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So good afternoon. And we are-- hopefully, we'll finish the topic on liquid-vapor equilibria today. Now, we have seen that everything is contained in the chemical potentials. And so this summarizes, for example, for a pure substance, when you have the two phases in mutual equilibrium, like liquid and vapor, the equality of chemical potentials for the pure liquid and the pure vapor gives a relation between pressure and temperature, which we call p_{sat} , or the inverse function is T_{sat} .

That's what you find in, for example, the steam tables for water or every other substance, as this establishes the boiling point at a given pressure. So the equivalent for a binary mixture is that now we have-- if both substances are volatile and condensable, then you have two chemical equilibrium-- chemical potential equalities that are required for a mutual stable equilibrium between the two phases. Of course, the chemical potential is now not only a function of temperature and pressure, but also of composition.

But because the mole fractions add up to 1, you just need one independent mole fraction to represent the composition. But you need one mole fraction for the liquid phase and another mole fraction for the vapor phase because they are not necessarily equal. So these two equalities in the four variables, T , p , y_1 , and y_2 , can be solved to give these relations.

So you only have a variance of two, it gives a phase-rule variance of two, meaning that, for example, if you fix temperature and pressure, that automatically fixes a unique composition for the liquid and a unique composition for the vapor that are not equal. And the Raoult's law that we have developed establishes the relation between the composition of the vapor and the composition of the liquid.

You can also rewrite-- solve these equations for other independent variables. For example, you keep T and the mole fraction of the liquid, and you get from these relations a function, which we call the bubble line. Or if you instead like to keep the temperature and the composition of the vapor, you get the dew line, which can be expressed as pressure as a function of temperature, but also temperature as a function of pressure.

So these are all equivalent forms. And here is sort of a three-dimensional representation of how these things look. Of course, in the limit of the pure substances, you get the usual p - T diagram for that substance. This is for one. This is for two. But halfway, when the mole fractions go from between 0 and 1, then you get these relations, as we have seen, gives rise to gaps.

So to regions that are forbidden, they cannot be obtained-- in which the substance doesn't behave in-- doesn't exist in stable equilibrium. It likes to separate. So today, to finish up, we need to see a little more about this. So the first result that we can talk about is called Henry's law, which is a byproduct of Raoult's law.

So remember, Raoult's law was a relation here, this one. That gives us, as we just said, the composition of the vapor phase in equilibrium. It is a function of the composition of the liquid phase, with which it is in mutual equilibrium. And the saturation pressure of the pure substance enters in Raoult's equation.

We derive this by equating the chemical potentials of substance one. And, of course, if you have-- if your mixture is ideal at all compositions and both substances are volatile and condensable, you have also Raoult's law for the second substance. And so you have the same expression, like here, only with the subscript 2 instead of 1.

However, very few mixtures in the liquid phase are really ideal at all compositions. But we know that in the dilute limit, so therefore a dilute solution, we argued that every liquid solution is always in that limit behaving as ideal. So that means-- Let's consider component 1 as the solvent for which this equation is valid in the limit of $y_1 \rightarrow 1$ -- That means the liquid composition-- is very close to the pure substance. So that's a dilute solution limit.

Substance 2 does not behave as Raoult's law. But we will see that now, the next lines are going-- we're going to need to prove this relation here, which is Henry's law, which looks similar to Raoult's law, except that instead of the saturation pressure of the substance, of the second substance, you have another function of not just temperature, but temperature and pressure, which is called Henry's volatility constant. And it's going to be given by this relation here.

So how do we obtain this? And this is valid for any mixture in the dilute solution limit. There is a constant like that. It's called Henry's constant, but it's really something that it is independent of composition, and it's a function-- but it is a function of temperature and pressure. So it's constant once you fix temperature and pressure.

So where does it come about? It comes about from the Gibbs-Duhem relations because they can-- they must always hold. Do you remember, Gibbs-Duhem relations are the ones that we use also to derive the Gibbs phase rule and the Clausius-Clapeyron relations for the pure substances.

For a binary mixture, the usual summation becomes just two contributions here. So this is minus $s \, dT$ plus $v \, dp$ plus the summation-- minus the summation of the mole fractions times the d of the chemical potentials. Now, suppose that we fixed temperature and pressure. So we set dT and dp equal 0.

Then you see, this gives a relation between how the chemical potential of the second substance, so of the solute in the dilute solution, changes as you have changes in the chemical potential of the solvent. So they are not independent. So since the solvent behaves like this, it's ideal. So it obeys this ideal relation for chemical potentials.

If you do the differential of that at constant T and p , you are left with just the differential of $\log$ of y , which is dy over y . So that's dmu_1 in the liquid phase. So you can substitute in this relation here. So you see, this relation can be rewritten this way. And then here, for this one, you substitute what we obtained from the ideal solution.

And here is what you get. You get a similar relation. So you get that, also, the chemical potential of the second substance in the liquid solution behaves logarithmically with the composition. So that means that if it is logarithmic-- see, for the ideal solution, this is the logarithmic dependence. And here you have the pure substance. So the constant here is the pure substance.

Oops. Whereas, for this other case, if you integrate this relation, you get something similar to the one up there, but with a different integration constant that is not necessarily equal to the pure component chemical potential. It is equal to the pure component chemical potential in the limit of ideal solution at all compositions.

But in general, this is some other function of temperature and pressure, which nevertheless can be measured. And therefore, if you use this relation to obtain-- like we did for obtaining Raoult's law, you obtain Henry's law. And here is the explicit expression that derives for Henry's constant in terms of the saturation pressure of the second substance.

There is this correction factor. And this correction factor can be very large. For example, one important example in some practices is the one for nitrogen. So Henry's constant has a value which is 85,000 atmospheres. It's a very high pressure. From the point of view of-- graphic point of view, suppose this one is mole fraction of the solvent. Say that we are talking about water.

So this is-- the dilute limit is in this area. So mole fraction of water is very close to 1. And so what is missing to get to 1 is the mole fraction of the solute. And suppose solute is nitrogen. The Henry's slope-- if you had ideal behavior, this line represents the partial pressure.

So it's the product of mole fraction and pressure. And it's a straight line because that's a linear relation. That takes you to the saturation pressure of nitrogen. Since this constant is very high, the Henry's constant is very high, the actual slope here is much steeper. And that is sort of the tangent of this non-ideal behavior bubble line.

Now, why nitrogen is important? For example, for divers-- you know that there's this problem of decompression. And if you dive and you stay for a long time at high pressures, nitrogen-- you see, here, if I increase the pressure, the mole fraction of nitrogen that can stay in the liquid, so let's say the-- let's call it the solubility of nitrogen in the blood gets higher. So the longer you stay, the more nitrogen goes into your blood. And this happens in the lungs.

Now, if you come up to sea surface too quickly and you don't let the necessary time to adjust back through the lungs, this nitrogen will evaporate from your bloodstream and form bubbles all over. And these bubbles typically collect in joints and gives you a lot of pain, especially when you move the joints. And that's why the disease is called, also, the bends. When you bend, you suffer.

But of course, the Henry's constant has also some other applications that also have to do with atmospheric and ocean science. And so this is-- for example, it determines the composition of clouds, cloud droplets. And also, it is important in how, for example, some pollutants are absorbed in wastewater management plants, treatment plants. So this was an example of application of the Gibbs-Duhem relation, which has some practical applications.

Before we go on, I have to stress again something that we have already discussed. So I'm not going to go into too many details here, but I leave it, this slide, for reference because when we-- like we're going to do next, we deal with models of mixtures to describe this non-ideal behavior,

we are going to have to be concerned with the stability or the solubility limits, the stability conditions, for these mixtures because sometimes, for example, liquids, you know, oil and water, don't mix, at least not at all compositions. So that is an effect of the fact that at certain compositions, a homogeneous mixture of oil and water is unstable, at most compositions.

All right, well, so our models will give expressions for the Gibbs free energy. And you can express the Gibbs free energy as the total value or the specific value. And of course, if we are talking about large systems with large numbers of particles, so we can apply the Euler relation. And this is the fact that the specific Gibbs free energy is essentially-- you can write it as the weighted sum of the chemical potentials weighted by the mole fractions of the components.

But we have to remember that-- you see, you might be tempted to say that, therefore, the chemical potential is the derivative of little g with respect to y , but it is not. That's why you have to be careful. The chemical potential, when you want to write it in terms of the Gibbs free energy, is the partial of the Gibbs free energy, capital G , with respect to n at constant T , p , and all the other n 's. And if you do all the correct steps, here it is. Here is the expression in terms of the specific Gibbs free energy.

There are lots of contributions. It's not just the partial of g with respect to y . There are other stuff. For example, if you assume-- if you apply this to the Gibbs free energy of the ideal solution, which we discussed last time also, which is given only by this term plus the mixing entropy type term, and you do this derivative here, you see that this derivative of the lowercase g with respect to the mole fraction is equal to the pure component plus something like that.

So there is an RT term, too many, which makes it different from the ideal chemical potential. But if you put this expression into here, then you get the proper expression for the chemical potential. For a binary mixture, which is something-- so these are relations that we will need in a few moments.

For a binary mixture, the specific Gibbs free energy is function of only one mole fraction, of course, because the other is $1 - y_1$. The chemical potential, if you use this expression, can be written this way. And for the second component, it can be written this way, in terms of the derivative of little g with respect to y .

And so where do we need these two expressions? We need them when we want to apply the conditions for mutual equilibrium between two phases because, if we have the two phases in equilibrium, component 1 must have the same chemical potential in both phases, and component 2 also. So this gives two relations. And these two relations can be written-- from these two relations, you can obtain these-- by substituting the expression above-- these two expressions here.

So it tells you that the partial of g with respect to y must be equal for the two phases. Even if this derivative doesn't represent the chemical potential, but only a part of it, still, it has to be equal for the two phases. And plus, it represents a slope of a geometrical construction that looks like this. So if I have-- I plot g with respect to mole fraction, y , sometimes, we will see-- you get expressions-- plots like this.

We will see that the condition for mutual equilibrium, the first one, this one, says that there are going to be-- if you find a line, which is tangent both here and there-- almost-- this slope is dg/dy , also there. But here it's evaluated at y prime first-- phase one. And here it is evaluated at y double prime. So finding this tangent line identifies those two mole fractions that are in mutual equilibrium.

And also, see, this is g prime. And that's g double prime. And as you see, the equation of this line is precisely this equation here. So that construction helps us identify for a given temperature-- because here we have fixed a given temperature and pressure. It helps identify these two points.

So, again, that means, suppose I fix now the pressure. And I take that temperature. So at this temperature, T , I'm going to plot these two points that I have found, y_1' and y_1'' . This represents the two phases in mutual equilibrium. So this would be, say, y_1^f for example, for the phase, this would be y_1^g and this is y_1^g if you're talking about liquid-vapor equilibrium.

Now, if I change the temperature and make another plot of the same kind, I'm going to identify by the same way the two other compositions that correspond to the mutual equilibrium and so on, until I get to a temperature in which these points are going to coincide. So I'm going to obtain a curve like that. Maybe it's a bit smoother in practice. This is called a critical point.

It's critical in what sense? It's critical in the sense that above that temperature, you can see that all compositions are possible for equilibrium. Whereas, below here, there is a gap. So this area here is forbidden. And it's called the miscibility gap. There are no stable situations inside here. But as we have seen for the pure substance, we may have metastable situations, which is now what we want to analyze.

So let's try to do that construction with one of the models that we have assumed, the simplest, the one-parameter Margules model for the binary mixture, so just parameter A . So the Gibbs free energy is the sum of an ideal part and an excess part. The ideal part is given here.

Something-- it can be computed from the pure substance properties-- something is related to the entropy of mixing. And then here, the excess part is related to the composition and to this constant A , which you remember is essentially the mixing enthalpy of the two components, which in this model are equal, for the two components. So that's the model.

Now we apply the stability conditions because you remember that for mutual-- for stable equilibrium, we derived a while ago general conditions for stability that are not just-- yes, they are theoretical things, but which have practical consequences and that, therefore, allow to describe some physical reality.

So the second differential of g , if I move out from a state in which the system is in mutual equilibrium with a reservoir at temperature T and p , and I move out by changing the composition while keeping T and p constant, this differential must be greater than 0. So that implies that if I keep, also, n among the various possibilities, I can-- of changing the composition, I'm taking the simplest. So I take--I keep constant the total amount and just change the relative composition.

So I just changed the mole fraction of component 1. And this second differential gives rise-- well, maybe here, more than an equal sign, there should be an arrow because this is not an equality. It's wrong mathematically, but because here we should have also dy_1^2 , which being squared has a positive sign. So it doesn't-- it is always positive.

So I have to correct that. And so this is the second derivative. And on this graph, the second derivative is the convexity of the curve. It has to be positive. So we see here that it's positive here, it's positive here, it's positive up to a certain point here, but then it becomes negative, the second derivative. So from where it becomes negative to where it comes back positive, this is the region of instability.

And these two points here are going to define-- see, they're not-- they are at different mole fractions than the two phases in mutual equilibrium. So see, this is a different mole fraction and a different mole fraction. So this will identify another curve inside here. So the locus of all these other points, these other curve, is what we will call the spinodal curve. So usually, one calls-- this one is called binodal. And the one inside, that's the spinodal.

So we have the expression for the Gibbs free energy. We can take derivatives. Let me skip the steps and go to the result here. This is the second derivative. It's in terms of the mole fractions, RT , and A , the constant A . For this to be greater than 0-- and see, this subtracts. So you need that A should not be too large. The maximum value of this fraction is 1-- is 2. No, it's 4 because half and half. And therefore, A equals 2 is the maximum allowed value.

So the stability condition is satisfied if A is less than 2. The critical situation is when A is equal to 2. And if A is greater than 2, you can still satisfy this condition, but only in a certain range. See, this is the expression. It's like a second order equation. So you can solve it, and you find this range. So this is this mole fraction and that is this other mole fraction as a function of parameter A .

So this is one part of the condition for-- it's a necessary condition for stability. But the other condition is that the two phases are in mutual stable equilibrium. And therefore, you also have the conditions that the chemical potentials must be equal. And these two conditions essentially correspond to this construction of the tangent line that we just described. So these equations here, if you fix an A , you find the mole fractions of the phases in mutual equilibrium.

This is easy enough that you can implement it, for example, in an Excel file. So you see the Gibbs free energy, little g molar, is given by this relation. It's the sum of the two contributions, the ideal, which is this, and the excess, which is that. In this case, for A less than 2 at all compositions, the second derivative of g is positive and we have stability.

So in general, this A depends on temperature. So at these temperatures, the two liquids are completely miscible. As you decrease the temperature, the value of A changes, and eventually you reach the critical value, A equals 2. At that moment, you still are OK in terms of stability. But at the minimum here, you have a second order derivative equal to 0. Not a minimum at this-- at some point, you get a second order, second derivative, equal to 0.

Of course, for these plots, we had to assume something about the properties of the pure substances. So I assumed these values, 0.2 for one substance and 0.4 for the other. If you set a lower temperature, so you go to A greater than 2, then you get partial miscibility. You get this miscibility gap.

So from the spinodal composition here to the spinodal composition there, for the liquid and the vapor, there is this entire range of compositions in which the mixture doesn't want to stay. So if you find-- if you manage to produce a mixture with this composition at these conditions of temperature and pressure, it will separate spontaneously in search for stability.

And it will form two phases. It will form a phase which is rich in component 1, this one, and a phase which is lean in component 1, which is this. And eventually, it will reach mutual equilibrium-- it will phase separate to two phases that are in mutual equilibrium at these compositions. These equations are, again, that constructions that we have already done.

So if you-- by some means, for example, one possibility is to start from a mixture at a temperature above critical, say here. And then you find a way to quench it, much like what we discussed also for the van der Waals spinodal decomposition. So you quench to this point here.

So here is the temperature. At this point, the instability triggers what you see here. It triggers the fact that from homogeneous, the phases begin to separate because substance 1 either wants to be close to a lot of substance 1 or a little of substance 1. So you get diffusion process.

And this is fast because, as we have seen for the van der Waals case, we have a lot of free energy available to create the surface that separates the two phases. And then once that happens, coalescence makes-- uses up that surface energy and tries to find configurations of lesser free energy by making drops or bubbles, drops, in this case, bigger and bigger.

And also here, if you do the separation, if you do this quenching at exactly the critical composition, then the mixture, the separation, as you see, doesn't either-- neither do drops nor-- doesn't do-- yeah, in the van der Waals, it's neither drops nor bubbles here. It's drops in all cases. But you see, instead of drops, it's continuous regions that became gross and grosser. If you instead are off critical on either side, you get drops of one into a continuous region of the other.

Now, there is also this region here of metastable states between the spinodal and the binodal curve. There is metastability. And these metastable states are interesting because sometimes they can be used for applications. For example, this is-- I know that one of you is Greek, and so certainly knows this ouzo effect.

But in the Mediterranean, there is these liqueurs that have very different names. So let's see. I wrote them down because I forgot. In France, you get Anisette or Pastis. And in Italy, Sambuca. That one I know. Turkey is Raki. In Colombia, there is some kinds of aguardiente, which is flavored with anisette, with anise. Mexico, also, has its own. And also, some of the Egypt and Israel have Arak.

So essentially, this is-- the funny thing of these liquors is that they are transparent. And when you mix it with water, which is another transparent liquid, they become-- they give you a milky kind of opaque thing. So that's always sort of a mysterious effect if you see the first time.

It turns out that this effect, it has been named the ouzo effect only relatively recently, maybe 20 years ago, when somebody-- some real scientist visited the Mediterranean, but-- and it is not spinodal decomposition. It is just the fact that you start, you generate a mixture-- this has to do-- this is more complicated because it's not a binary mixture.

It is a three-component mixture. It has water, it has alcohol, which is ethanol, and it has a little amount of this oily thing that you extract from the seeds of a plant, of a flower that is called anisette or something like that. No, I don't have the name of that.

I think the chemical composition of this oily thing that gives the flavor is trans-anethole, and it's $C_{10}H_{12}O$. You find all these in this nice article that give the scientific explanation, and from which I have extracted these pictures. So the idea here is that you have three substances. So let me just see.

They call it DVB in that graph, that plays the role of the anise oil, but I don't think-- they prefer to do it with a polymer that has-- polymeric oil that-- so they use divinylbenzene. So this is divinylbenzene, at least in their experiment.

So let's say this is substance C. Now, it turns out that this substance is soluble in alcohol. It's not soluble in water. So let's call water B and alcohol A. So essentially, here we have the mole fraction of the organic oil. That's our C.

And this is the mole fraction of the ethanol, which is our A. This is how the equivalent of this diagram looks at a fixed temperature as a function of these compositions. Of course, the mole fraction of water is 1 minus the sum of these two, hence the triangular line here. So up here, we got just pure water.

If you plot this, it is very skewed. If you plot it in a logarithmic scale, in the composition of the organic oil, this is how it looks. It opens up.

So what you typically have is-- ouzo is 40% by volume, meaning about 35% or 34% by weight. And here is by weight. So this is the alcohol content. And let's say the content of this oily anisette organic oil extracted from these flowers, from these seeds, suppose it's this much. What happens is when you add water, you dilute the solution. And so the fraction of ethanol goes down from 35, say, to-- you cross this line, and you get into the metastable region.

In that metastable region, you get an immediate separation or formation of these minute droplets, which then, because you-- so you release the excess Gibbs free energy that forms those minute droplets. Those droplets are the reason why, then, light does not get through, gets diffused by these droplets. So that's why the liquid loses the transparency to light. The reasons are these droplets.

But differently from spinodal decomposition, if you had generated this kind of situation from the unstable state, the separation would have been much more vigorous and it would generate-- have more energy, so generate bigger drops in the end. And eventually, the mixture will separate. Or maybe, in any case, it will form bigger drops.

Whereas, in the ouzo effect, you generate-- you produce very small droplets. They remain in sort of an emulsion that is relatively stable. In other words, it survives hours. And in some cases, this kind of process is wanted because there are applications in which you want to generate emulsions, which is precisely a mixture of a solvent with a lot of small droplets in it. Like when you do vinaigrette, that's an emulsion.

And many times, in order to produce emulsions, you need surfactants. But this is instead a way to produce emulsions without surfactants. And chemical industry is full of processes that go back and forth with these kind of effects in order to separate or mix and generate things.

Also, I think that this method has also been used in order to generate scaffolds for biological applications, for example, because if you-- once you have this emulsion, you freeze it in such a way that-- if you freeze it in such a way that the bulk phase remains liquid and the droplets become solid, then you've generated small spheres.

So in this-- this is a way in which you produce small spheres. Or conversely, if you-- perhaps not these ones, because they are not connected. And so if you freeze this and the liquid droplets remain liquid, you still have droplets and you are not-- there is no path for the liquid to go away.

But if you use a situation like this one, generated by a spinodal decomposition, and you freeze, then you-- because there is a path in which, say, the dark phase becomes solid and the liquid in the white phase can drain away. And then you produce a porous material, which can be used-- a high surface material that can be used for enhancing or studying biological, but also for other applications in which you need a lot of surface for things to happen, like catalysts.

All right, so with this, I think we can terminate the mixture stuff, at least of that kind. But we start with mixtures that are subject also to chemical reactions. So this is the two main situations that we will approach at the beginning here. It's two kinds of systems in which we have chemical reactions. One is a closed system and the other is an open system.

So this is a model for a batch process. And this is a model for a steady state flow process, or flow reactor. In the closed system situation, you have a box. The application that I like to have in mind is the internal combustion engine. So you imagine that this wall is the piston of the cylinder of your internal combustion engine.

And so this wall goes up and down. And at the top dead center, it will be at a certain volume. And suppose the piston stops there for a while. So at that moment, you have a mixture inside your combustion chamber, which is a mixture of air and your fuel, and some water vapor sometimes because air is humid.

And so there is a water vapor content also at the beginning of the combustion process. It has some temperature, some pressure, because the piston has compressed that mixture. Of course, since we are in a stable equilibrium state, it also has chemical potentials. And if we want to compute the energy and the entropy, because they will enter in the energy and entropy balances, we know how to do it because we've dealt with mixtures for a long time now.

So the energy in general is simply given. Well, simply, is given by the weighted sum weighted on the amounts of the partial properties. And the partial properties depend on composition. And here we can apply all our theories about ideal mixtures or other models and so on. And the same holds also for the other properties, like entropy, which is the other one that is needed for the entropy balance.

Now, what's new here is that next, you sort of turn on chemical reactions. So the composition is allowed to change according to one or more chemical reaction mechanisms. We will describe them. I'll go into detail of this description in the next slide, but we will describe it by this general notation. And what will happen is that the process, the fact that you turn on the possibility of a chemical reaction, makes the state evolve towards equilibrium and the composition will change.

So in the end, you will have a composition that is different from the beginning. So here you have the reactants. So R stands for reactants here, not for reservoir. And P stands for products. See, these are the products of combustion, for example, in which case you have air, of which you've consumed some of the oxygen. And then you have carbon dioxide, water vapor, and maybe some nitrogen oxides.

Because the reaction occurs irreversibly, spontaneously, there will be some entropy produced by irreversibility. You can compute once you have-- or at least in terms of the final composition and the final temperature and pressure, you can compute the energy and the entropy the same way. Only, of course, relative to the new composition.

Maybe not all the final things are known. If you can use up only the energy and the entropy balance, and perhaps also the volume balance, if you assume that these volume remains constant or relatively constant because that reaction at the top dead center occurs very quickly, and so the piston doesn't move a lot, then you have three equations, energy, entropy, and volume balance, with which you can solve for three unknowns. So the various possible problems that can be solved are variations of this thing.

And of course, even though that happens quickly, maybe there is some exchange of heat between your mixture and the walls of the container, like the cylinder, because the internal combustion engines are cooled, water cooled or air cooled. And so some of the energy can be exchanged with heat to the wall temperature. And also, if the piston is moving while this is happening, there may also be some work due to the pressure times the volume change.

So that's the setup of the closed system, so internal combustion engine. Here instead is a steady state burner, or reactor. Again, if I have in mind combustion of hydrocarbons, this is a steady state burner, which is typically inside a power-- combustion fossil fuel power plant.

Here, the idea is that you have a flow, bulk flow. One, if all the substances are pre-mixed. Or maybe you have several if you have some of the substances that are injected, for example, air. You could have an injection of air through one stream, so one bulk flow interaction, and then your fuel injected from another pipe that goes in. So I indicate here a single arrow, but of course, you may have many.

The properties for bulk flow interactions-- what enters in the energy balance, as you remember, is the enthalpy. And so we need the enthalpy, the rate of enthalpy, brought in by this inlet bulk flow interaction, which has to do with the partial enthalpies of the components in the mixtures for those that are mixed. And that would be the specific if they are injected as pure components.

And the same for the outlet. So the outlet here would be the hot product, for example, the hot products of combustion. But in other configurations, it could be-- if this reactor contains not only just-- it's not adiabatic, but it contains also the machinery, and the thermal cycle that extracts the energy, and so on. This would be just the products that get exhausted at the chimney or the stack of your power plant.

All right, and so then, in that case, we may have heat interactions and work interactions while this complex power plant is evolving. There is, of course, entropy produced by irreversibility. And again, the new aspect that we need to deal with is the fact that inside here, a chemical reaction or chemical reactions can occur, changing the composition from the inlet to the outlet.

The energy balance equation for a steady state says that the rate of change of the energy is 0 because it's steady state. And therefore that must be-- so the rate at which the energies are exchanged in and out must balance to 0. So the enthalpy of the inflow-- this is positive-- the enthalpy of the outflow. The heat flow, positive if-- if it has the arrow inside, it means positive, if received, minus the work, which has the arrow outward. And so it's positive if it is produced.

And similarly for the entropy balance. The rate of change of the entropy of the reactor, because we are making a balance equation for this reactor here, if it is steady state, the properties don't change, so the rate of entropy change is 0. And so then you have a balance between the net amount of entropy that comes in and out and the entropy that is produced by irreversibility.

Now, if you look at these ones, if you look at these equations and compare them, you are often tempted to, for example, rewrite these ones with H_P minus H_R on the left-hand side, which is OK, just a legitimate mathematical step. However, it should be--you shouldn't be confused because, otherwise, you say, well, why do I use enthalpy here? Why do we use energy there?

You're not using enthalpy here the same way. It doesn't play the role of-- the energy, the rate of energy change, is this 0 here. That 0 is important. So if you do that mathematical step, you sort of kill a 0. That is important and gives you a reminder that you're talking about a steady state process.

How about notation? So let's take an example of the reaction in which you have two hydrogen molecules, this and that, and an oxygen molecule. And they get reassembled by this mechanism into two molecules of water. So I use the equal sign here to say that this refers simply to the mechanism.

It doesn't say which direction it will go. It simply defines the mechanism. And therefore, you can go one direction, but also the opposite. And there is, therefore, some arbitrary choice. You could put on the left-hand side hydrogen and oxygen. Or you could put on the left-hand side the water, the symbol for water. Either one is OK.

Once you have written that this way, you can also put them all on the left-hand side, and with the stoichiometric coefficients positive for what you will consider the products of the reaction and negative for those that you will consider the reactants. Now, the meaning of the stoichiometric coefficients are that they determine the possible changes in composition.

So if I start with a composition which is given by these numbers, anything, and then I want to see how the composition, that composition, can change according to this reaction mechanism and only this one, then you can write-- these changes are not completely arbitrary because you have to have the fact that the ratio of the change of one component to the respective stoichiometric coefficient must be equal to the same ratio for all the other components.

So this ratio, we are going to call the reaction coordinate or change in reaction coordinate. That defines the reaction coordinates, the change over the stoichiometric coefficient. Notice that the stoichiometric coefficient must be taken with the sign, the proper sign, negative for the reactants and positive for the products.

So with that in mind, then in order to introduce a notation that is typically used in software that deals with the calculations of chemical equilibrium or chemical kinetics, we can define a symbol, A_i , A_1 , A_2 , A_3 , to represent the chemical symbols in the list.

So for example, we make a table. 1, 2, 3. We decide to call the first component to make it H_2 . The second component is oxygen and the third is water. So the stoichiometric coefficient, we use the symbol ν_i for the stoichiometric coefficients. It's minus 2 for hydrogen, minus 1 for oxygen, and 2 for water.

And then you see that this equation here that represents the chemical reaction mechanism translates into this summation, which we can write in the summation this way. The advantage of that is that so I have, say, this for my first reaction. But suppose I have-- because in general, life is not simple and very few things can be described with just a single chemical reaction.

For example, even for that formation of water, just for the combustion of hydrogen, I think that the mechanism-- you have to consider at least, I forget now, probably eight mechanisms (actually, it's 24, see later). And for the combustion of methane, it's probably 250 or more that play a role and determine the kinetics. Different thing is for equilibrium. But for the kinetics, you need many mechanisms. So for example, suppose we have, also, another important equation for combustion, which is the dissociation of CO₂ in CO and oxygen.

If, together with my initial reaction, which is 2H₂ plus O₂ equals H₂O, which we already represented in our list, if we also have that one, we can keep going in our list of chemical species that are relevant to our problem. We add CO₂ and CO. Of course, they don't play a role in the first reaction, so we'll have stoichiometric coefficients for reaction 1. Let's say this is reaction 1. So I'm putting a superscript 1 for the first reaction.

And then I put here the chemical-- stoichiometric coefficients for the second reaction. So for the second reaction, I have plus 1, since it's a product for CO. So CO is 1. Oxygen, 1/2, so 0.5 positive. Then CO₂, it's on the left-hand side, so it's negative. It's minus 1.

Of course, the others are 0 because, in reaction 1, there is no play by CO₂ and CO. And reaction 2, there is no play by water and hydrogen. And so you see, I have just put a j there. And I have a system of as many chemical reactions as we want. Now, the proportionality relations, namely these relations here that represent the role of stoichiometric coefficients in order to represent what changes in composition are possible, are written this way.

Or also, in generic terms, like $\Delta n \text{ over } \nu_i \text{ equals } \Delta \epsilon$, which we can write more explicitly, for example, if we--like in the previous examples, like in the batch process, the composition goes from that of the reactants to that of the products.

So the change Δn is equal to final minus initial. So this is n_P minus n_R is equal to $\nu_i \Delta \epsilon$ sorry, ν_i times ϵ . And this ϵ here could be-- it's actually a Δ . It's the difference between the value of the reaction coordinate that describes the products and the value of the reaction coordinate that describes the reactants composition.

If we have instead a steady state flow continuous reaction, then we talk about the rate of change of the composition. So we take-- we define-- we divide this by Δt . So $\Delta n \text{ by } \Delta t$ is the stoichiometric coefficient times $\Delta \epsilon \text{ over } \Delta t$. Let's call it $\epsilon \dot{\epsilon}$.

And so you find that the rate at which the-- the difference between the rate at which the products and the reactants come out and in is related to this rate of change of the reaction coordinate, which somehow is related to the reaction rate or rates. And in fact, do I have it in the next slide? No.

So in fact, so we have $\dot{n}_i$ is equal to $\dot{n}_R$ plus-- so if you have only one reaction, it's the summation of $\epsilon \dot{\epsilon} \text{ times } \nu_i$. But if I have several reactions, then each one has its own reaction coordinate. And I have to sum up the contribution to the change of the various reactions in play.

So now let's go back-- sorry, let's go back here to the structure of the balance equations. In the balance equations, we have to deal with differences between the energy, between products and reactants, the entropy between products and reactants, also here, the enthalpy between reactants and products, the entropy.

These differences, yes, it is true that we can write and we know how to write them, except that we have to learn a proper way to deal with the fact that the composition is changing here. So some molecules are disappearing and some are appearing that have different properties. And therefore, we have to be careful in how we take a reference value for these properties. And this is done here.

For example, of those differences, let's take one, which is the energy. So we write the energy difference between products and reactants, as we said. So this is just the implementation of what we said in terms of partial properties. Now, let's add and subtract something, which will not change, therefore, the result, and which we select to add and subtract for each constituent the specific property of pure component of that constituent at some reference.

And here, let's say, at some reference, temperature and pressure. I'm going to call the pressure p_0 because, typically, it's taken-- the standard pressure is 1 atmosphere. Whereas, here for temperature, let's use the generic temperature for the moment. If it will be the standard temperature, 298.15, we will denote it by T_0 . But for the moment, this can be done at any temperature. And this temperature is not necessarily equal to either T_R or T_P .

So we add and subtract. So here it is. So we subtract from this summation. We subtract from that summation. But then we realize that since we put it in this summation here, it is multiplied by n_P . And here it is multiplied by n_R . So we have to add up what we subtracted, so this multiplied by the corresponding amounts here.

So in this summation that compensates for those subtractions we recognize the difference between composition, between products and reactants. And that's related to the reaction coordinate through the proportionality relations. So the epsilon doesn't have a subscript. It goes out of the summation. And here, we are left with the summation of the stoichiometric coefficients, which multiply this reference-- these pure component properties, specific properties at those reference of temperature and pressure.

This summation, we call it the energy of the reaction at standard pressure and at that temperature. And we denote it by this symbol here. So that defines the energy of the reaction. You can do that for all the other differences here. For example, this is for the enthalpy, the rate of enthalpies.

Add and subtract the pure component specific enthalpy. In this final term, you get the proportionality relation for the continuous process. Epsilon dot goes out of the summation. This summation, you also call it the enthalpy of the reaction at-- it is the enthalpy of the reaction because it refers to a specific reaction because it depends on the stoichiometric coefficients of that reaction.

So I'll have an enthalpy of this reaction and another enthalpy for that reaction. So each reaction has its own value for these properties of reaction. We call them properties of reaction. And here is the list. You can do that for all properties, including energy, entropy, enthalpy, Gibbs free energy, and even volume.

And of course, since these are pure component properties, the relations that hold between properties also hold between the properties of reaction. So since the Gibbs free energy, you can write it as $h - Ts$, it turns out that the Gibbs free energy of reaction is equal to the enthalpy of reaction minus T times the entropy of reaction. Or since the enthalpy is equal to energy plus $p v$, there is a relation also between the enthalpy of reaction, the energy of reaction, and the volume of reaction.

This is for a generic temperature T . At standard temperature and pressure, also the temperature is fixed. We drop the symbol function of T . And for simplicity, we just, by convention, say, well, if there is no dependence of T , it means that we are at T_0 . So the 0 here has two meanings, pressure and also temperature are at standard values.

Now, it turns out that if you want to compute the properties of reaction, you see, as we've said, every reaction has its own properties. Should they be all measured? So if you are interested in one reaction, you have to find the experimental values from somebody who measured the properties for your reaction?

Well, the answer is no, fortunately, because of the Hess relation, which we will prove in a moment, whereby it turns out that there is a minimal set of measurements that you have to make, which is the measurement of the reactions of formations of the various components.

Once you have those, using these relations, Hess relations, you can find the properties of reaction for any reaction by just taking the weighted sum with the stoichiometric coefficients of your reaction, of the reactions or formations of the various molecules that play in your reaction.

So essentially, here, I'm interested in energy. Yeah, the f goes before. f_0 . And then I'll have to list somewhere here the values of the energies of formation for these various components. And these ones, I find tabulated in the handbooks of chemical physics. Before we prove the Hess relation, let's see the meaning of this Δu and Δs -- well, actually, this is for enthalpy and entropy.

And so let's consider one particular reaction, like that in which a hydrogen molecule splits into two hydrogen atoms. So here I'm drawing the E versus S , or actually, the enthalpy versus S curve, for the stable equilibrium states of atomic hydrogen, this is atomic hydrogen, in the amount of one, fixed amount, 1 mole, and at standard pressure, 1 atmosphere.

This other curve represents half a mole of molecular hydrogen, H_2 , also at standard pressure. Then I take a slope equal to 298.15 kelvin and search for the point on this curve where I have that temperature. It turns out that the derivative of that, of H with respect to S at constant p , is equal to the temperature. So also on this diagram, the slope is the temperature. And here, I find it here. And for this other substance, I find it there.

Now, these two curves until yesterday or-- until we didn't consider chemical reactions, were sort of independent. If we needed to describe the properties of this molecule, we just draw this curve anywhere, taking an arbitrary 0 for the enthalpy. It didn't matter. But now, instead, what matters is the fact that with a chemical reaction mechanism, you can go from one substance to the other.

So you cannot arbitrarily choose reference values for the properties for both, because-- for example, if you look at-- suppose we were at 0 temperature. In order to split this molecule of molecular hydrogen into two hydrogen, you have to break a bond, chemical bond. And the strength of this chemical bond corresponds to an energy that you have to provide in order to detach these two atoms that compose the molecule.

This bond energy is what you have to plot here. So that is the number that allows you to place in relative position the two curves because, this value, you measure. And therefore, these two curves must be at this distance here. Then using the properties of the substances, of the pure substances, here, using specific heats and so on, you can compute what would be the value of the enthalpy at this temperature.

And then also, using the specific heats of this other substance, you can integrate the equation, the fundamental relation, and get to this point. These correspond to the standard conditions. And the enthalpy of formation of atomic hydrogen, so of this state here, from molecular hydrogen is given by the difference in the enthalpy between here and there.

This is the amount of energy that you have to provide in a steady state reactor, where as input you have hydrogen at standard conditions, and as output you have atomic hydrogen also at standard conditions. And this also, there is a difference in entropy.

This difference in entropy corresponds to the entropy of formation. Now, the strength of the bonds, we will return on this graph, but just-- the strength of the bonds is also describable using, for example, a Lennard-Jones potential. But the strength and the distances in play are very different.

For example, this would be the Lennard-Jones potential that describes the covalent bond, which is what happens when this hydrogen atom gets close to the oxygen and gets to share-- they get to share two electrons. And these two electrons form a negative charge enough to cover up the repulsion between the positive charges of the nuclei. So then this is the repulsion of the nuclei, this is the attraction, and this is very heavy dip. It is 459 kilojoules per mole.

You compare it with the van der Waals forces that you can calculate for water molecules in-- that describes the liquid and vapor phase for water molecules using the Lennard-Jones fluid model that we discussed. The value of the epsilon is-- you see it's-- what is it? 4,000 times smaller. 5,000 times smaller. So much that in order to show it in the plot, I have to multiply it here by a factor of 1,000. And still it's smaller.

And also, the minimum here for the van der Waals forces, the attraction between molecules, which are also of electrostatic nature, but from a different source-- has very large-- much larger characteristic distances. So it's like three Angstrom here or 300 picometers here. And instead, for the covalent bond, it's of the order of 74. So they have to get much closer in order for these much stronger forces to get in play and hold the molecule.

So this is-- to say that, yes, you can use Lennard-Jones. Although, it's not really a great model for these kind of bonds, but it gives you the first order idea. But you have to realize, also, of the different order of magnitude, of the strengths of the bonds with respect to the van der Waals forces. So yeah, let's stop here, I guess, yeah.