[SQUEAKING]

[RUSTLING]

[CLICKING]

GIAN PAOLO BERETTA: OK, good morning. So we started talking about systems with chemical reactions. And we-- to just go quickly over what we have done so far, we considered the two most representative setups, the closed system up here and the open system setup, for which, of course, when we analyze, we have to make at least the energy and the entropy balance, and sometimes also-- here also the volume balance.

And these balances take these forms, where these differences between properties of the products and the reactants, energy, entropy-- here, the enthalpies because we have bulk flow interactions-- are important.

And they have the feature that we need to-- we need to deal with the fact that the composition changes now because as the process proceeds, we have a chemical reaction in place-- one or more chemical reactions in place.

We introduced the notation for stoichiometry and the proportionality relations. And we defined the properties of reaction as a way to concentrate the part of the change in the properties that has to do with the change in composition in this last term, where we have the product of the reaction coordinate and what we called the property of reaction.

For example, this is the energy of reaction, the enthalpy of reaction. But the same way we can define also the entropy, the Gibbs free energy, and the volume of the reaction. And remember that if-- the 0 here means standard pressure, so 1 atmosphere. And the 0 here without the temperature dependence means also standard temperature. So STP means-- is standard temperature, 25 degrees C, and 1 atmosphere.

It may seem that we have to measure properties of reaction for every reaction that we have to deal with. But fortunately, that's not necessary. All we need to do is to measure the properties of reaction for what we will define as the reactions of formation.

The properties of reaction-- for example, this is the reaction of formation from molecular hydrogen, which is the most stable species for hydrogen at STP. And it's the formation from that to atomic hydrogen, which is not-- which is also an elemental species, but it's not the most stable.

And in order to go from here to there, we have to break this hydrogen bond. And that requires energy. And this is why the curve that represents the equilibrium state for hydrogen, even at 0 temperature, is above the curve that represents the molecular hydrogen states. And at 0 temperature, this difference is precisely what we call the bond energy.

Instead, what we call the property of reaction doesn't refer to 0 temperature. It refers to standard temperature, T0. So it is the difference between that property-- in this case, the enthalpy, if we go vertical-wise, or the entropy, if you go horizontal-wise, from-- the difference in the enthalpy or entropy between this state and that state. OK, so these represent graphically the enthalpy of reaction and the entropy of reaction.

We ended the last lecture with this graph that wants to point out that even the bond energies can be described somehow by means of the Lennard-Jones potential. That is a possible, reasonable model-- perhaps not the best, but it is simple enough that one can use it.

And the values of the parameters, the Lennard-Jones parameters, for atomic bonds, bond energies, bond energies are at least three orders of magnitude stronger than the van der Waals forces. They are all electrostatic forces, but the ones that you need in order to form this bond are much stronger.

Not only they occur at closer distances-- you see, this is at 0.7 Angstrom with respect to the bottom of the Van der Waals forces, which is about 3 point something Angstrom for the liquid-- for example, this is liquid water.

And also notice that, yes, I have plotted this, but in order to make it visible, I had to multiply it by a factor of 1,000. Otherwise, it would be almost flat as compared to the strength of the atomic bonds, covalent bonds.

OK, now, the properties of reaction, as we have seen, at 0 temperature, are related to the bond energies. So, for example, if I take-- this is the reaction of formation of water, of two molecules of water, from two molecules of hydrogen, of molecular hydrogen, and one molecule of oxygen.

In order to go from this configuration to this configuration, you have to break these two hydrogen bonds and the oxygen bond and then reassemble in this other way. At the end, in this other way, in two water molecules, you have four times an oxygen-hydrogen bond, OK? Four times.

The strength of these bonds are listed-- are plotted, are measured. You find tables that provide this strength and also the typical distance between atoms, between the nuclei in these bonds. For example, the blue one is the hydrogen. It's the closest. It's at 74 picometers-- that's 0.74 Angstrom.

The oxygen is here. And in the middle, we have the hydrogen and oxygen bond.

And, in fact, if you take the depth-- so the strength of these potentials-- so the epsilons for the Lennard-Jones for these bonds, and you do the simple counting of what's the difference between having four of these ones, four of these ones that are worth 459, as compared to two of these ones, the hydrogen that are 432 and one oxygen, 495, you find that the difference is in favor of this one.

So these are more stable. They are less-- they are more strongly bound. And this number, which is by the accounting of the bonds, is very close to the enthalpy of formation of 2 moles of water.

The difference stays mostly in the fact that whereas the bonds are computed at 0 kelvin, the enthalpies of formation are listed at standard temperature and pressure. So you have to correct in going from here to here for the specific heats from 0 temperature to 298 K.

And if you do that correction, you get closer to this number. So in a sense, this is to say that the Lennard-Jones representation is not bad for giving a first look at what these properties of formation, and at least the enthalpy of formation, comes from.

Now, this slide wants to describe what's behind the Hess relation and these properties of formation.

So it turns out that we don't need to measure all the properties of reactions, but only those of a formation from a set which is complete enough that-- so we define a complete set of independent chemical species from which you can construct any other molecule.

So these are like the building blocks of chemical compounds. And typically, they are called the elemental species.

In order to define this set, you need to request two conditions. The first is that, yes, every molecule must be-- you construct any chemical species, and you have to be able to construct it from these elemental species, according to a chemical reaction of formation, which is this one.

Now, in our notation, where we put everything on the left-hand side with the plus stoichiometric coefficient for the products and with the negative stoichiometric coefficient for the reactants, this is the way we would write our reaction.

But you could also write it this other way. And formally, these will be useful in one step below. The other condition that you want to impose is that the set of these species be independent from one another so that it is impossible to convert one into the other or several into the other.

That condition is written by saying that if you ever write a chemical reaction that involves only elemental species, that reaction has to be identically trivial-- so 0. All the stoichiometric coefficients must be 0. Otherwise, it would be possible to transform gold-- I mean, lead in gold, like-- instead of chemistry, you do alchemy.

So the practical choice is to select-- the practical-- the conventional choice is to select as elemental the species that have only one type of nucleus. For example, the oxygen molecule has two nuclei, but they are of the same kind, so only one kind.

And plus, since you know that-- for example, oxygen, you can find it in several molecular configuration, like atomic oxygen, the ion, or ozone, O3, and O2-- you pick the one that is most stable at standard condition. So in this case, for oxygen, you take O2.

And it turns out that you have to select one species for each atomic number in the periodic table. I'm sure you remember the periodic table. And Z is the number of protons in the nucleus of the atom.

And the actual-- the isotopes, which has to do with the number of neutrons that are in the nucleus of the atom, don't count for chemistry, because chemistry is mostly-- what's responsible for chemical reactions is the electrical-- the electrons and the protons and not the weight of the nucleus, which is instead important for nuclear reactions.

And, of course, I think you can proceed in a similar way also if you are interested in nuclear reactions. So you want to apply this same kind of reasoning to the properties of formation of nuclei.

You would have to define a set of complete and independent nucleons. And typically, you would choose the proton, the neutron, and the electron, and-- what else? I don't know. Maybe quarks are the different level.

Anyway, so then, for this reaction of formation, you select your compound, and you find the stoichiometric coefficients in terms that are needed in order to construct your compound from the elemental species. These are the alphas.

And then you write down according to our rules-- so the summation of the stoichiometric coefficients times the properties of the pure components that appear in the reaction at STP. And this gives you the property of reaction. And since it's the reaction of formation, we call it the property of formation of your compound i.

Now, it turns out-- and this is the good-- the practical aspect of this choice-- it turns out that you can safely arbitrarily select the reference value for the property at STP of the elemental species.

And since it's arbitrary-- in other words, it will not-- it will cancel out your calculations in chemistry-- you can set you can select any number. So the simplest is to set it equal to 0.

Why so? Well, because in your chemical problems, you will have to deal with chemical reactions that have this generic form equal to 0. So 0 equals the stoichiometric coefficients times the chemical compounds.

Now, each chemical compound, like here, can be obtained from the elemental species. So we can formally substitute this formula here for the compound in here. And we get the chemical reaction that involves only the elemental species. By the condition of independence that requires that this set of stoichiometric coefficients be all identically equal to 0.

This is more or less the formal expression of what you do when you fix the stoichiometric coefficients in a reaction. And you balance the reaction by putting the proper stoichiometric coefficients. That's what you're searching for, the nu sub i's that satisfy-- that solve this equation.

So now, since we are interested in general in this kind of reaction, the property of that reaction-- for example, the energy of reaction for that reaction-- is given, is defined this way.

If you substitute this expression here-- because, you see, here we have these pure component energies at STP for your substances that appear in your reaction. And you can write them in terms of the properties of formation and these other summation that you take on the other side. So this is the substitution.

And then you bring the summation in, and you find that this second contribution has coefficients that are identically 0 for the reason that we just mentioned before. So this summation cancels away.

And therefore, you find that the property of your reaction is equal to the weighted sum on the stoichiometric coefficients of your reaction of the properties of formation of the various components that appear in your reaction. This is called the Hess relation.

And the fact that these things are multiplied by 0 allows you to select any-- their value being not important. So you conventionally select those equal to 0. And also, you could safely select that the STP value for the pure components are equal to their properties of formation, like we do here, setting these equal to 0.

There is another minor but dangerous complication-- dangerous if you forget about it in your calculations-- that most of the tables have-- since much of this has been developed, when people dealt with combustion problems, and the products of combustion are in the gaseous phase, in practical applications, people are listing the values of formation of the species when they are in the gaseous phase.

But many species-- for example, water-- at standard conditions is not in the gaseous phase because at 25 degrees C and 1 atmosphere, water is liquid. Yet in the table, you find the property of formation of water in the fictitious gaseous state.

So what's that? OK, that is sort of an extrapolation of water vapor from the range of states in which it behaves as an ideal gas for which you know the properties-- for example, the specific heats at constant pressure. And you know them as a function of temperature. They are given by correlations. We'll see some in a moment.

And what you do is to extrapolate those properties down to standard conditions as if that substance kept behaving as an ideal gas down to those STP. And that's how you compute this, from this temperature T where it behaves as an ideal gas down to here.

And also, for the entropy, you just apply the laws of ideal gas and extrapolate down to STP. OK, so these are details.

And when you compute-- yeah, these tables give values for the enthalpies of formation of a number of compounds, from which you can cook up all sorts of chemical reactions.

For example, we are interested in combustion of methane or the combustion of isooctane. Isooctane is close to gasoline, and methane is natural gas, the main component in natural gas. So these are important for energy applications, as you know.

So in order to write this-- this is the representation of the complete combustion, so the simplest model for oxidation of the fuel, complete oxidation of the fuel.

And so the stoichiometric coefficients are minus 1, minus 2, plus 1, plus 2. Then you pick from this table the values of the enthalpies of formation. So, for example, you look for CH4, which is methane. It's up here. It's minus 74.9. So that's where you get this number.

The elemental species have no value for the property of formation. It's 0 for them. So you can recognize them here. These are the elemental species-- hydrogen, nitrogen, molecular oxygen. So you get 0.

Then you have CO2. So you look for CO2, which is here, minus 393.8. And then you get water, which is here at the bottom, 242. Then you can calculate this.

These numbers are in megajoules per kilomole-- or, say, kilojoules per mole. And if you divide by the molecular weight for methane, 16, you get this number, negative 50 megajoules per kilogram.

For isooctane, it's a much higher molecular weight. So mole-wise, it's a much higher enthalpy of reaction. And that's because you have many more bonds to break per molecule.

But if you divide by the molecular weight, you get a number which is of the same-- very close, same order of magnitude as this one. And actually, this turns out to be true for all hydrocarbons. I thought I had it in the next slide. We don't. It will come up in a moment. OK.

So negative means that the reaction is exothermic. And we will see now what the sign of these properties imply in determining the direction of spontaneous evolution of the reaction.

So let's take the steady-state reactor setup. And let's assume that we want the reaction to occur at constant temperature and pressure, meaning that the inlet flows and the outlet flows are going to be kept at the same temperature and pressure.

And this is going to be done with a heat interaction at some temperature TQ. For this moment, for this slide, this temperature of the reservoir is not necessarily the same temperature of the inlet at which you want the reactor to operate.

We do our energy balance and our entropy balance. We combine them by eliminating Q dot. And here's the outcome.

It gives the entropy production by irreversibility multiplied by TQ, the temperature of the heat source-- or, say, heat bath or heat reservoir, thermal reservoir, whatever you want to call it, is equal to minus epsilon dot, which is the reaction rate, the rate of the reaction coordinate, times this combination of the enthalpy and the entropy of reaction, which looks like the same kind of combination that we have in available energy, or, actually, exergy.

If you look back into when we did a review of exergies in bulk flow, the difference in enthalpy minus the temperature of the reservoir times the difference in the entropies between inlet and outlet, that is the exergy of your flows. So this is the exergy related to-- the exergy difference between the products and the reactants with respect to that reservoir at temperature TQ.

Now, when epsilon dot is positive, the reaction is forward. It means that it's proceeding into producing products, consuming reactants. So the fact that, of course, entropy cannot be destroyed-- so that this has to have always a positive sign if it has to really occur-- gives you a criterion to decide whether the reaction will be forward or backwards at that temperature, because if you want it forward, you need epsilon dot to be positive.

So if that's positive, in order for this to be positive, you need this linear combination to be negative. So in this table, you can summarize the possibilities.

So if you want that to be positive, and you want it to be positive at all combinations, you could make sure that the enthalpy of reaction is negative-- so that is an exothermic reaction-- and also that this term doesn't influence the sign of the overall linear combination.

So certainly, if the entropy of reaction is positive, you're safe because this also gives a negative contribution. You're also safe if it is negative, but not too negative, because this will-- with the minus sign in front, if it is negative, it will be positive.

It eventually could cancel out the negativeness of the enthalpy. And so you could reverse the fact, which happens if this is not satisfied-- or, actually, if this is satisfied.

OK, so, you see, these properties of reaction give you the key to understand whether the reaction will go in the direction you want, because, typically, you bother constructing reactors because you want to consume some products in order to-- some reactants in order to produce some products that you want.

Now, if we repeat the same, but with the same temperature as-- so the heat bath or the thermal reservoir has the same temperature at which the reaction occurs.

So when you have your reaction, for example, placed in a calorimeter or in a thermostat-- so it's a thermostatted reaction at constant pressure, again-- and this pressure is the atmospheric pressure-- again, your balance equations is exactly like before, only the TQ now is becoming equal to T.

And then this makes-- this linear combination is the Gibbs free energy of reaction because h minus Ts is the Gibbs free energy.

So this is why they typically say that the reaction occurs in the direction of negative Gibbs free energy. Yes, you need the Gibbs free energy of reaction to be negative in order to the epsilon dot to be positive.

However, this depends on temperature because the Gibbs free energy is a function of temperature. And actually, in the next slide, we will prove this relation here, that the way the Gibbs free energy changes in temperature is this way, is related to the enthalpy of the reaction.

So the rate of change of the Gibbs free energy divided by RT with respect to temperature is equal to the enthalpy of reaction divided by RT squared. This is that relation.

And that is the proof. The proof comes from an old friend of ours, which is this relation that gives the enthalpy in terms of the chemical potential for the pure substance. The chemical potential is the Gibbs free energy. If you go back in your notes, you find this relation. And if you put it inside here, out comes this thing.

And this plot has here-- it plots versus-- this is not temperature. It's 1 over T. It's a 1 over T scale. So actually, the scale is here is 10 to the 4 over T. So it's a 1 over T scale, which is precisely the thing with respect to which we're doing the derivative.

And this axis instead shows delta g over RT. Yeah, there is the logarithm of 10 because this is done on-- this is the log of-- the Napierian log instead of log of 10.

But apart from this factor, this shows the dependence of delta g over RT versus 1 over T. It's almost linear. And these slopes, the slopes are represented by the negative of the enthalpy of reaction.

So for the exothermic reaction, this is positive. So you see these ones that go up are the exothermic reaction. For example, CO plus 1/2 O2 is CO2, or water is here, H2 plus 1/2 O2 is H2O, and so on.

And you see that-- so if this is positive, because the relation that we proved in the previous slide was that the entropy produced by reversibility divided by the reaction rate-- so if this is positive, that is also positive. You need this number to be positive.

So from here up, you have all product-favored reactions. But for each reaction, for even that of formation of water, if you go sufficiently high in temperature-- and as I go down-- high in temperature means 1 over T goes down.

So if I go down here, eventually, I will find a temperature-- for water is of the order of, what, maybe 5,000 K. It becomes negative. So it becomes reactant-favored. So water dissociates instead of--

And the same is for true for CO2. CO2 also dissociates at higher temperatures-- high temperatures.

This, of course, is important because in combustion, it's true that the oxidation of a fuel produces CO2 and water. But if you are very high in temperature, like in an adiabatic flame setup like the one we will consider in a moment, the temperatures are so high that the reaction-- that CO2 and even water, a little part dissociates.

And of course, if it dissociates, it consumes some energy in order to break those bonds that are particularly stable.

Another setup that is important is precisely the adiabatic setup in which we have a reactor which is insulated-- so no heat, no work interaction. Just the reaction itself makes things happen.

And this time, of course, you cannot have the same temperature of the outlet. So in the outlet, you have a different temperature of the products. And we call it T ad for adiabatic.

Of course, you have to write an energy balance. And the energy balance this time will be simply that the net of the enthalpy coming in with this bulk flow must be equal to the enthalpy going out with this outlet bulk flow. So these must be equal, too.

So this gives you one relation that allows you to solve for the adiabatic temperature-- adiabatic product temperature. And once you solve for that, you go into the entropy balance. And that allows you to compute this difference.

And you can write this S dot irreversible-- one way is to write it this way. Yes, here it is.

Yeah, you essentially add a 0. You add the entropy balance-- i'm sorry, the energy balance, which is 0. So you can add it. It doesn't change the entropy balance.

And you multiply the entropy balance by T so that it becomes dimensionally an energy. And then what you get, you can split the outcome as two parts. One is our familiar Gibbs free energy of reaction term multiplied by the epsilon dot.

And these other terms are essentially-- as they're written here-- are essentially the difference in the exergy of your products at this temperature from the reactants. I'm sorry. I take it back.

It's the difference between the exergy that the products have at this temperature-- you see, this is still P-- and that they have a temperature of the reactants. So it's the difference, between Tad and T, of the exergy of your products.

And so you see if you want the reaction to occur in that direction, you need delta g to be negative. But it must be negative enough to overcome this exergy here.

And this exergy is what will be-- you could deploy in applications. For example, if this is high temperature, you could use it to run the heat exchanger of a thermal cycle to produce electricity and so on. We will do the calculation for fuels.

Again, another setup is the exergy kind of discussion. Here we use TQ as a different temperature, as the temperature at which you want your reaction to occur.

And you assume also that this-- I shouldn't really call it a reactor, but it's a reactor that is going to be part of some more complex system that contains also machinery, thermal cycles, whatever you want, in order to produce some work.

So this is like a box, which could be a power plant that takes in reactants, produces your products. It could be a materials processing plant that takes in raw materials and produces your material, what you desire to manufacture.

Now, in some cases-- you write, as this is ?] usual, the energy and entropy balance, and you compute now the work. So the work, in some cases, depending on the conditions and the values of these properties of reaction, sometimes, you can do work. And the maximum work you can do is given by this.

And if you have entropy produced by irreversibility, that will detract from the maximum you can do. So your actual work will be less than the maximum because there is a minus sign here. Sometimes, you cannot extract work, but you actually need to spend work in order to make that occur. This is the minimum work you need to spend.

And if you have irreversibility, that will detract. And now the sign becomes plus, and it will add up to the minimum. So in practice you'll spend more work than the minimum requirement.

So let's do something more specific about the oxidation of hydrocarbons in this very simplified view in which we consider the overall basic reaction mechanism of complete oxidation of a hydrocarbon as if there were only that one, which is not true.

But in this simplified view, you already can do a lot of interesting considerations and calculations.

First of all, you notice that the mechanism involves a fuel, a hydrocarbon. k is the number of carbon nuclei in the molecule, and l is the number of hydrogen nuclei in the molecule.

You need oxygen. And the two main products are CO2 and water. And that's the balanced stoichiometric coefficients.

Typically, when you burn a fuel like this, you don't do it in pure oxygen, although you could do oxy-combustion. But you do it in-- you use air as an oxidant. And so oxygen is going to be only one of the components in the mixture of your oxidant. The mole fraction of oxygen in air is about 21%.

So if you want 1 mole of oxygen to be available for your fuel, you need this divided by-- so 1 over this is, like, 4.77 moles of air. And therefore, the stoichiometric amount that you need, since for 1 mole of the fuel, you need k plus l over 4 molecules of oxygen, that means 4.77 times this of air.

So this gives the stoichiometric air/fuel ratio. The s stands for stoichiometric. If you are more interested in weight fractions, this is the air-to-fuel ratio mass-wise. You have to multiply by the molecular weight of air and the divide by the molecular weight of the fuel.

Also, if you need to completely burn your fuel, you want to make sure that if you have a combustion application, you don't leave unburned hydrocarbons around.

So, for example, if you think of a combustion chamber in the internal combustion engine, yeah, it's loaded with fuel. And you have the molecules of fuel spread around in the combustion chamber.

And if your air is just the stoichiometric amount, chances are that the last molecule of fuel will be on one side and the last molecule of oxygen on the other side, and they will not encounter. So you miss that. And so you're going to have some unburned fuel.

So for this reason, you provide extra air, extra oxygen. You provide some excess air. So the actual fuel/air ratio that you use is more than the stoichiometric amount. And the ratio of what you actually put over the stoichiometric is called equivalence ratio.

We already talked about the heating values of fuels being in the range-- more or less in the range. And now, hopefully-- OK, here is the list for the various hydrocarbons with molecular weights that range from 2 of hydrogen to 16 of methane, 114 of isooctane, and up.

And you see that the enthalpy of reaction, except for hydrogen, which is much higher, or for carbon, which is lower, in terms of megajoules per kilogram, the others are all in the range between 40-- this one-- but between 44 and 48, more or less-- 50 for methane.

And also, you could compute the entropies. Notice that the entropy of reaction-- of combustion does not necessarily have to have a positive sign. For some fuels, it's negative.

What's important for the application that you have already used in your homework is that the difference between the enthalpy and the Gibbs free energy is small, percentage-wise in terms of the Gibbs free energy, which is related to the exergy of the fuel.

You see that this ratio is between plus and minus 2.4%. So this allows you for simple calculations to neglect the difference and say that the exergy of the fuel, which is the Gibbs free energy-- minus the Gibbs free energy, is almost equal to the lower heating value of the fuel, which is the enthalpy.

This other table provides more specific values for heating values, and also the air/fuel stoichiometric ratios for some practical fuels, and introduces to the idea that heating values-- as you know, if you buy a burner for your house, you have to deal with the salesperson that gives you efficiencies.

And sometimes-- most of the times, the efficiencies are based on the lower heating value. But nowadays, they're selling a lot of condensing burners where they exploit also the heat of condensation of the water that is in the products of combustion.

And therefore, the proper reference for computing efficiencies there would be the higher heating value. Sometimes, they play with this difference because that difference can be large. For example, for natural gas, it's about 10%, which is not an unimportant amount.

So where does that difference come from? So we have to distinguish between lower and higher heating values. And we have to therefore consider how much of the water that is present in the products of combustion condenses.

Now, the setup here is the setup of Raoult's law. We are at pressure p. We have water vapor plus-- let's call it 2-- the other products of combustion. And water vapor is the one that can condense-- that condenses, at least part of it, at a given temperature.

And, of course, we have dealt with this problem, and we proved the Raoult's law, that the Raoult law tells you what is the amount of water vapor that is in the gaseous phase when there is equilibrium with the liquid phase.

And there cannot be more water vapor here. So that amount given by the Raoult's law is the maximum that can be dissolved in the gaseous phase. If you have instead less than that amount, then there is no condensation.

It's like for today. Today, we have rain. So that means that moist air has more water than it can stay there. And therefore, it drops, condensates, and then we get rain.

On a drier day, there is less water vapor, and it's below the threshold for condensation. So this is all in this expression here. But, of course, it's Raoult's law with the mole fraction in the liquid phase equal to 1, because we assume that this liquid phase is just pure water. There's no salt dissolved or other things.

All right, so Raoult's law gives us the maximum. So the actual amount is called the relative-- the actual amount divided by the maximum is called the relative humidity, relative to the maximum that you can dissolve.

And the saturation pressure is that of pure water. And at standard temperature, 25 C, that pressure is about 3.17 atmospheres (slide was wrong, I meant kiloPascals). So you see that by taking the pressure down here-- so you can-- this is about 3 atmospheres (read kiloPascals) divided by 101, which is atmospheric pressure. This ratio is equal to the maximum.

So the maximum-- instead of y1s, this should be y1gmax-- is 3%. So out of 100 moles of stuff in the products of combustion, at most 3 can be water molecules. If you have more, your combustion reaction produces more water, then the extra will condense.

So if you do the inventory for water, this is the amount produced by your reaction. So in the products, that's the amount. Some of it remains in the gaseous phase. Some of it goes into the liquid phase. It condenses.

And the stoichiometry tells you that per unit amount of fuel, the amount of water produced is l over 2. So this l over 2 will be split into partly condensed and partly water vapor.

The mole fraction in the water vapor is defined as the amount of water that remained in the vapor phase divided by the overall amount in the vapor phase. And so the overall amount is the overall products of combustion minus the water that has condensed. So it went away from the gaseous phase. So this is the mole fraction. And the total amount is given by this stoichiometry.

So if you combine all that, you get that the maximum amount of water that can stay in the gaseous phase is limited by this combination of the l and k's that describe how many carbons and hydrogens you have in the fuel molecule.

And when you have condensation, which happens when l over k is greater than 0.4, this is the amount that condenses.

OK, so if that amount condenses, it releases the enthalpy of vaporization of water. And that enters into your balance equation.

And so the heat that you need to-- when you compute the heating value at standard temperature, you're actually making an experiment in which you have your reactants come in at STP, produce your products, and you need to put some heat out at temperature T so as to cool the products down again to this temperature here. So that's the setup in which you measure this value.

And this is the entropy balance-- I'm sorry, the energy balance. That defines per unit-- so the amount of heat that you have to extract per unit of amount of fuel that you have burned in that experimental setup is the actual heating value.

And part of it is equal to the negative of the enthalpy of reaction. And part of it is due to the condensation enthalpy. So if you do the calculation, for example, for methane, the value is, in megajoules per kilogram, 54.7. If you neglect this condensation, it's only 50.1.

And the other extreme is if you want to have an even quicker calculation and forget about the amount of water that remains in the gaseous phase and assume that everything, every single molecule of water that has been produced, condenses, then you put l over 2 here. And you get what is called the higher heating value. It's 55.5.

So there is heating value and heating value. So the actual-- the lower if you neglect condensation, and the higher is you a bit overestimate condensation.

So this reactor that we just considered, it's represented again here. And in this setup, with this setup, we can consider three possible cases. The one is the heating value, the one that we just did, in which there is no work, and you set the outlet temperature of the products to be standard, like the inlet in this setup that defines the combination from which you measure the heating value.

The exergy setup, the exergy of the fuel, is one in which, again, you have the products out at atmospheric or standard temperature. But your reactor has some system inside that allows you to extract work, and actually does it reversibly.

So if you do it reversibly-- so in order to obtain the maximum work, you set the entropy produced by irreversibility equal to 0 in your entropy balance. And the outcome is this one. The exergy of the fuel turns out to be equal to the negative of the Gibbs free energy at STP.

And notice that in this calculation, see, while here you only have the enthalpy difference-- and in the enthalpy difference, then you need to account for condensation-- here you have the enthalpy difference, but also the entropy difference, and they are multiplied by the temperature T0.

So one brings in the enthalpy of vaporization. The other brings in the entropy of vaporization. And they are related to one another. For a pure substance, you have this identity that h fg is equal to T s fg at every temperature because of the condition of mutual equilibrium between the liquid and the vapor.

So these two contributions cancel out. So this delta g negative does not have contributions from condensation. The condensation doesn't play a role in the exergy of the fuel.

If you want, what I'm neglecting here is the mixing entropy terms that are here, depending on how you put in your fuels. Certainly, the air is a mixture of oxygen and nitrogen.

Sometimes, you put in your fuel premixed. So you mix the fuel with the air. So you have a mixture. And in the entropy balance, you should consider the mixing terms.

And then also the products of combustion is a mixture. And so you have an entropy term. So somehow, these are approximations in which we are neglecting mixing entropies.

The final setup of this is one in which you compute the adiabatic flame temperature-- no heat, no works, just an adiabatic insulated reactor in which you just have this combustion reaction occur.

The energy balance is this one. Now the enthalpy of the products has to be computed at temperature T ad, T adiabatic.

We can add and subtract the enthalpy of the products at standard temperature so that this difference here is the same that appears here in this other setup. And we've already computed it. It's the heating value times epsilon dot.

And this is just the sensible heat that is-- sensible, yeah, heat that is required to heat up the products from standard to adiabatic flame temperature. And you can compute that by simply using the properties of an ideal gas.

You can actually start even from standard temperature, even for water, because in the heating value, which is on that part, you assume that water is in the fictitious gaseous state. So you can use those correlations for specific heats and integrate.

Of course, this gives you an equation in which T adiabatic is the only unknown. And you can solve for it.

Once you find it, you can put it in the entropy balance. Also, the entropy balance, which is this one, entropy of the outlet, is greater than that of the inlet. And the difference is the entropy produced by irreversibility. You can add and subtract the entropy of the products at standard conditions.

And so this last difference is equal to the entropy of the reaction times the reaction coordinate. And this initial difference you can obtain by integrating the formulas for an ideal gas mixture.

When you do these kind of calculations-- and we have a couple of tables that show these numbers later on-- you compute the entropy of-- these typical values are in the range between 26% and 30% of the negative of the Gibbs free energy of-- so if you take T0 and put it on the other side, T0 times S irreversible is the waste of-- the exergy destruction-- is the source of inefficiency of your system.

And that is equal to about 26%, 30% of the exergy of the fuel. So that means that by burning your fuel in a steady-- in a reactor like this, you're wasting about 25% to 30% of the availability of the fuel without having consumed one single unit of energy.

And this is, if you remember, the reason why I told you that if we ever will follow history and we'll have power plants or a production of electricity that will exceed our current 65% of the best available technology, we will have to find alternatives to burning fuels this way, in adiabatic flames, because we need to overcome this 25% loss of efficiency-- of potential efficiency.

Now, if you've seen in the previous slide, we need to do those integrals to compute the enthalpy and the entropy, the difference for the products of combustion between the standard and adiabatic flame temperature.

One way to do that calculation-- this is just a detail, but you can find correlations for the specific heats of the various substances. And one way-- one correlation that is given in the book and from which I have extracted some of these numbers, this kind of correlation is able to cover with a single correlation the range from standard to 5,000 K with very good approximation.

Otherwise, in typical software they use, they split the range with a correlation that holds between standard, say, 25 C and, say, 1,000 K, and another correlation from 1,000. So you have to split the integral into two parts.

The thing that was into these integrals here, you see, it's the summation of the specific heats of the various products weighted on their mole fractions in the product stream. And also, for the entropy, it's the same thing, only divided by T.

So you need to compute these. And with that kind of correlation, you can do it simply by using a correlation with similar fractional powers of the temperature with the coefficients that are weighted sum of the individual coefficients of the various molecules which you take from this.

And then also the integral of these fractional powers of temperature can be done explicitly. So here's the result of this integral. That's the result of that integral.

And so that is the actual expression that you will have to solve numerically in order to obtain the adiabatic flame temperature from the energy balance.

I am mentioning these details because I'm not going to go over other details, but in the past, I have developed this Excel file that I will share with you on Canvas, just in case in the future you have to maybe teach a course like this. Then you may have your students play with these equations.

This is several sheets. It allows you to compute-- to use all the equations that we have seen. It allows you to compute, for example, the enthalpy versus entropy diagram for reactants and products.

It can allow you to identify-- for example, in this case, the temperature. I assume the reactants are at 700 K-- and to compute the adiabatic flame temperature, so the temperature of this other state for the products. So you can play with this if you like.

Of course, we left it alone, but we are not always working with steady-state flow reactors. Often, like in an internal combustion engine or in bombs-- not necessarily used for wars. You use bombs also to measure in the lab, like, the heating power of fuels or the flame propagation rates.

So you have a closed system set up. And you can perform exactly the same reasoning that we've done. The only difference is that you have to perform a volume balance.

And if you can assume that both the initial and final states are in the gaseous phase, the ideal gas law gives you the volume. And then, if the volume remains constant, like VP equals VR, then you find that the ratio of the final temperature over the final pressure is equal to the initial ratio. But there is also the ratio of nP over nR.

So, for example, for the heating value, you could measure a heating value at constant volume. You would have no heat exchange. You would have-- I'm sorry, no work exchange. And you would have heat exchange enough to bring your products down to the environmental temperature.

But you have to accept that since it's a closed volume setup, the final pressure will not go down to atmospheric. And it will be a pressure p that-- determined by the ideal gas law is determined by this thing.

OK, so if you do the energy balance, you get the heating value. The heating value this time, in this setup, is equal not to the enthalpy, but the internal energy of combustion plus the amount of energy that is involved in condensation.

And I presume that here I should change this into a U. That's the internal energy of condensation and not the enthalpy.

Or if you consider an adiabatic setup, like a true bomb setup, where there is no work, no heat, this is the final pressure in terms of the final temperature. And you compute the final temperature by, again, the energy balance.

The only difference is that instead of the specific heats at constant pressure, since the energy for a gas depends on the specific heats at constant volume, it's the cv that you have to integrate here.

And you can then compute the pressure. Once you have the temperature, you can compute the pressure from here. And then you can compute the entropy produced by irreversibility with the entropy balance.

And you find that this time the loss of-- the exergy destruction-- so the loss of efficiency-- is a bit smaller. Well, why? Because you are left with products that are in a container and at very high pressure. And that high pressure has some availability. You could use it to expand and, therefore, to make work.

So that is has transformed part of the exergy of the fuel into that. And that's why-- These are the numbers. So here are numbers for a closed combustion chamber.

Temperatures are very high, and pressures of the order of 10 atmospheres. And here that ratio is indeed in the range that I said.

For the steady-state flow burner, the adiabatic flame temperatures are lower. And the irreversibility is higher.

Actually, these calculations are done not using simply the reaction of oxidation of the fuel, but also using the other two reactions, that of dissociation of CO2 and of H2O, because those two reactions are important at high temperatures and are also energy-intensive in the sense that they consume up some of the energy released by the combustion reaction.

And therefore, they are important. Otherwise, if you neglect those, you would get even higher values for the temperatures here.

And in the Excel file, you find that in some of the sheets you are neglecting this dissociation of CO2 and H2O. And some other sheets, you find them. Those are the ones where you also compute the equilibrium because-- at the moment we haven't done yet.

Next time, we'll talk about chemical equilibrium. And those reactions are assumed to be in chemical equilibrium at these temperatures. So let's summarize.

For the closed system setup, what we have seen in this energy versus entropy diagram, this is the curve that represents the stable equilibrium states of the reactants. And this is the one that represents those of the products.

T0 is this slope here, which touches the reactants at this point. So these are the reactant mixture. So it would be your fuel, including the air that you're using to oxidize the fuel at 25 C, 1 atmosphere, so in this state here.

And these are the products of reaction after you cool them down at standard conditions. So the difference in energy between this and that is these blue arrows. That's the energy of reaction.

And the difference in the entropies-- these black arrows here-- is the entropy of the reaction. And, again, sometimes, this point will be to the left of that one. Sometimes, for other fuels, it will be on the right. There is no fundamental reason why it should be left or right.

We start with the products-- I mean, with the reactants at STP. And we run our adiabatic constant energy combustion-- adiabatic flame temperature setup. So the energy remains constant. And in the final state, we end up here, with this state that has a temperature, which is represented by this slope, which is higher.

Now, talking about-- I mean, yes, available energies. So let me call omega, as we did in the initial part of the course-- omega, the available energy, with respect to a reservoir. So the 0 up there means with respect to a reservoir at standard temperature.

So in any place of this diagram, which you remember, at any point, we can compute the energy and the entropy-- this is the expression for the available energy-- energy minus the energy when the system is in mutual equilibrium with the reservoir.

But now we have two options here. One is with the off case-- no reactions. So for no reactions, the composition cannot change.

And so at our reference state-- the reactants are in mutual equilibrium with our reservoir at this state here. So this is the state with energy U0R and S0R, so it's here.

If, instead, we allow the chemical reactions, then the mutual equilibrium with the reservoir will be this one. The most stable is when the products have occurred, the reactions have allowed to go to a more stable mutual equilibrium, which is this one, the state at T0 of the products.

So I can compute-- of course, this state has zero availability with respect to the off situation. But with respect to the on situation, so with the reactions, it has an availability which is given by this blue line here. So that's the available energy of the inlet state with respect to the outlet state.

When I do the flame, the adiabatic combustion, I end up with this state here and its availability, its available energy-- you remember the construction, you have to go down here geometrically until you reach the line that has the slope of the temperature of the reservoir.

So this is the blue-- this is the available energy. It's less than the initial. And what's missing is related to the amount of entropy that you generated by irreversibility. If you look at this triangle, this tangent is T0. And so this side of the triangle is equal to T0 times this length, which is S irreversible.

Now, sometimes-- well, first observation here is that these two curves approach each other as you go high in temperature. So if we could have the combustion occur by preheating our reactants at a higher temperature-- for example, T1R here-- when I do the oxidation, the adiabatic flame, I produce less entropy by irreversibility, and therefore, I consume less exergy.

That increases the efficiency. So preheating the reactants is a way to improve the efficiency. Of course, preheating requires some availability, some available energy, this much. And this is the available energy of the heated reactants with respect to the reactants themselves. So I'm using the off expression for the available energy.

And then, when I have obtained these products, of course, at a higher temperature, see, T1 prime, they have this much available energy. And even if I pay off what I spent in order to do the preheating, I'm still gaining in terms of the fact that, of course, if I do things reversibly, I have less energy waste than-- exergy waste than in the previous case.

And the last observation is the following, that, OK, well, could we keep preheating and so get closer and closer? This concept has been-- so the question is, is it possible to go to an extreme to where these two curves, one of the reactants and one of the products, touch each other?

And they do, at a certain temperature, provided you do what-- you have to mix some of the products with your reactants. In fact, this is also done in internal combustion engines. It's called exhaust gas recirculation.

You take some of the gases and mix them with the reactant mixture. That makes these curves get closer to one another and, therefore, reduces the irreversibility and increases the efficiency.

Of course, if you do too much, this mixing involves an entropy of mixing. So what you gain by getting these two curves close, you lose in the mixing entropy. And that's also irreversible.

These concepts are very theoretical, of course. You know Keenan has brought up this question in 1941. Also Obert, 1948 and then also 1973.

And later on, every 10 years or so, people go back to this one. I haven't been following, so I don't know if the frequency of 10 years is still respected. But at least we are talking about it now.

We ourselves-- you can go to this reference-- we worked on some calculation. And we computed the amount of water that you have to dissolve in-- this was the combustion of hydrogen.

And we wanted to look at what dilution you should dilute your products of combustion, which in this case is just water, in order for the temperature at which they touch not to be too high, because if it is too high, the problem here is that you want to do the preheating. And while you're preheating, you should be able to contain the reaction.

You should freeze the reaction and allow the reaction-- only, so to speak, turn it on only when you are here. Then you turn it on, and nothing happens because the reactants and products are in equilibrium. But then, as you cool down the products, you go down this curve.

So you obtain more than-- you obtain the exergy, essentially, of the fuel with respect to this one. So in the preheating, you spend this exergy. And in the cooling down of the products, you obtain this energy. And the difference is the exergy of the fuel.

But the problem in practice is that as you go above a certain temperature, any mixture will have a self-combustion-- an auto-combustion limit. And it will burn by itself.

And that's why we were looking for a way to dilute enough so by diluting you reduce the temperature at which this happens. And therefore, you have to go below the self-combustion temperature. And here is this.

So, for example, we could find that-- I think we did, like, 1,500 or maybe 1,000. This is the amount of water molecules that you have to put in.

I don't think anybody has ever done this kind of thing practically. But conceptually, it's something to be kept in mind. So I think, yes, we can stop here today. And next time, we'll do chemical equilibrium. OK.