

Chapter 3

Controlling Fire

Up until this point in our story, we have been primarily concerned with the “natural” world - a world situated within a universe whose underlying physics appear to obey the First Law of Thermodynamics. In Chapter 2 we learned about how this law applies to the Earth’s climatological system via a number of *constitutive* relationships between the system’s various properties (e.g. ideal gas law), and how over millions of years, these relationships guided the evolution of the many ecosystems that comprise the climate in a delicate balance between incoming solar energy and internal energy - and thus global temperature.

One key constraint of this “natural” world, whose timeline spans the majority of the Earth’s 4.5 billion year history, has been that organisms only consume the energy that is immediately available to them. Chemosynthetic organisms derive their energy from hydrothermal vents, photosynthetic organisms from the sun, herbivores from these organisms, and the food chain continues up through the *apex predators* at the top. Looking back down the chain from the perspective of one of these top predators like a megalodon or velociraptor, as far removed as we seem from the initial source of energy, we are truly not far removed from the source *temporally*. Indeed, the time between when some phytoplankton first used solar energy to convert CO₂ into sugar and when the thing eats the thing that ate the thing that ate the thing...that ate the phytoplankton is on the order of months to years - instantaneous compared to the rate of the Carbon Cycle, which operates over millions of years.

As a result of these extremely disparate timescales, the Earth’s natural feedback loops were able to drive not just the evolution of the climate as it pertains to temperature, atmospheric compositions, etc., but even life as well. For instance, when early photosynthetic life began to explode in numbers, it quickly and dramatically altered the composition of the atmosphere, leading to

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a climate cooling event that resulted in major glaciation, freezing much of the oceans and slowing the expansion of life. The balance swung back and forth between rapid growth and swift climatological resistance, each time getting less severe as ecosystems became more diverse and therefore more robust to change. Over billions of years, this rhythm, whose tempo was set largely by the constant influx of solar radiation, shaped the Earth. More importantly, this harmonious relationship between energy and growth prevented the system from going too far in either direction, as had happened with Venus for instance.

This leads us to the advent of the “unnatural” world almost 2 million years ago when humans discover they can control fire. At this precise moment, life became no longer bound to using energy that arrived at the Earth via sunlight over just the previous month or year. Instead, burning branches from a felled tree releases tremendous amounts of solar energy stored over hundreds to potentially thousands of years. Burning coal left over from the Carboniferous period in the Paleozoic era 300 million years ago or oil from the Mesozoic Era 100 million years ago releases solar energy stored over millions of years - now comparable to the rate of Carbon Cycle itself. With the control over fire - and later ambivalence to natural signals that something was awry - came the relinquishing of control over the natural tempo that had reliably guided the planet’s development up to that point¹.

Just as thermodynamics explains the goings on of the “natural” world, it also governs the physics of the “unnatural” world, which should be the case since the only difference between the two is of sociological and cultural construction. The physics is exactly the same. As such, we will spend this chapter delving into the thermodynamics of fire and some of the consequences of heat transfer to various substances. We will learn about the chemistry of combustion, including concepts like enthalpy, heating values, and adiabatic flame temperature. Finally, will we conclude this chapter with a few related concepts and some of the early uses of fire to relate the concepts back to climate change and foreshadow what is to come.

3.1 Combustion

As before, it will help us to define a few terms. First, *fire* and *combustion* refer to the same phenomenon - a rapid and *exothermic* chemical process that releases heat via *oxidation*. An oxidation reaction is simply one in which an element or molecule loses electrons and has nothing intrinsically to do with

¹see Bill McKibbin’s *End of Nature* for a now slightly outdated but still insightful discussion of this concept

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oxygen, other than the fact that oxygen is a very common *oxidizer*. Water, for instance, is also a strong oxidizer that is responsible for rusting, another type of oxidation reaction.

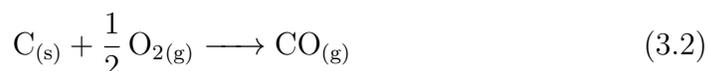
Combustion, however, mainly refers to hydrocarbons or metals reacting exothermically with oxygen. For example, plain elemental carbon² will react with oxygen via the following reaction:



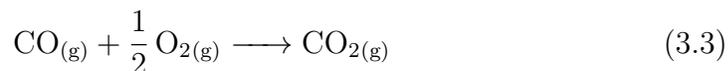
releasing a significant amount of heat in the process. This reaction in particular, releases roughly 33 megajoules of heat per kg of carbon. Notice that the carbon here is just a single atom - it has no chemical bonds to break to release that energy; however, the CO₂ product has less energy in its bonds than the oxygen has in its own, giving the pure carbon a potential energy of sorts. The reason for this will become evident later.

The reaction in Eq. 3.1 is typical of hydrocarbon combustion in general and as a quick aside about chemical equation notation, reads “one mole of carbon reacts with one mole of oxygen to produce one mole of carbon dioxide”³. We call this type of reaction *complete* hydrocarbon combustion in which all of the carbon in the *reactants* ends up in carbon dioxide in the *products*. CO₂ is *fully oxidized*, meaning that no more energy can be extracted from it. In fact if want to break those bonds, we must put energy back into it. This is exactly what happens in photosynthesis, with the energy coming from the Sun.

Hydrocarbons can also undergo partial or *incomplete* combustion where instead of producing CO₂, the reaction produces the intermediate, carbon monoxide (CO). With our pure carbon example, this looks like



and is also exothermic, but does not release as much heat as the reaction in Eq. 3.1 since CO has a slightly higher *energy state* than CO₂. We can subsequently combust CO via



to release the additional heat. If we measure and sum the heat released in Eqs. 3.2 and 3.3 it will exactly equal that released in Eq. 3.1.

²graphite or coal

³In the majority of the chemical equations we look at in this text, mass is conserved. Therefore we must have the same number of moles of each element on either side of the arrow.

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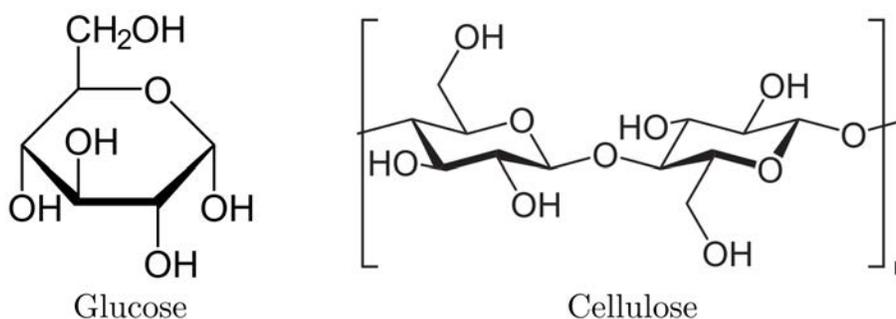
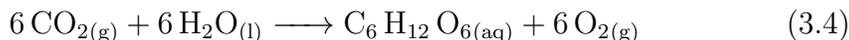


Figure 3.1: Molecular structure of glucose ($C_6H_{12}O_6$) and cellulose ($C_6H_{10}O_5$).

And so this notion of potential energy again arises in which a substance gives us the ability to create an exothermic reaction with a widely available oxidizer, releasing net energy in the form of heat. This becomes additionally evident if we look at where pure carbon or coal comes from on Earth. Let's start with a molecule of CO_2 in the air, which is happily floating around in its lowest possible energy state - it will remain as is if left untouched⁴. Chloroplasts in photosynthesizing organisms take this CO_2 and react it with water to produce a long chain of carbon, hydrogen, and oxygen called *glucose* via the following reaction:



where because glucose ($C_6H_{12}O_6$) is in a higher energy state, this reaction requires energy be added, in this case via solar radiation.

Some of this sugar is consumed (oxidized) by the plant for its own energy needs, releasing some carbon back out as CO_2 , while the rest is stored in molecules like cellulose, a complex *organic*⁵ compound with repeating base units of $C_6H_{10}O_5$. After this organism dies and begins to decompose, over time, some of the carbon contained in these molecules turns into methane gas (CH_4)⁶ and CO_2 , and under the right conditions, the remainder gets pushed deep underground. Over millions of years, the heat and pressure underground provides additional energy to these molecules, slowly breaking more and more bonds until just pure carbon is left. So to recap from an energy perspective, CO_2 in a low energy state was brought to progressively higher potential energy states, first via input energy from the sun and then from geothermal energy

⁴ignoring quantum effects for now

⁵any molecule comprised of some combination of carbon, hydrogen, and oxygen.

⁶see the end of the chapter for more about this process

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deep in the Earth's crust. One can imagine the final carbon product as a ball pushed up a hill, waiting for oxygen to come along and knock it back down, converting that potential energy back into heat. From a time perspective, what took millions of years to process is undone in an instant via combustion.

In all of these combustion reactions, there is some *activation energy* required for the combustion to begin. In the ball on the hill example, there is a slight bump in that keeps the ball from easily rolling back down. In combustion, the energy required to overcome this bump typically comes from thermal energy, and the hotter the environment, the more likely individual particles have enough thermal (microscopic kinetic) energy to kick off a chain reaction. Most substances therefore have an *autoignition temperature* above which the reaction is likely to spontaneously ignite. Dry wood for example will nearly immediately ignite above 427 °C.

3.1.1 Combustion Stoichiometry

In nature, the majority of combustion that occurs - including the early fires set by humans - involves the reaction of a hydrocarbon with air. Oxygen is the oxidizer in these reactions but only comprises about 21% of air by mass. The primary component is nitrogen, comprising 78% of air by mass, with the rest made up of trace amounts of several other gases. A good model for combustion is to lump these other gases together with nitrogen, giving us the general *ideal* hydrocarbon combustion stoichiometric equation:



whose coefficients ensure that mass is conserved across the reaction. As a result, z , for this ideal case can be solved for explicitly as

$$z = x + \frac{y}{4} \quad (3.6)$$

Similarly, for alcohols or carbohydrates, which contain complex molecules of carbon, hydrogen, and oxygen, the ideal general combustion equation is given by:



where

$$\beta = x + \frac{y}{4} - \frac{z}{2} \quad (3.8)$$

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Metal oxidation reactions are typically much simpler and involve a pure, *reduced* metal and oxygen reacting to form that metal's oxide. For example, aluminum and air react to form aluminum oxide by the following reaction:



While these examples show ideal combustion stoichiometry, in reality there are many other molecules that can be made with carbon, hydrogen, and oxygen, for example, than just CO_2 and H_2O . Specifically in hydrocarbon or alcohol combustion, the reaction products also typically include carbon monoxide (CO) and hydrogen (H_2) as well. Thus, in pure oxygen, for example, the actual reaction equation might look like



where we can relate the stoichiometric coefficients a , b , and c to x and y by applying conservation of mass to the carbon, hydrogen, and oxygen respectively to find

$$a + b = x \quad (3.11)$$

$$2c + 2d = y \quad (3.12)$$

$$2a + b + c = 2z \quad (3.13)$$

Notice here that given x , y , and z we have 3 equations but 4 unknowns: a , b , c , d . We can gain additional information from knowing that some CO will react with additional oxygen or with water vapor to form carbon dioxide and hydrogen, but will need some additional chemistry knowledge to determine the proportions.

3.1.2 Chemical Kinetics

Most chemical reactions can go both ways under the right conditions, and in fact, many naturally occurring chemical reactions do. In general, such a reaction can take the form



where the double arrows indicate that A and B can react to form C and D and vice versa. If we were to zoom in on the molecules during this reaction, we

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would find that both the *forward* reaction, where C and D are the products, and the *backward* reaction, where A and B are the products, are actually happening at the same time. From chemistry, though, we know that depending on the compounds and the temperature and pressure of the reaction, one of these reaction is happening more often than the other, skewing the concentrations⁷ accordingly.

For the forward reaction in this general case, we observe that the time derivative of the concentration of the products is proportional to some constant, k_f - which is a function of temperature - multiplied by the concentration of both the reactants such that:

$$\frac{d[\text{C}]_f}{dt} = ck_f(T)[\text{A}]^a[\text{B}]^b \quad (3.15)$$

and similarly for the backward reaction:

$$\frac{d[\text{C}]_b}{dt} = -ck_b(T)[\text{C}]^c[\text{D}]^d \quad (3.16)$$

where the exponents come from the fact that a moles of A, for example, means we need to multiple the concentration of A by itself a times.

Because the forward and backward reactions are happening simultaneously, the net rate of change of [C] is the sum of these two rates, equal to

$$\frac{1}{c} \frac{d[\text{C}]}{dt} = k_f(T)[\text{A}]^a[\text{B}]^b - k_b(T)[\text{C}]^c[\text{D}]^d \quad (3.17)$$

We also know that mass must be conserved, and by the stoichiometry, if this rate changes by some factor, λ , so too must the rate of change of the other species, each scaled by their stoichiometric coefficient. Expressed mathematically,

$$\frac{1}{a} \frac{d[\text{A}]}{dt} = \frac{1}{b} \frac{d[\text{B}]}{dt} = -\frac{1}{c} \frac{d[\text{C}]}{dt} = -\frac{1}{d} \frac{d[\text{D}]}{dt} \quad (3.18)$$

In thermodynamics, however, we mainly care about what happens in equilibrium - when the time derivatives of all the individual species' concentrations go to zero. Thus, in equilibrium we can set the left-hand side of Eq. 3.17 to zero and rearrange to find that

$$\frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} = \frac{k_f(T)}{k_b(T)} \quad (3.19)$$

⁷as used here, *concentration* has units of mass per volume

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It is important to note that we could have started with the time derivative of any of the species' concentrations per Eq. 3.18 and gotten the same expression.

If all of our reaction species are ideal gases, which is often the case in combustion reactions, we can relate the concentration of species i to its mole fraction, X_i , which is the number of moles of the species divided by the total number of moles, in the solution by the following:

$$[i] = \frac{n}{V} X_i = \frac{P}{RT} X_i \quad (3.20)$$

where the second equality is derived by substituting in the ideal gas law. Using this relationship, we can rewrite Eq. 3.19 as

$$\frac{X_C^c X_D^d}{X_A^a X_B^b} \left(\frac{P}{RT} \right)^{(c+d)-(a+b)} = \frac{k_f(T)}{k_b(T)} \quad (3.21)$$

and divide both sides by $\left(\frac{P_0}{RT}\right)^{(c+d)-(a+b)}$ to get

$$\frac{X_C^c X_D^d}{X_A^a X_B^b} \left(\frac{P}{P_0} \right)^{(c+d)-(a+b)} = \left(\frac{RT}{P_0} \right)^{(c+d)-(a+b)} \frac{k_f(T)}{k_b(T)} \quad (3.22)$$

where the right hand side of this is defined as the temperature-dependent *equilibrium constant*:

$$k_p(T) \equiv \left(\frac{RT}{P_0} \right)^{(c+d)-(a+b)} \frac{k_f(T)}{k_b(T)} \quad (3.23)$$

giving us our final relationship:

$$\boxed{\frac{X_C^c X_D^d}{X_A^a X_B^b} \left(\frac{P}{P_0} \right)^{(c+d)-(a+b)} = k_p(T)} \quad (3.24)$$

or in the general case:

$$\frac{\prod_{i=1}^{n_p} X_i^{\nu_i}}{\prod_{i=1}^{n_r} X_i^{\nu_i}} \left(\frac{P}{P_0} \right)^{(\sum_{i=1}^{n_p} \nu_i - \sum_{i=1}^{n_r} \nu_i)} = k_p(T) \quad (3.25)$$

where ν_i is the stoichiometric coefficient for species i , n_p is the number of product species, and n_r is the number of reactant species.

This principle that the environmental conditions can shift the balance of concentrations in a chemical reaction is known as *Le Chatelier's Principle*. It is highly useful because if we know the equilibrium constant, the pressure at which it was calculated, P_0 , and the pressure that reaction occurs at, we

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have another expression that relates the equilibrium concentrations for this reaction. Combined with our earlier combustion example, this gives us the final equation we need in addition to the mass conservation equations to solve our problem, as we will soon see.

In practice, the equilibrium constant $k_p(T)$ is a function of temperature derived from experimental data and is specific to every reaction. Because there are too many chemical reactions that *can* occur, instead of tabulating this value for each reaction, it is instead computed from species-specific constants tabulated for every commonly used substance such that

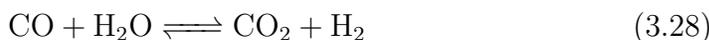
$$\log_{10} k_p(T) = \sum_{i=1}^{n_p} \nu_i \log_{10} k_{p,i}(T) - \sum_{i=1}^{n_r} \nu_i \log_{10} k_{p,i}(T) \quad (3.26)$$

which is written in this form as the equilibrium constants for each species are typically tabulated as $\log_{10} k_{p,i}(T)$. These values can also be found in NASA or JANAF data.

Going back to our incomplete combustion example, recall that we needed an additional equation to determine the concentrations of the products. Again, the reaction in question is



but we know that CO, H₂O, CO₂, and H₂ can undergo an additional two-way reaction called the *water-gas shift reaction* such that



Using our equilibrium constant equation for Eq. 3.28, we get the final equation needed to solve for the concentrations of the products in Eq. 3.27. If we have $n_p = a + b + c + d$ total moles, the mole fraction for each species is simply the stoichiometric coefficient for that species in Eq. 3.27 divided by n_p . Plugging this into Eq. 3.25 and noting that n_p will cancel out in the numerator and denominator, we get

$$\frac{cd}{ab} \left(\frac{P}{P_0} \right)^{(1+1)-(1+1)} = \frac{cd}{ab} = k_p(T) \quad (3.29)$$

where k_p is computed from the individual given species equilibrium constants using Eq. 3.26.

3.2 Enthalpy

To help us quantify the amount of heat released in these combustion reactions, it is helpful to define a quantity called the *enthalpy* of a substance. Enthalpy, H , is defined simply as

$$H \equiv U + PV \quad (3.30)$$

and while this definition may seem arbitrary, we can work it into our differential First Law equation to see its utility. Writing the law and then adding $d(PV)$ to both sides:

$$dU = dQ - dW \quad (3.31)$$

$$d(U + PV) = dQ - P dV + d(PV) \quad (3.32)$$

noting that $U + PV$ is our enthalpy, H , as defined in Eq. 3.30. This gives us

$$dH = dQ - P dV + P dV - V dP \quad (3.33)$$

If we look at just constant pressure processes - of which many combustion processes are - for the time being, we find can also set dP to zero giving us the final relationship that

$$dH = dQ \quad (3.34)$$

Therefore, for a constant pressure process the change in enthalpy tells us directly how much heat is absorbed or released. Enthalpy in fact has units of energy. Substituting Eq. 2.33 into Eq. 3.34 for dQ gives yields

$$dH = C_p dT \quad (3.35)$$

where C_p is the heat capacity at constant pressure.

3.2.1 Enthalpy of Formation

As we saw with the carbon combustion example, some net potential energy is transformed into thermal energy in the formation of CO_2 . This heat is given by Eq. 3.34 as the change in enthalpy between the products and the reactants:

$$Q = \Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}} \quad (3.36)$$

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which for this example is equal to -393.5 kJ/mol carbon at 300K. The negative sign here means that heat is *released* (i.e. the reaction is exothermic). In general, the change in enthalpy for reactions like this one that produce a single species is called the *enthalpy of formation* or *heat of formation*, denoted as ΔH_f , and in reality is a function of temperature since C_p is a function of temperature as we learned in Chapter 2. If the reaction occurs at 298.15 K, we refer to it as the *standard* enthalpy of formation, ΔH_f° .

An important point to make here is that enthalpy is a state variable and property, but because it also represents a *transfer* of heat, it is a *relative* quantity. That is, it is defined in relation to some reference value that we all agree on, usually specified at 298.15 K. This allows us to measure and tabulate the changes in enthalpies of commonly used substances as functions of temperature. Also to make the math easier, these enthalpies are defined such that single elements or molecules with multiple of the same element - C, O₂, N₂, etc. - have an enthalpy of exactly 0 J/mol at 298.15 K. If we take care to reference all species in our reactions at the same temperature, these will cancel out on both sides. For reactions that incur a temperature change, however, this cancellation cannot be made.

To illustrate this, let us look at a more complex reaction - the combustion of methane, which occurred naturally in the early Earth atmosphere when photosynthesizing plants came on the scene and began releasing massive amounts of oxygen and is thought to have caused the first major ice age. This reaction occurs as follows:



where now because we are combusting a *hydrocarbon*, we also get water as a byproduct. For this reaction, we can write the change in enthalpy for this reaction accounting for the reference values as

$$\Delta H_{\text{reaction}} = (2\Delta H_f^{\text{H}_2\text{O}}(T_2) + \Delta H_f^{\text{CO}_2}(T_2)) - (\Delta H_f^{\text{CH}_4}(T_1) + 2\Delta H_f^{\text{O}_2}(T_1)) \quad (3.38)$$

where T_1 and T_2 are the temperatures of the reactants and products respectively and may not be equal. The factors of 2 in Eq. 3.38 come from applying the *stoichiometric* coefficients in Eq. 3.37⁸. For each of the enthalpies of formation for those compounds, which again are all functions of temperature. To compute ΔH_f , we can look to literature to find equations that model each individual enthalpy of formation for these various compounds. NASA, for

⁸We did the same thing with the carbon reaction equation, but the coefficients were all 1.

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example, has polynomial fits for the majority of elements and combustible compounds [1]. If we work out these numbers, we find that the combustion of one mole of methane at 300 K releases 890 kJ. Note that this reaction releases more than double the heat of the carbon reaction and produces the same amount of CO₂.

It is also important to emphasize that because c_p is a function of temperature, enthalpy is also a function of temperature, and sometimes only the enthalpy of formation at standard temperature and pressure is provided from experimental data. If we also know the heat capacity at constant pressure, however, we can compute the enthalpy at the new temperature via

$$H = \sum_i n_i \left[\Delta h_{f,i}^\circ + \int_{T_0}^T c_{p,i}(T) dT \right] \quad (3.39)$$

where the lowercase variables indicate a *specific*⁹ quantity. Notice that this comes directly from integrating Eq. 3.35 with the appropriate initial conditions. Note that the same can be done for internal energy, yielding:

$$U = \sum_i n_i \left[\Delta u_{f,i}^\circ + \int_{T_0}^T c_{v,i}(T) dT \right] \quad (3.40)$$

which is required for characterizing combustion at constant volume instead. For these processes, the heat of reaction is the change in internal energy as was previously shown in Chapter 2.

3.2.2 Enthalpy of Phase Change

Because combustion often involves the phase change of some substance - typically from liquid to gas - it is important to understand how thermal energy is transferred as *latent heat* during this process. Because phase change is a *constant pressure* process in many cases, especially the ones that concern our work in this course, the latent heat can be often characterized using enthalpy. Just as before, the heat transfer is represented by a difference in enthalpy between the final state and initial state, though this time the states represent different phases of matter. From liquid to gas, for which we will use the subscripts f and g respectively as is common practice, this latent heat is given as

$$\Delta h_{fg} = h_g - h_f \quad (3.41)$$

⁹per mass

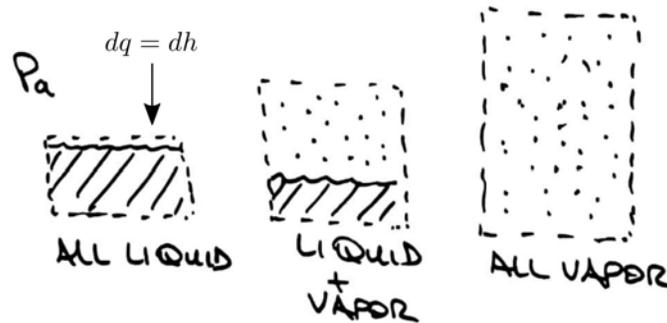


Figure 3.2: A vaporization process at constant pressure. As heat is added, the control volume expands to encapsulate the vapor such that the total system remains at constant pressure P_a .

which is typically called the *latent heat of vaporization*. The *latent heat of fusion* from solid to liquid is similarly given as

$$\Delta h_{sf} = h_s - h_f \quad (3.42)$$

As before, these are all quantities that are measured experimentally and given as functions of temperature. For some substances, this latent heat can be substantial, resulting in a significant energy transfer throughout the process and must therefore be carefully included in analyses. For example, the latent heat of vaporization for water at 100 °C is 2.3 MJ/kg, while its latent heat of fusion at 0 °C is only 334 kJ/kg. This is one of the many reasons why an atmosphere like Venus is so stable - it requires a lot of energy to condense water vapor, but not nearly as much energy to melt ice.

3.2.3 Liquid-Vapor Equilibrium

With the discovery of fire and the subsequent control of *heat*, early humans now had the ability to turn ice into liquid water and liquid water into steam. The latter involves the incredibly important phenomena of *evaporation* and *boiling*, which are both fundamentally *vaporization* - turning liquid into gas. The opposite process of turning gas into liquid is called *condensation*. As discussed previously, at the molecular level, if enough heat is absorbed by molecules at the surface of a liquid, they can be liberated from the bonds that are holding them together in liquid phase, which in the case of water molecules are *hydrogen bonds*. Conversely, gas molecules near the surface of a liquid of the same species can reject heat, reducing their kinetic energy to where they

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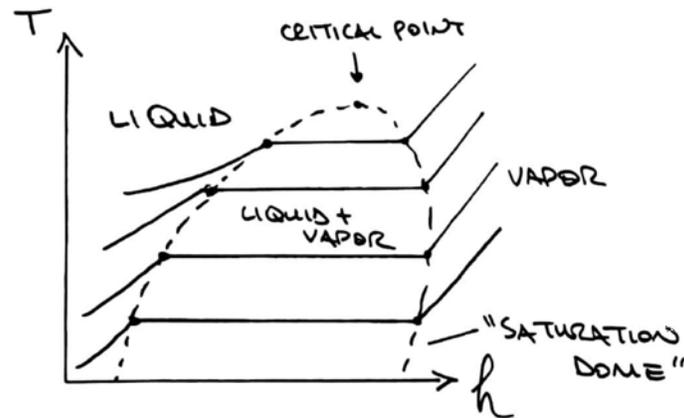


Figure 3.3: Multiple evaporation curves at different constant pressures are plotted on a T - h plot, showing that the points at which liquid begins to turn into vapor lie on the left side of the dotted curve, called the *saturation* or *vapor dome*. Under the dome, both liquid and vapor can exist, and to the right of the dome, only vapor can exist. The width of the dome at a particular pressure is exactly h_{fg} , the latent heat of vaporization.

can join the liquid phase. In reality, both processes are happening simultaneously, and there are several factors that determine whether net vaporization or condensation is occurring.

First, if we look at a constant pressure vaporization process, as we incrementally add heat dq - the heat per unit mass of substance - to a pure liquid, as we would expect, the liquid at first will increase in temperature until at some point the temperature remains constant and the phase change starts to take place. As the change from liquid to gas phase continues, the temperature and pressure remain constant¹⁰ as more molecules are liberated from the liquid surface until finally all of the liquid is turned to gas and the temperature continues to rise. We discussed this process in Chapter 2 as a means of storing heat and showed in Fig. 2.9 the progression of the temperature of the system as a function of the heat added. Since for a constant pressure process, $dq = dh$ as we showed here, this plot is equivalent to same process plotted on T - h axes, as shown in Fig. 3.3.

We can go one step further and plot the constant-pressure temperature-enthalpy curves for vaporization occurring at different pressures, also shown in Fig. 3.3 as the solid curves. As we can see, both the points at which the

¹⁰We assume here that this process happens slowly such that the temperature and pressure are always uniform throughout the control volume.

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vaporization starts to occur and finishes changes as the pressure increases. If we connect these points with a curve, we get what is called the *vapor* or *saturation dome*, shown in this figure as the dashed curve. In this *phase diagram*, to the left of the dome, the substance only exists in liquid phase, under the dome the substance exists in both liquid and vapor phase, and to the right of the dome, only vapor phase can occur. Above the highest point of the dome, which is called the *critical point*, the substance exists as a *supercritical fluid* for which all of the properties - density, specific enthalpy, internal energy, etc. - of both the liquid and vapor phases are identical and thus cannot be told apart. From our definition of the latent heat, h_{fg} , we can see directly from this plot that the width of the dome at a particular constant pressure curve¹¹ is exactly $h_g - h_f = h_{fg}$.

During the vaporization process, under the saturation dome there can exist both liquid and vapor phases in equilibrium, which can make analysis of this process a bit more difficult. To characterize how much of the substance has been vaporized in a particular state, we define the *vapor quality*, x , defined as

$$x \equiv \frac{m_{\text{vapor}}}{m_{\text{vapor}} + m_{\text{liquid}}} \quad (3.43)$$

which is the ratio between the mass of the substance in vapor phase to the total mass of the substance across both phases. This allows us compute the total enthalpy - and all other state properties - at a given point under the dome as

$$h = xh_g + (1 - x)h_f \quad (3.44)$$

If we look at the change in enthalpy between where the substance is pure vapor ($x = 1$) and pure liquid ($x = 0$), we get

$$\Delta h = [1 * h_g + \overset{0}{(1-1)} * h_f] - [0 * h_g + (1 - 0) * h_f] \quad (3.45)$$

$$= h_g - h_f \quad (3.46)$$

$$= h_{fg} \quad (3.47)$$

which is to be expected. Similarly, the total *specific volume*¹², v , is given as the quality-weighted sum of the specific volumes of the substance in gas and liquid phases - v_g and v_f respectively - as

¹¹called an *isobar* which we will explore in detail later

¹²volume per mass equal to $1/\rho$

3.2. ENTHALPY

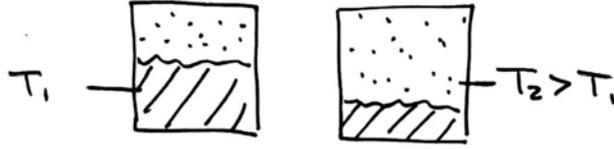


Figure 3.4: A constant volume vaporization process where both the temperature and pressure increase as more liquid is vaporized. Note that at every state, the vapor and liquid phases must be in equilibrium with one another.

$$v = xv_g + (1 - x)v_f \quad (3.48)$$

If we know the total volume and the values for v_g and v_f at a given temperature, we can solve for the quality.

Finally, we can look at vaporization at constant volume to get a sense for the relationship between the temperature and pressure in the two phase region, represented on the T - h plot in Fig. 3.3 under the saturation dome and on the T - P plot in Fig. 3.5 as the *saturation curve*. It can be shown that the relationship between temperature and pressure in this regime - T_{sat} and P_{sat} respectively - obeys the following expression:

$$\frac{dP_{sat}}{dT_{sat}} = \frac{h_{fg}}{T_{sat}(v_g - v_f)} \quad (3.49)$$

which is called the *Clausius-Clapeyron* relation. Typically the density of the vapor phase of a substance at temperatures and pressures reasonably below the critical point is much less than the density of the liquid phase density at those same conditions. Thus, in that case, $v_f \ll v_g$, and Eq. 3.49 can be simplified as:

$$\frac{dP_{sat}}{dT_{sat}} \approx \frac{h_{fg}}{T_{sat}v_g} \quad (3.50)$$

$$\approx \frac{h_{fg}}{T_{sat} \left(\frac{RT_{sat}}{P_{sat}} \right)} \quad (3.51)$$

$$\approx \frac{h_{fg}P}{T_{sat}^2 R} \quad (3.52)$$

or

3.2. ENTHALPY

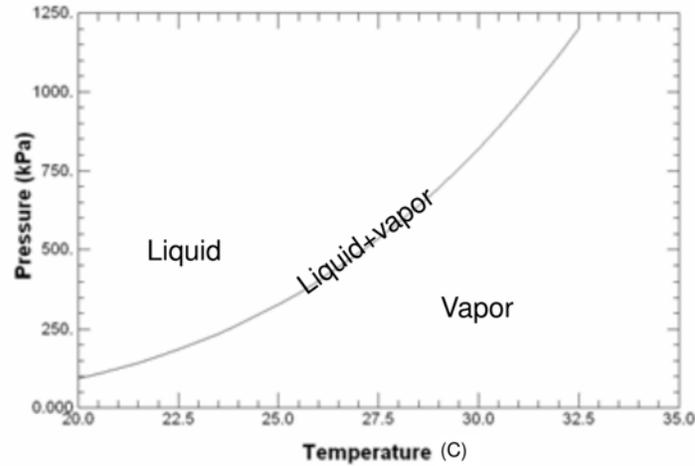


Figure 3.5: Pressure-temperature phase diagram for water. The curve represents the line on which both liquid and vapor can coexist and is typically called the *saturation curve*.

$$\frac{dP_{sat}}{P_{sat}} \approx \frac{h_{fg}}{R} \frac{dT_{sat}}{T_{sat}^2} \quad (3.53)$$

$$\int \frac{dP_{sat}}{P_{sat}} \approx \int \frac{h_{fg}}{R} \frac{dT_{sat}}{T_{sat}^2} \quad (3.54)$$

$$\ln P_{sat} \approx -\frac{h_{fg}}{RT_{sat}} + C \quad (3.55)$$

$$\Rightarrow P_{sat} \approx e^{-\frac{h_{fg}}{RT_{sat}} + C} \quad (3.56)$$

where C is some integration constant. This equation is often modeled from experimental data as the following:

$$\log_{10} P_{sat} = A - \frac{B}{C + T_{sat}} \quad (3.57)$$

where A , B , and C are tabulated for different substances in different temperature ranges. This expression is called the *Antoine Equation*. Fig. 3.5 shows an example of this curve plotted for water.

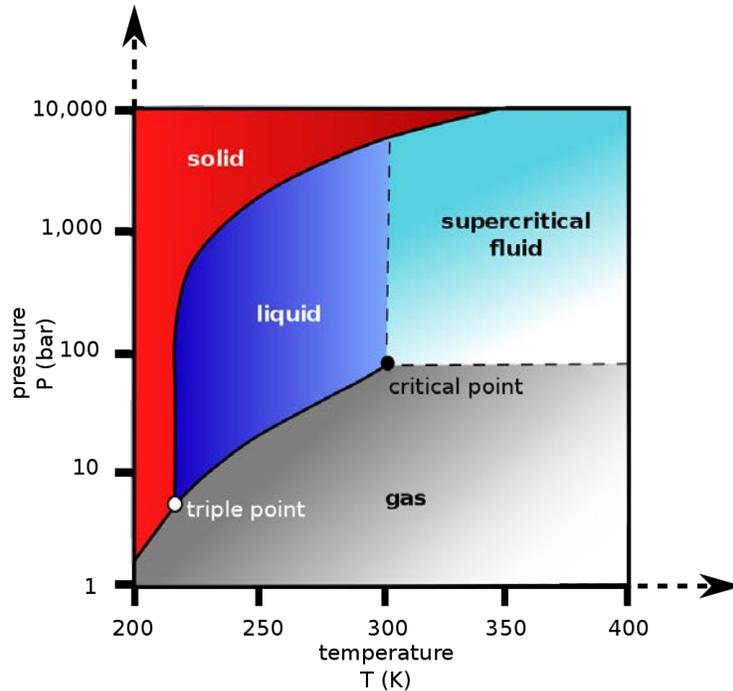


Figure 3.6: Generalized phase diagram for a pure substance.

Raoult's Law

These equations were all derived for a *pure* substance containing only one species. For a mixture, however, we have the simple expression - which closely mirrors Dalton's Law - that relates the total vapor pressure, $P_{sat,total}$, to the individual vapor pressures as

$$P_{sat,total} = \sum_i P_{sat,i} \quad (3.58)$$

where $P_{sat,i}$ is the vapor pressure of species i in the mixture and is given as

$$P_{sat,i} = X_i P_{sat,i}^{\circ} \quad (3.59)$$

where X_i is the mole fraction of species i and $P_{sat,i}^{\circ}$ is the vapor pressure of the pure species. Note that an *ideal mixture* is one in which this law is obeyed, but that is not always necessarily the case.

3.2.4 Gibbs Phase Rule

Stepping back and looking at the two-phase equilibrium conceptually, these expressions for the saturation pressure and temperature tell us that for a closed volume containing both liquid and vapor phases of a substance, the temperature alone can tell us the pressure in the volume and vice versa. Recall that for an ideal gas, in order to nail down the total state, we need to know two of the state properties: (v, P, T) . But if both liquid and gas are present, the state collapses to a single P - T curve. The number of variables required to fully describe a thermodynamic state is called the *degrees of freedom*, and is given by the *Gibbs Phase Rule* as

$$F = (\# \text{ Species}) - (\# \text{ Phases}) + 2 \quad (3.60)$$

where F is the number of degrees of freedom of the system.

So for an ideal gas with one species, we have $F = 1 - 1 + 2 = 2$ as we know. For our two phase equilibrium, $F = 1 - 2 + 2 = 1$, which again is to be expected. For an ideal gas mixture, we know that the total pressure is given by the sum of the individual partial pressures and so would expect we need an additional variable, the mole fraction, to fully describe the system. Indeed, for this case, $F = 2 - 1 + 2 = 3$. In general, the number of phases present can be determined by the phase diagram for a species. A generalized phase diagram is shown, for example, in Fig. 3.6.

3.3 Fuels

With this basic understanding of fire and combustion and how heat is released from combustion reactions and can interact with other surrounding substances, we can begin talking about combustible materials - wood, coal, oil, etc. - as *fuels*. Fuels have a several properties that facilitate calculations involving the energy they contain and, more importantly, their impact on climate change.

3.3.1 Heating Value

Now that we can compute the concentrations of combustion products for even incomplete combustion reactions where not all of the carbon in the reactants goes into CO_2 , we can figure out precisely how much heat is released in the reaction using what we learned earlier about taking the difference in enthalpies of products and the reactants. As should be familiar by now, this *heating value*

is also a function of whether the combustion is constant volume or constant pressure and the phases of the products. Also, by definition, the heating values presented as follows are given for ideal stoichiometric combustion reactions, though a non-ideal reaction heat release can be computed in the same way.

First, in Section 3.2.1, we showed that for constant pressure processes, the change in enthalpy is equivalent to the heat released in the reaction. This heat release is called the heating value at constant pressure and per unit mass is given by

$$q_p(T) = - \left[\sum_i (n_i \Delta h_{f,i}(T))_P - \sum_i (n_i \Delta h_{f,i}(T))_R \right] \quad (3.61)$$

where the negative sign ensures that q_p is positive for exothermic reactions. For constant volume processes, the heating value at constant volume per unit mass is given by

$$q_v(T) = - \left[\sum_i (n_i \Delta u_{f,i}(T))_P - \sum_i (n_i \Delta u_{f,i}(T))_R \right] \quad (3.62)$$

In nature, forest fires burning in the open or the combustion of methane in the atmosphere, for instance, are well-described as constant pressure processes.

Additionally, any combustion reaction that produces water - which includes all hydrocarbon, carbohydrate, and alcohol combustion reactions - has what are called a *lower heating value* (LHV) and *higher heating value* (HHV), which depend on the phase of the produced water. The LHV is the value that assumes all of the water generated is in vapor form, and thus the sensible heat released is lower as a significant amount of heat is contained within that phase change. Conversely, the HHV assumes that water produced is in liquid form, resulting in a greater quantity of sensible heat. As we saw earlier, the latent heat of water can be substantial and thus these values differ by a non-negligible amount. Methane, for example, at constant pressure has a LHV of 50.1 MJ/kg and a HHV of 55.6 MJ/kg. In reality, the actual heating value for the combustion of methane will fall between these values. In general, constant pressure combustion tends to be closer to the lower heating value as the conditions are not suitable to maintain liquid water.

3.3.2 Adiabatic Flame Temperature

As discussed in detail in Chapter 2, there is a fundamental difference between heat and temperature - though they are closely related. In the previous section, we learned about the heat associated with fire and combustion, but how can

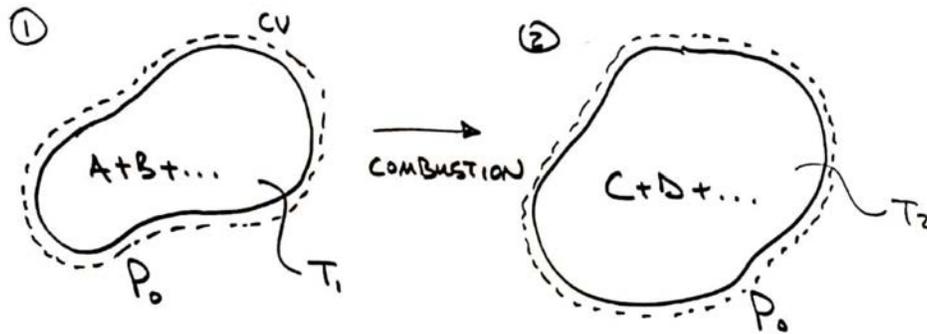


Figure 3.7: Constant pressure adiabatic flame temperature. No heat is transferred from the control volume but the control volume may do some work on the environment.

we define the temperature of such a reaction? The answer as we would expect is complex and depends precisely on the ambient conditions of the reaction, in particular how much other “stuff” is present to absorb the thermal energy. That said, we can compute an upper bound for the temperature if we assume all of the heat is contained within the reaction products themselves.

Because no heat is transferred in our idealized combustion reaction, we call this maximum temperature that can be achieved the *adiabatic flame temperature*. To compute this first for the constant pressure case, whose CV is given in Fig. 3.7, we start with the First Law:

$$\Delta U_{CV} = \emptyset - W \quad (3.63)$$

where we are given that $Q = 0$. Substituting our definition for enthalpy as before, we find that

$$\Delta H_{CV} = H_2 - H_1 = 0 \quad (3.64)$$

and thus that

$$\sum_i (n_i h_i(T_2))_P = \sum_i (n_i h_i(T_1))_R \quad (3.65)$$

which says that the enthalpy of the products must equal that of the reactants across the reaction. Because the products are different species than the reactants and therefore have different individual enthalpies, T_2 - the adiabatic flame temperature - must increase to satisfy Eq. 3.65. This is represented graphically on the H - T plot in Fig. 3.8. Typically, this problem must be solved numerically with a computer as the functions for h can be highly non-linear.

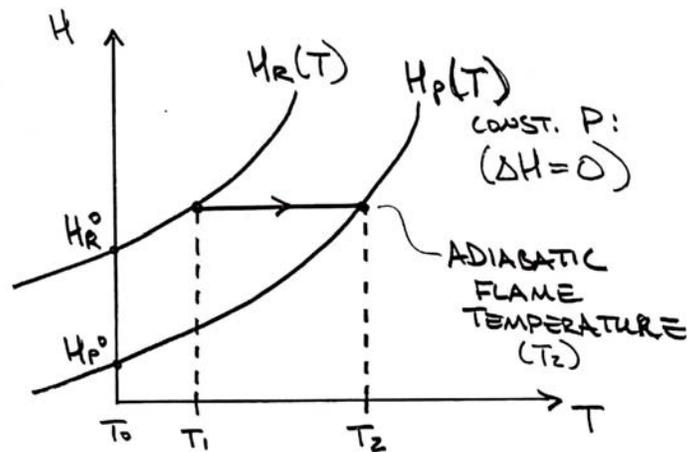


Figure 3.8: Adiabatic flame temperature (T_2 here) for constant pressure combustion.

Similarly, for the constant volume combustion case, we can start with the First Law, noting this time that because the volume of the control volume does not change over this process, there is no work done.

$$\Delta U_{CV} = \dot{Q} - \dot{W} \quad (3.66)$$

and thus that

$$\Delta U_{CV} = U_2 - U_1 = 0 \quad (3.67)$$

$$\sum_i (n_i u_i(T_2))_P = \sum_i (n_i u_i(T_1))_R \quad (3.68)$$

from which we can solve for T_2 numerically if we have functions for the internal energy of the products and reactants as functions of temperature. Fortunately, these values and values for $h_i(T)$ are typically available for most common species involved in combustion¹³. As with the constant pressure case, the constant volume combustion process can be represented graphically on a U - T plot as shown in Fig. 3.9.

¹³There are so many data on combustion reactions due to the work of NASA and the US Air Force in trying to figure out rocket propellants and jet fuel.

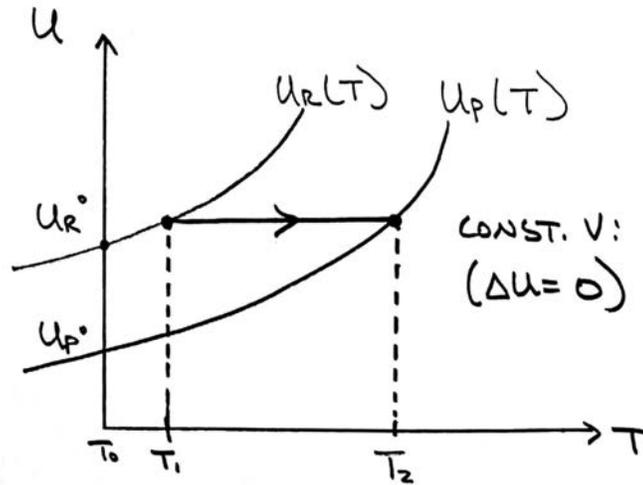


Figure 3.9: Adiabatic flame temperature (T_2 here) for constant volume combustion.

3.3.3 Carbon Intensity

The control of fire has come at the cost of a climate destabilized by the associated carbon emissions. We can quantify the carbon footprint of various fuels using the notion of *carbon intensity*¹⁴. While this value can be defined in several ways, we will define here as the mass of carbon dioxide produced per unit of thermal energy released. As an upper bound, the carbon intensity, $I_{\text{CO}_2\text{e}}$, is approximately

$$I_{\text{CO}_2} = \frac{m_{\text{CO}_2}}{q_p \text{ or } v} \quad (3.69)$$

and in general is bounded by

$$\frac{m_{\text{CO}_2}}{\text{HHV}} < I_{\text{CO}_2} < \frac{m_{\text{CO}_2}}{\text{LHV}} \quad (3.70)$$

where m_{CO_2} is the mass of carbon dioxide emitted per unit mass of fuel.

Looking at ethanol¹⁵ combustion at constant pressure, for example, it will react ideally with oxygen by the following:

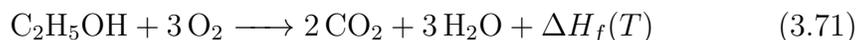
¹⁴also called *emission intensity*

¹⁵a naturally occurring alcohol produced in the *fermentation* of corn and other starchy vegetables

3.4. RELATED CONCEPTS

Table 3.1: Carbon intensities of common fuels

Fuel	Carbon intensity [gCO ₂ /MJ _{thermal}]
Wood	115
Peat	106-110
Coal	88-94
Oil	73
Ethanol	63-70
Methane (natural gas)	51-68



From this equation, we see that 2 moles of CO₂ are produced per mole of ethanol combusted, which is equivalent to 1.87 gCO₂/g ethanol. Working out the enthalpies for each of the products and reactants yields a LHV of 26.8 kJ/g and a HHV of 29.8 kJ/g, giving us an ideal carbon intensity between 63-70 gCO₂/MJ. For comparison, some common carbon intensities are given in Table 3.1.

3.4 Related Concepts

While “combustion” involves the breakdown of organic molecules using an oxidation reaction, there are other similar processes that either differ in the direction of heat transfer or in the usage of oxygen in the reaction. We will briefly discuss a few of the most common related concepts here.

3.4.1 Anaerobic Digestion

The combustion of an organic molecule requires that oxygen be used to break it apart - however, it is often possible break the same molecule down in the absence of oxygen. Glucose, for example, can be decomposed *anaerobically*¹⁶ via:



which occurs in specially evolved bacteria called *methanogens*. This reaction is exothermic, which you can verify experientially by noticing that compost -

¹⁶in the absence of oxygen

3.4. RELATED CONCEPTS

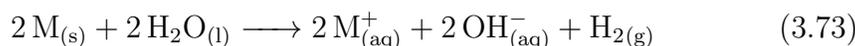
decaying plants and vegetables - is warm to the touch. Instead of being full broken down, however, considerable potential energy remains in the methane product of this reaction, as it can later be oxidized further by oxygen.

This reaction happens extremely frequently in nature due to the ubiquity of these bacteria. For example, this process occurs in the digestive tract of termites, which are capable of breaking down complex sugars in wood. In fact, termites alone are responsible for 1-3% of global methane emissions. In reality, they produce much more than this initially, but much of this methane gets oxidized to CO₂ inside the termite mounds before being released into the atmosphere [2]. Cows and other mammals that eat cellulose-rich plants as the majority of their diet also emit significant amounts of methane from their digestive processes. Consequently, global meat consumption has a significant impact on the climate, accounting for nearly 40% of human-activity-related methane emissions [3].

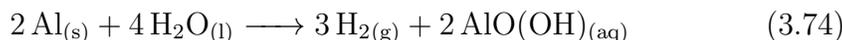
3.4.2 Hydrolysis

Hydrolysis is another anaerobic process capable of breaking down carbohydrates and even metals. Such a process is simply defined as an oxidation reaction that uses water as an oxidizer. In nature, this reaction is also extremely common and is often a precursor to digestion that occurs in living organisms. For example, many plants naturally produce sucrose (C₁₂H₂₂O₁₁), a *disaccharide* molecule containing both glucose and fructose and what is commonly referred to as table sugar. In order for other organisms to metabolize this sucrose into the more readily usable glucose, this molecule must first be split apart. This process occurs in digestion via hydrolysis.

The reaction of metals with water to produce hydrogen and a hydrated metal oxide - a process colloquially referred to as *rusting* or *corrosion* - is another example of hydrolysis. In general, this reaction can be carried out via:



where M represents a generic alkali metal. Aluminum will also react with water via



which is highly exothermic. Given the high abundance of aluminum on earth

3.4. RELATED CONCEPTS

and its high energy density, it is potentially ideal energy storage mechanism¹⁷ [4].

3.4.3 Pyrolysis

Many organic compounds when heated in the absence of oxygen will decompose in a process called *pyrolysis* whereby all volatile compounds like water are driven off and hydrogen and oxygen atoms are liberated, repeatedly breaking long carbon chains into smaller ones. This process is responsible in nature for turning dead plant matter into coal. In fact, most of the coal used today was formed over millions of years from plants that were once alive during the carboniferous period. As the plants decayed and their sugars were pushed deep underground, the high pressures and temperatures in the Earth's crust over time degraded these carbohydrates into nearly pure carbon.

3.4.4 Liquefaction

Liquefaction or *hydrothermal liquefaction* is a process that functions like pyrolysis but in reverse. Instead of converting complex organic molecules into charcoal, biomass is instead turned into even longer hydrocarbon chains under high pressure and temperature conditions. In nature, the crude oil and its derivatives that humanity has been burning for a couple centuries now, was formed as decaying biomass - mainly from algae and zooplankton that lived millions of years ago - got buried deeper and deeper in sediment at the bottom of large bodies of water. Under the intense pressure and in the presence of water, the carbonaceous remains of these critters reacted with water to form long chains of carbon, hydrogen, and oxygen. This added thermal and pressure work greatly increases the energy content of the original fuel¹⁸.

3.4.5 Gassification

The final related concept to look at here briefly is *gassification*, which utilizes the reaction of elemental carbon with carbon dioxide to produce carbon monoxide by the following equation:

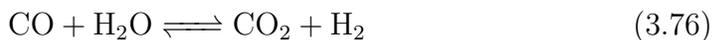


¹⁷though current carbon emissions associated with its reduction process currently limit its utility as a carbon-neutral storage mechanism.

¹⁸for more information see *catagenesis*

3.5. EARLY USES FOR FIRE

which can then be reacted with water to recover the carbon dioxide and produce hydrogen gas via the previously discussed water-gas shift reaction:



It is important to note here that not all of the carbon monoxide can be converted to carbon dioxide here, and thus this is not nearly a carbon-neutral process in practice. Also, if we look at the change in enthalpy across reaction 3.75, we find that this process is endothermic, requiring an input of heat equal to 173 kJ/mol carbon at 600 K. Typically, the heat required for this reaction comes from the burning of additional coal.

3.5 Early Uses for Fire

In our story of climate change, the discovery of fire - or more accurately, the ability to set fires - marked a new era of energy usage for life on Earth. Despite the long-term consequences of consuming stored solar energy in organic matter faster than it could be replenished, fire provided great utility to early hominids. First, fire simply provided warmth, allowing humans to greatly expand their reach into territories that were previously too cold to survive in. This also allowed permanent settlement to be established as they no longer had to migrate with the seasons. Additionally, fire could be used to ward off predators that previously created too hostile of an environment for survival.

In these early settlements, fire was also used to prepare land for what was to eventually become organized agriculture. The early humans likely found that burning large swaths of forests and other areas of dense growth was a convenient way to clear the land for farming. With farming came additional breakthroughs in diet and food preparation. The ability to cook food and purify water in particular reduced risks of infection and disease, and it also allowed for food to be stored for greater periods of time. The once hunter-gatherers were transitioning into farmers, and the control of fire played a significant role in that shift.

3.6 Summary

In this chapter we looked at the chemistry and thermodynamics behind fire - one of the key tools used by early humans to transform their evolution, expansion, and ultimately their world and climate. Fire (*combustion*) describes a wide variety of reactions between organic molecules or even metals and oxygen.

The heat produced in these reactions at constant pressure can be expressed as the change in enthalpy between the products and reactants. More generally, the enthalpy is an important thermodynamic properties derived from the sum of the more fundamental internal energy and the product of the substance's pressure and volume. Similarly, for constant volume combustion, the change in internal energy can be used to quantify the heat released.

We then looked at the stoichiometry of common combustion processes, including how various hydrocarbons can be oxidized to varying degrees of completion. To that end, we also learned about reaction equilibria to give us the tools necessary to determine the equilibrium concentrations of the products, allowing us to accurately determine the heats of reaction under different environmental conditions.

With an understanding of the basic chemistry underlying combustion, it is then possible to discuss substances as potential fuel sources¹⁹. We saw how these substances could be characterized by their heating value and carbon intensity - how much thermal energy is released relative to the quantity of carbon dioxide produced in the process. In this way, we can begin to quantify the impact of human development on the climate in terms of their production of greenhouse gases. As we will soon see, burning these fuels can be used to power mechanical work with the advent of the engine, providing additional motivation to keep producing such gases.

Bibliography

- [1] Bonnie J. McBride, Michael J. Zehe, and Sanford Gordon. NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species. Technical report, NASA Glenn Research Center, 9 2002.
- [2] Philipp A. Nauer, Lindsay B. Hutley, and Stefan K. Arndt. Termite mounds mitigate half of termite methane emissions. *Proceedings of the National Academy of Sciences of the United States of America*, 115(52):13306–13311, 12 2018.
- [3] R. John Wallace, Goor Sasson, Philip C. Garnsworthy, Ilma Tapio, Emma Gregson, Paolo Bani, Pekka Huhtanen, Ali R. Bayat, Francesco Strozzi, Filippo Biscarini, Timothy J. Snelling, Neil Saunders, Sarah L. Potterton, James Craigon, Andrea Minuti, Erminio Trevisi, Maria L. Callegari,

¹⁹The desire to look around and ask which of these things can be used as fuel is eminently human.

BIBLIOGRAPHY

- Fiorenzo Piccioli Cappelli, Edward H. Cabezas-Garcia, Johanna Vilkki, Cesar Pinares-Patino, Kateřina O. Fliegerová, Jakub Mrázek, Hana Sechovcová, Jan Kopečný, Aurélie Bonin, Frédéric Boyer, Pierre Taberlet, Fotini Kokou, Eran Halperin, John L. Williams, Kevin J. Shingfield, and Itzhak Mizrahi. A heritable subset of the core rumen microbiome dictates dairy cow productivity and emissions. *Science Advances*, 5(7):8391–8394, 7 2019.
- [4] Peter Godart, Jason Fischman, and Douglas Hart. Kilowatt-Scale Fuel Cell Systems Powered by Recycled Aluminum. *Journal of Electrochemical Energy Conversion and Storage*, pages 1–14, 3 2020.

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