum_k^N \Delta Y_k \Delta h_{f,k}^0 = - \int_{298\text{ K}}^{T_{\text{prod}}} c_{p,\text{prod}}(T') dT' + \int_{298\text{ K}}^{T_{\text{reac}}} c_{p,\text{reac}}(T') dT'$$

where $\Delta Y_k = (Y_{k,\text{prod}} - Y_{k,\text{reac}})$. For lean combustion, using Eq. (3.21) and noting that at lean conditions $\Delta Y_F = -Y_{F,\text{reac}} = -Y_F$ (no fuel left in the products), we obtain:

$$-\frac{Y_F}{\nu_F W_F} \sum_k^N \Delta \nu_k W_k \Delta h_{f,k}^0 = - \int_{298\text{ K}}^{T_{\text{prod}}} c_{p,\text{prod}}(T') dT' + \int_{298\text{ K}}^{T_{\text{reac}}} c_{p,\text{reac}}(T') dT'$$

For the way $\Delta \nu_k$ was defined, we can recognise that for each k , the term inside the sum operator is the standard enthalpy of formation per unit of moles ($W_k \Delta h_{f,k}^0$) times the number of moles at stoichiometric condition in the reactants or in the products. Recalling Eq. (3.7), this sum gives exactly the enthalpy of reaction at standard conditions ΔH_R^0 . By further multiplying by -1 the equation becomes:

$$\frac{Y_F \Delta H_R^0}{\nu_F W_F} = \int_{298\text{ K}}^{T_{\text{prod}}} c_{p,\text{prod}}(T') dT' - \int_{298\text{ K}}^{T_{\text{reac}}} c_{p,\text{reac}}(T') dT' \quad (3.23)$$

By repeating all the steps using Eq. (3.22) in place of Eq. (3.21), we obtain the analogous equation for rich combustion:

$$\frac{Y_{Ox}\Delta H_R^0}{\nu_{Ox}W_{Ox}} = \int_{298\text{ K}}^{T_{\text{prod}}} c_{p,\text{prod}}(T')dT' - \int_{298\text{ K}}^{T_{\text{reac}}} c_{p,\text{reac}}(T')dT' \quad (3.24)$$

We can further simplify the notation in the following way. Assuming that the heat capacity varies smoothly with the temperature (which is the case), we can define an temperature-averaged coefficient as:

$$\langle c_p \rangle = \frac{\int_{T_0}^T c_p(T')dT'}{T - T_0}$$

Substituting into Eq. (3.23) we obtain:

$$\frac{Y_F\Delta H_R^0}{\nu_F W_F} = \langle c_p \rangle_{\text{prod}}(T_{\text{ad}} - 298\text{ K}) - \langle c_p \rangle_{\text{reac}}(T_{\text{reac}} - 298\text{ K})$$

By rearranging for T_{ad} we finally obtain, for **lean** combustion:

$$T_{\text{ad}} = 298\text{ K} + \frac{Y_F\Delta H_R^0}{\nu_F W_F \langle c_p \rangle_{\text{prod}}} + \frac{\langle c_p \rangle_{\text{reac}}}{\langle c_p \rangle_{\text{prod}}}(T_{\text{reac}} - 298\text{ K}) \quad (3.25)$$

Similarly, for **rich** combustion:

$$T_{\text{ad}} = 298\text{ K} + \frac{Y_{Ox}\Delta H_R^0}{\nu_{Ox}W_{Ox} \langle c_p \rangle_{\text{prod}}} + \frac{\langle c_p \rangle_{\text{reac}}}{\langle c_p \rangle_{\text{prod}}}(T_{\text{reac}} - 298\text{ K}) \quad (3.26)$$

and of course the two equations needs to give the same value at $\phi = 1$. Note that the equations still have to be solved iteratively as the temperature-averaged heat coefficient in the products depends on the final temperature T_{ad} . However, we can more easily study this equation and make the following observations:

- The standard enthalpy of reaction is an extensive quantity, so it is proportional to the actual amount of fuel in the reaction. In tables this quantity is given usually either per mole of fuel ($\Delta H_R^0/\nu_F$) or per kilogram of fuel ($\Delta H_R^0/(\nu_F W_F)$);
- At lean conditions, as ϕ increases Y_F also increases, therefore the adiabatic temperature increases with ϕ . At rich conditions, as ϕ increases Y_{Ox} decreases, therefore the temperature decreases with ϕ . It follows that the adiabatic temperature is maximum at $\phi = 1$ in the assumption of complete combustion. This is not what is observed in experiments, where the peak is for ϕ slightly above unity (1.05 to 1.1). Moreover, near stoichiometry the adiabatic temperature for complete combustion overestimates the experimental observations, and this overestimation increases for oxyfuel combustion;
- When the temperature of the reactants is the standard temperature ($\approx 298\text{ K}$), the heat of reaction is equal to the standard heat of reaction and the last term on the RHS of

equations (3.25) and (3.26) vanishes. Since $\langle c_p \rangle_{\text{reac}} < \langle c_p \rangle_{\text{prod}}$ due to the significant difference in temperature between products and reactants, an increase in temperature in the reactants ΔT_r produces an increase in temperature in the product of a lesser extent, $\Delta T_p < \Delta T_r$. This is also observed in experiments, but in the latter the increase of temperature is less than linear, implying the adiabatic temperature increase is even lower.

- There is no dependence on pressure. T_{ad} is observed to increase with pressure instead in experiments, and this behaviour is more marked for oxyfuel combustion and at high temperatures.

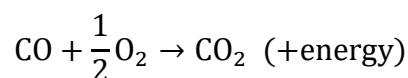
These observations allow us to also understand the limitations of the complete combustion approximation. The reasons behind these limitations will become obvious after the analysis of chemical equilibrium in next section. In particular, the big player missing is the effect of endothermic dissociations, which ‘steal’ energy from the system and were not taken into account.

Exercise 4. Plot the variation of T_{ad} with equivalence ratio for hydrogen/air and $T_{\text{reac}} = 600$ K. Repeat the exercise for hydrogen/oxygen (oxyfuel) combustion. What are the differences?

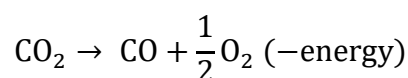
Exercise 5. Plot the variation of T_{ad} with T_{reac} for hydrogen/air combustion for $\phi = 0.6$ and $\phi = 1$. Compare the two variations.

3.2. Chemical equilibrium

Complete combustion does not account for the endothermic dissociations occurring at high-temperature. We discussed in Section 1 that reactions in combustion are characterised by high activation energies. When this activation energy is provided, the reactions start, providing sufficient energy to activate further reactions and so on. As the energy liberated to the system increases however, there may be at some point enough energy to activate the reverse reaction. To understand this, let’s suppose we have the following reaction:



This reaction occurs at some stage during the combustion of hydrocarbons and is exothermic, since the formation enthalpy of the carbon dioxide is lower than that of the carbon monoxide and thus, which means we have liberated energy. This is what is shown in Fi. 3.3, going left to right along the curve. As the combustion progresses, however, there is a point in which there is enough energy in the system also to trigger the reaction in the reverse direction:



The activation energy in this case is higher as shown in the figure, which is why the reverse reaction is more likely at higher temperatures. As the reverse reaction packs energy from the system, the final temperature also decreases, which lowers again the probability of the reverse

reaction. There must be thus a point of equilibrium in which the forward and reverse reactions balance. In the case of complete combustion, we had no chances in predicting this effect.

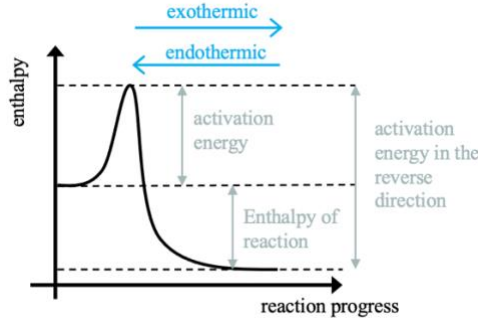
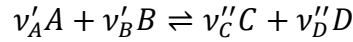


Fig. 3.3. Reaction progress for a generic reaction

Let's better formalise the concept of chemical equilibrium. Let's consider an adiabatic and homogeneous system, and a generic stoichiometric reaction j where two species A and B react to form products C and D.



We have used one apex to indicate the stoichiometric coefficients of the reactants, and two apices to indicate the stoichiometric coefficients in the products. The conservation of mass applies to this system, and can be written as:

$$\nu'_A W_A + \nu'_B W_B = \nu''_C W_C + \nu''_D W_D$$

For a generic reaction j and any number of reactants or products, this equation can be generalised as:

$$\sum_k^{\text{reac}} \nu'_{k,j} W_k = \sum_k^{\text{prod}} \nu''_{k,j} W_k$$

We can rearrange the above equation summing over all species (reactants + products):

$$\sum_k^N \nu_{k,j} W_k = 0 \quad k = 1, \dots, N \quad (3.27)$$

where $\nu_{k,j} = \nu''_{k,j} - \nu'_{k,j}$ is the net stoichiometric coefficient of species k in the reaction j . Let's now introduce the net **reaction rate** of species k in reaction j :

$$\dot{\omega}_{k,j} \equiv \frac{dY_{k,j}}{dt} \quad (3.28)$$

The reaction rate is measured in kg/s and is the speed at which the mass of a species k is produced or destroyed. As we discussed, as the reaction starts a reactant is being destroyed at a faster rate than it is produced in the reverse reaction. As the temperature increases, the reverse

speed also increases until equilibrium is achieved. Before achieving the equilibrium, however, the two speeds are different, and thus the net reaction rate also changes as the reaction is progressing. In general, species k is present in many reactions, therefore the net reaction rate of species k in the entire combustion process is the sum over all reactions M :

$$\dot{\omega}_k = \sum_{j=1}^M \dot{\omega}_{k,j}$$

At this point the mass conservation can be re-formulated in terms of the reaction rates. For example, if 1 mole of reactant A is consumed over a time Δt , the other reactants have to be also consumed of an amount given by the proportion of stoichiometric coefficients. Similarly, during the same Δt products have been formed. We already expressed this concept for Eqs. (3.21) and (3.22). From any of the two, dividing by Δt and in the limit of $\Delta t \rightarrow 0$, we obtain for a reaction j :

$$Q_j \equiv \frac{\dot{\omega}_{k,j}}{W_k \nu_{k,j}} \quad (3.29)$$

The quantity Q_j is the rate of progress of reaction j and because of mass continuity it is independent of the species k . At equilibrium, forward and reverse reaction rates must be the same, i.e. $Q_j = 0$. Note that the equilibrium is dynamic, i.e. reactants are still transformed into products, but at the same rate at which products are reverted back into reactants. To be useful, we would need to find an expression for the reaction progress. This depends on many factors such as concentration of species, temperature and pressure, which in general also vary throughout the reaction. These expressions are found by looking at chemical kinetics and with the help of experimental measurements. However, does the equilibrium point really depend on the rate of reactions? Is there another way to find it by a simple use of thermodynamics, thus avoiding the chemical kinetics?

In order to obtain such a result, we need to find a way to tell whether, for any condition of temperature, pressure and species concentrations, the reaction would progress in the forward or reverse direction. If we find this criterion, at that point we can imagine also to find the point at which the reaction does not progress either in a direction or the other, and thus find the equilibrium point. Luckily, we have a criterion for spontaneity, which is given by the second law of thermodynamics. This tells us that the entropy of the universe, or more precisely any part of the universe that to good approximation can be considered a closed system, always increases. To make this useful, we need to be able to write this statement in terms of our system of interest. Let's thus express the entropy of the universe as the sum of that of our system and the surrounding:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \quad (3.30)$$

We need to express the variation of entropy ΔS in the surrounding in terms of what we know. Gibbs realised that for a reaction, a certain amount of energy goes to an increase in entropy of a system and a certain amount goes to a heat exchange for a reaction. Let's define the Gibbs energy G as:

$$G = H - TS$$

Since G is a combination of state functions, it is also a state function. By differentiating Eq. (3.31) we obtain

$$dG = dH - T dS - S dT \quad (3.31)$$

To understand its meaning, let's suppose the process is isobaric, so that $\delta Q = dH$.

Let's now make some assumptions:

- Reversible process. From Eq. (2.23) then $\delta Q = T dS$;
- Closed system (no exchange of mass with the surrounding);
- Isobaric process. In this case $\delta Q = dH$;
- Temperature remains constant.

Let's remember that for functions of state what actual process we undergo is only a matter of convenience, as the variation only depends on initial and final states. At these conditions, the system is in equilibrium and, by using the assumptions into Eq. (3.31), we have $dG = 0$, i.e. the Gibbs free energy remains constant. To relate this result to entropy, let's rewrite Eq. (3.30) using infinitesimal increments as:

$$\begin{aligned} dS_{\text{universe}} &= dS_{\text{system}} + dS_{\text{surrounding}} \\ &= dS_{\text{system}} + \frac{\delta Q_{\text{surrounding}}}{T} \end{aligned}$$

The variation of heat in the entire universe is $\Delta Q = \Delta Q_{\text{system}} + \Delta Q_{\text{surrounding}} = 0$, therefore:

$$dS_{\text{universe}} = S_{\text{system}} - \frac{\delta Q_{\text{system}}}{T} = dS_{\text{system}} - \frac{dH_{\text{system}}}{T} \quad (3.32)$$

Multiplying by T the final expression for the system of interest becomes (omitting the subscript for simplicity):

$$dH - T dS = dG = 0$$

If now the system is not in equilibrium, then $\delta Q \leq T dS$, and the above is replaced by:

$$dH - T dS = dG < 0 \quad (3.33)$$

We can now understand the meaning of the Gibbs free energy. For an isobaric process that is not in equilibrium, G always decreases, and its variation represents the “excess energy” liberated at non equilibrium conditions. Part of the heat $dQ = dH$ thus goes into an increase of entropy (and temperature also more in general, using Eq. 3.31), but at non-equilibrium conditions part of the heat also is used for the reaction progress (free energy). This heat represents the part of the energy packed into the system that is available to the system itself. If the reaction would have been isochoric rather than isobaric, the same identical concept would

apply by using the free Helmholtz energy $F = U - TS$ in place of G . From now on, however, we will only consider isobaric processes.

Exercise 6. Determine whether the free energy is larger for an isobaric or isochoric process.

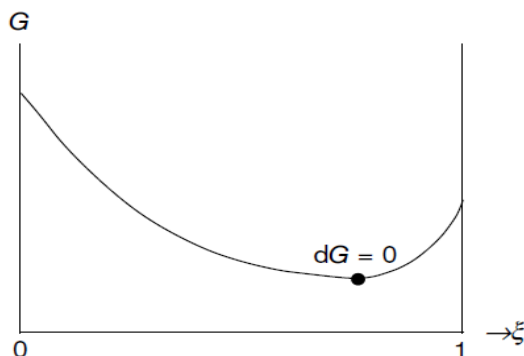


Figure 3.4. Variation of Gibbs function for a generic reaction

The variation of Gibbs function for a generic reaction is shown in Fig. 3.4. When $\Delta G < 0$ the process is *exergonic* and will proceed spontaneously in the forward direction to form more products. When $\Delta G > 0$, the process is *endergonic* and, according to Eq. (3.33), not spontaneous in the forward direction. Instead, it will proceed spontaneously in the reverse direction to make more starting materials. When $\Delta G = 0$ the system is in equilibrium and the concentrations of the products and reactants will remain constant. Recall this is a dynamic equilibrium, and implies that the change of Gibbs function in the products equals the change in the reactants. From Eq. (3.33) we realise that the spontaneity of a process depends on temperature and entropy, other than the enthalpy variation. Therefore, the process can be spontaneous or not independently of whether the reaction is exothermic or endothermic. This is a great result as it allows us to predict when reverse, endothermic reactions, can occur. We can distinguish four scenarios:

- $\Delta H < 0$ and $\Delta S > 0$. In this case ΔG is always negative and the reaction is always spontaneous. This is the case for most combustion reactions, since the reactions are prevalently exothermic ($\Delta H < 0$ between products and reactants) and we usually move from large molecules to small ones, so increasing the number of possible microstates (thus the entropy).
- $\Delta H < 0$ and $\Delta S < 0$. In this case $\Delta G < 0$ (for a fixed negative variation of entropy determined by the process) provided that the temperature is low enough. This is the case of condensation: the process is exothermic, but at constant temperature and the entropy decreases because the degrees of freedom decrease from gas to liquid or solid. An example is the contrail formation in the wake of an airplane.
- $\Delta H > 0$ and $\Delta S > 0$. In this case the process is endothermic and $\Delta G < 0$ provided that the temperature is high enough. This is the case of dissociation reactions, for example the reaction $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$. As the number of molecules increases from left to right, so does the entropy. If the temperature is high enough, the reaction will thus be spontaneous in the forward direction (endothermic), which is equivalent to having enough energy to win the activation energy for the dissociation of CO_2 .

- $\Delta H < 0$ and $\Delta S > 0$. In this case ΔG is always positive and the process is never spontaneous. This does not imply that the process cannot manifest in nature, but we need to provide energy from an external source to make it happen. A natural example of this is the photosynthesis in plants.

Now that we have understood the significance of Gibbs function and free energy, we need to derive some mathematical form that allows us to predict the adiabatic flame temperature and concentrations in a reaction. Let's consider a closed system. From the definition of enthalpy, we have:

$$H = U + pV \Rightarrow dH = dU + p dV + V dp$$

Substituting into Eq. (3.31) we get:

$$dG = dH - TdS - SdT = dU + pdV + Vdp - TdS - SdT$$

if the system is reversible, from Eq. (2.24) we have $dU = T dS - p dV$. Substituting into the above equation then:

$$dG = \cancel{TdS} - \cancel{pdV} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT$$

and thus:

$$dG = V dp - S dT \quad (3.34)$$

Since G is a state function, we can quantify it by using the most convenient process. Let's for this purpose consider an isothermal transformation, so that the second term in the above equation is zero. By integrating Eq. (3.34) between the reference pressure $p_0 = 1$ bar and the final pressure p , and assuming perfect gas, we obtain, for a single species k :

$$G - G^0 = \int_{p_0}^p \frac{n_k R_0 T}{p'} dp' = n_k R_0 T \ln \frac{p_k}{p_0}$$

We can now find the expression for the variation of Gibbs function between products and reactants as:

$$\Delta G_R = G_{\text{prod}} - G_{\text{reac}} = \Delta G_R^0 + R_0 T \ln \prod_{k=1}^N \left(\frac{p_k}{p_0} \right)^{\nu_k} \quad (3.35)$$

where ΔG_R^0 is the standard Gibbs energy, i.e. the Gibbs energy at 1 bar. Since for a fixed temperature G is a linear function in H and S , the latter can be expressed in terms of the standard enthalpy and entropy of formation as:

$$\Delta G_R^0 = \Delta H_f^0 - T \Delta S^0 \quad (3.36)$$

It is to note that in Eq. (3.35) the net stoichiometric coefficients $\nu_k = \nu_k'' - \nu_k'$ have taken the place of the actual coefficients n_k . This is because even if the combustion is not stoichiometric,

the difference between the coefficients in products and reactants would give the same result. At this point by imposing equilibrium ($\Delta G_R = 0$) from Eq. (3.35) we obtain:

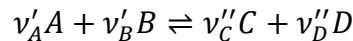
$$\prod_{k=1}^N \left(\frac{p_k}{p_0} \right)^{\nu_k} = K_p(T) = e^{-\frac{\Delta G_R^0}{R_0 T}} \quad (3.37)$$

where K_p is the equilibrium constant and the term on the left is named the reaction quotient. The constant K_p only depends on temperature, and is a sort of speed. If its value is very high ($> 10^3$) the reaction is strongly shifted towards the products and the combustion is almost complete. Vice-versa, if the constant is very low ($< 10^{-3}$) the reaction is strongly shifted towards the reactants, i.e. it is the reverse reaction that is about complete.

Note that in the above expression ΔG_R^0 is a function of the final temperature; and that it appears in the equation as an extensive quantity. Moreover, the partial pressures p_k depend on the species mole fraction as

$$p_k = p X_k \quad (3.38)$$

We have thus an explicit appearance in Eq. (3.37) of temperature, pressure and mixture composition. Let's try to understand the effect on the reaction of these three. To simplify the notation, let's suppose the following generic reaction:



In this case Eq. (3.37) becomes (min the sign of the net stoichiometric coefficients in products and reactants):

$$\frac{p_C^{\nu''} p_D^{\nu''}}{p_A^{\nu'} p_B^{\nu'}} = K_p = e^{-\frac{\Delta G_R^0}{R_0 T}} \quad (3.39)$$

where $p_0 = 1$ bar was omitted for simplicity. The partial pressures in Eq. (3.39) are thus non-dimensional. By substituting Eq. (3.38) into Eq. (3.39) we obtain:

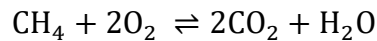
$$\frac{X_C^{\nu''} X_D^{\nu''}}{X_A^{\nu'} X_B^{\nu'}} p^{[(\nu''_C + \nu''_D) - (\nu'_A + \nu'_B)]} = K_p = e^{-\frac{\Delta G_R^0}{R_0 T}} \quad (3.40)$$

where the system pressure p also is non-dimensional (p_0 from Eq. 3.37 omitted for simplicity of notation). Let's now analyse the equation. Note that the value of the constant K_p can only change due to temperature as we said.

- **Increase of temperature.** The exponent on the RHS in Eq. (3.40) has a dependence on temperature of $(1/T)$. For a globally exothermic reaction ($\Delta H_R^0 < 0$) this exponent is positive so K_p decreases. Consequently, for a fixed pressure (isobaric process) the mole fractions of the products have to decrease or the mole fractions of the reactants have to increase. Thus, the reaction moves towards the reactants, i.e. the system reacts to the

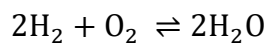
increase of temperature by favouring the reverse reactions (endothermic in this case), which would subtract energy and thus decrease the temperature.

- **Change of concentrations.** For a fixed pressure and temperature, if we increase the amount of reactants (by adding moles of fuel for example), or subtract a product (via a mass exchanger), the system has to react by reducing the concentration of the fuel or restoring the missing product to match the value of K_p (which depends on T so has not changed). Therefore, the equilibrium will shift towards the products.
- **Change of pressure.** The dependence on pressure is less obvious because of the exponent in the pressure term in Eq. (3.40). The behaviour depends on the sign of this exponent. There are three cases:
 - a) The pressure exponent is zero, i.e. the total number of moles is the same in products and reactants. This is for example the case of the 1-step methane combustion equation:



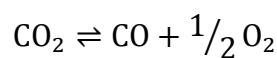
In this case pressure has no effect on the reaction.

- b) The pressure exponent is negative, i.e. there are more moles in the reactants than in the products. This is for example the case of 1-step hydrogen combustion:



In this case thus, if the pressure increases, the quotient would decrease, so the system has to react to re-increase it and match K_p . Thus, the reactant mole fractions decrease and those of the products increase. The equilibrium thus shifts towards the products (more efficient).

- The pressure exponent is positive, i.e. there are more moles in the products than in the reactants. This is for example the case of the following reaction:



In this case, if the pressure increases, the quotient would increase, so the system has to react to re-decrease it and match K_p (which has not changed). Therefore the equilibrium shifts towards the reactants. Since CO_2 tends to dissociate at high temperatures (endothermic reaction), the increase of pressure in this case contrast the inefficiency of the system.

All these changes are consistent with Le Chatelier's principle, which states that the system reacts to a change in the equilibrium condition by counter-acting the effect of that change.

Exercise 7. The effect of an increase of pressure in methane/air combustion on T_{ad} is shown from experiments in Fig. 3.5. Is this consistent with the analysis above? Discuss the reasons for the different behaviours.

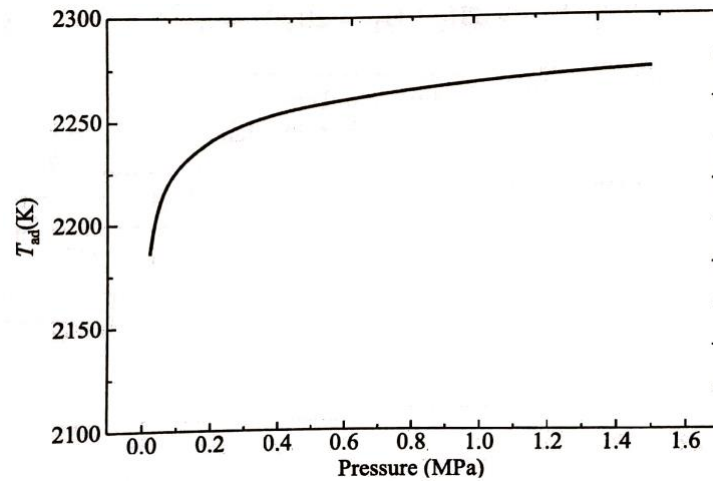


Figure 3.5. Variation of adiabatic temperature with pressure from measurements of methane/air combustion [D.P. Mishra, *Fundamentals of combustion*, PHI Learning, 2013].

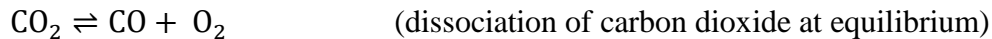
SAMPLE EXERCISES

Sample exercise 1

Find adiabatic flame temperature and mass fractions at the equilibrium for methane/air combustion at the following conditions.

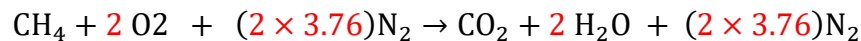
$$\begin{aligned}\phi &= 1 \\ T_{\text{reac}} &= 600 \text{ K} \\ p &= 1 \text{ bar}\end{aligned}$$

Use the following two-steps mechanism. Consider nitrogen inert.

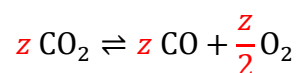


Execution:

Let's assume isobaric process, adiabatic and closed system, and perfect gas. First, we need to balance the chemical equations. For lean or stoichiometric mixtures, it is convenient to have the fuel coefficient 1. Also, nitrogen is needed to work out the equations even if inert. Thus:



Of the 1 mole of CO_2 , an amount z reacts in the second reaction, thus:



The equilibrium equation for the dissociation is (recall that exponents are the **stoichiometric** coefficients):

$$\frac{X_{\text{CO}}^1 X_{\text{O}_2}^{1/2}}{X_{\text{CO}_2}^1} p^{[1+\frac{1}{2}-1]} = K_p = e^{-\frac{\Delta G_R^0}{R_0 T}}$$

Note: the dissociation is occurring in a mixture of H_2O and N_2 (the products at the previous step). These do not take part to the reaction and thus do not directly appear in the above equation (they would cancel out in the quotient). However, their mole fraction affects the value of z and thus of X_{CO} , X_{CO_2} and X_{O_2} .

We need to express mole fractions in terms of z . Find first the total number of moles at equilibrium:

$$n_{\text{tot}} = n_{\text{CO}_2} + n_{\text{H}_2\text{O}} + n_{\text{N}_2} + n_{\text{CO}} + n_{\text{O}_2} = \\ = (1 - z) + 2 + (2 \times 3.76) + z + \frac{z}{2} = 10.52 + \frac{z}{2}$$

Note: If the first step was lean, we had to add the additional oxygen in the above count.

Conveniently rewrite equilibrium equation in terms of moles by substituting $X_k = n_k/n_{\text{tot}}$:

$$\frac{n_{\text{CO}} n_{\text{O}_2}^{1/2}}{n_{\text{CO}_2}} \frac{p^{1/2}}{n_{\text{tot}}^{1/2}} = \frac{n_{\text{CO}} n_{\text{O}_2}^{1/2}}{n_{\text{CO}_2}} \frac{p^{1/2}}{\left(\frac{z}{2} + 10.52\right)^{1/2}} = \frac{z \times \left(\frac{z}{2}\right)^{1/2}}{1 - z} \frac{1^{1/2}}{\left(\frac{z}{2} + 10.52\right)^{1/2}} = \\ = \frac{z^{3/2}}{\sqrt{2}(1 - z) \left(\frac{z}{2} + 10.52\right)^{1/2}} = K_p = e^{-\frac{\Delta G_R^0}{R_0 T}}$$

Let's now find $K_p(T)$. From tables:

$$\begin{aligned} \Delta H_{f,\text{CO}_2}^0 &= -393.5 \text{ kJ/mol} \times 1 \text{ mol} = -393.5 \text{ kJ} & S_{\text{CO}_2}^0 &= 213.68 \text{ J/(K mol)} \times 1 \text{ mol} \\ \Delta H_{f,\text{CO}}^0 &= -110.5 \text{ kJ/mol} \times 1 \text{ mol} = -110.5 \text{ kJ} & S_{\text{CO}}^0 &= 197.56 \text{ J/(K mol)} \times 1 \text{ mol} \\ \Delta H_{f,\text{O}_2}^0 &= 0 \times \frac{1}{2} \text{ mol} = 0 \text{ kJ} & S_{\text{O}_2}^0 &= 205.04 \text{ J/(K mol)} \times \frac{1}{2} \text{ mol} \\ & & &= 102.52 \text{ J/K} \end{aligned}$$

Therefore:

$$\begin{aligned} \Delta H_R^0 &= \sum(\Delta H_{f,k}^0)_{\text{prod}} - \sum(\Delta H_{f,k}^0)_{\text{reac}} = (-110.5 + 0) - (-393.5) = 283 \text{ kJ} \\ \Delta S_R^0 &= \sum(S_k^0)_{\text{prod}} - \sum(S_k^0)_{\text{reac}} = (197.56 + 102.52) - (213.68) = 86.4 \text{ J/K} \end{aligned}$$

Use tentative temperature (e.g. from complete combustion). $T = T_1 = 2300 \text{ K}$.

$$\Delta G_R^0 = \Delta H_R^0 - T \Delta S_R^0 = \left(283 - 2300 \times \frac{188.92}{1000}\right) \text{ kJ} = 84.28 \text{ kJ}$$

Note: The amount found is for 1 mol of reactant. Therefore, we will change the units to kJ/mol.

Thus, using the value of the universal gas constant $R_0 = 8.314 \text{ J/(K mol)}$:

$$K_p = e^{-\frac{84.28 \times 1000 \text{ J/mol}}{(8.314 \times 2300) \text{ J/mol}}} \approx e^{-4.41} \approx 0.012$$

Equilibrium towards the reactants. To find mole fractions, need to solve the equation in z:

$$\frac{z^{3/2}}{\sqrt{2(1-z)}\left(\frac{z}{2} + 10.52\right)^{1/2}} = f(z) = 0.012$$

$z \leq 1$ as $z = 1$ means that all CO_2 was burnt. After few iterations we find $z \approx 0.13$:

$$n_{\text{tot}} = 10.52 + \frac{0.13}{2} = 10.585$$

$$X_{\text{CO}} = \frac{n_{\text{CO}}}{n_{\text{tot}}} = \frac{z}{10.585} \approx 0.012 \quad X_{\text{H}_2\text{O}} = \frac{2}{n_{\text{tot}}} \approx 0.189$$

$$X_{\text{CO}_2} = \frac{1-z}{n_{\text{tot}}} \approx 0.082 \quad X_{\text{N}_2} = 1 - X_{\text{O}_2} - X_{\text{CO}_2} - X_{\text{H}_2\text{O}} - X_{\text{CO}} \approx 0.711$$

$$X_{\text{O}_2} = \frac{z/2}{n_{\text{tot}}} = 0.006$$

This means that at 2300K CO would amount to 1.2% in volume for the entire mixture. We need however to find out whether the guess temperature was correct, and can use the enthalpy balance for this:

$$h_{\text{prod}} = \Delta h_{f,\text{prod}}^0 + \int_{298\text{ K}}^{2300\text{ K}} c_{p,\text{prod}}(T') dT' = h_{\text{reac}} = \Delta h_{f,\text{reac}}^0 + \int_{298\text{ K}}^{600\text{ K}} c_{p,\text{reac}}(T') dT'$$

$$W = \sum_k W_k X_k = 0.012 \times 28 + 0.082 \times 44 + 0.006 \times 32 + 0.189 \times 18 + 0.711 \times 28 \approx 27.45 \text{ kg/kmol}$$

$$c_{p,\text{reac}} = \sum_k^{\text{reac}} Y_k c_{p,k} = \frac{1}{W} \sum_k^{\text{reac}} W_k X_k c_{p,k}$$

$$c_{p,\text{prod}} = \sum_k^{\text{prod}} Y_k c_{p,k} = \frac{1}{W} \sum_k^{\text{prod}} W_k X_k c_{p,k}$$

[Continue in Excel sheet using NASA polynomials].

Note: the dependence on reactants temperature only comes through the energy equation above.