[SQUEAKING]

[RUSTLING]

[CLICKING]

GIAN PAOLO BERETTA: OK, good afternoon. So we are back with chemical reactions, systems subject to chemical reactions. And today, we will talk about the statement of the second law and the small detail that is in there that regards chemical reactions. And then we'll start playing some more interesting physics of how chemical reactions happen.

So remember that, in order to describe the chemical reaction mechanism, we define an equation, which we can write in various forms. And formally, the generic chemical equation reaction mechanism can be written this way, where these are the chemical symbols, and these are the stoichiometric coefficients. And the proportionality relations-- relate changes, the possible changes in composition.

Now, let's go back to the statement of the second law. This is the same slide that we have seen long ago-- second lecture, I believe or maybe even the first, where I added some more specifics because we didn't stress it then, but in the statement we wrote that, in the subset of states of a system compatible with given values of the amounts of constituents-- we sort of skipped discussing what that compatible means because now we have the tools. So compatible means that the amounts of constituents may be different, may change, according to an internal mechanism such as a chemical reaction.

So in fact, when we fix-- when we say that there is a stable equilibrium state for each value of the energy, the amounts of constituents and the parameters, it's really-- it's not exactly the amounts of constituents. But it's a given set of compatible possible compositions corresponding to, for example, an initial set of amounts. So for example, suppose we say-- we characterize a set of compatible amounts of constituents by a given set of values of amounts, like an initial set. We put molecules in a box. Then we close the box.

But then the chemical reactions can change these amounts due to the collisions and the reactions themselves. So according to this relation. So that defines what we mean by compatible. And also, here, it says that, from any initial composition and the values of the parameters, we can reach a stable equilibrium state by means of a reversible weight process. That's really true, also, if you can change the composition compatibly with the chemical reaction mechanisms that you have defined as part of your model as being possible for your system.

Remember that we're always talking about a model. So in a model, you specify what the constituents are. And also, you have to specify what the allowed chemical reaction mechanisms are. You change one of these-- for example, you add one chemical reaction, that is a different system. So it's part of the definition of system is also this.

So what does that imply? Well, it implies that, since the composition can change, they become like properties. From state to state, you have different compositions. So you can measure what's the current composition. Something that you can measure corresponds to a property. So the amounts become properties.

And that stable equilibrium-- there is only one stable equilibrium state. That means there is only one composition that's stable that is a stable equilibrium for the given set of parameters, energy and compatible composition. So that means that, within that set of compatible composition, only one for each value of the energy is a stable equilibrium composition.

So we have to deal with these difficulties so we can somehow restate the state principle and the maximum entropy principle. What I just said is that any property-- and now that list of properties includes the amounts of constituents-- is uniquely fixed by the state so that, once you have a stable equilibrium state, you have one for each value of the energy, volume, initial amount, and stoichiometric coefficients that define what the mechanisms are in play.

OK, for that one, that fixes the state and therefore fixes the values of all the properties. Therefore, each property is only-- at stable equilibrium-- because this is true only at stable equilibrium-- is a function of these variables and only these. And among these properties is the amounts. So we call n sub 0 the amounts that prevail at stable equilibrium.

So in addition to the fundamental relation for the entropy, which is this one, with which we have played a lot in computing derivatives, properties, temperature, chemical potentials, pressure, and so on, we now have also another-- we could call it another fundamental relation for composition. Or equivalently, since composition and reaction coordinates are related this way, you can also write it equivalently-- this is not an extra equation-- in terms of the epsilon. And here I have to correct. This must be epsilon 0.

The maximum entropy principle then says that, among all the states-- and here in the slide, I didn't write it explicitly, so now we should go back and correct-- states compatible with given initial amounts of constituents parameters and energy-- so among all these states, and there are many-- the stable equilibrium state is the one with the maximum entropy. And we shall use this condition of maximum entropy in a moment to determine what the equilibrium composition is.

In order to do so, we have to define better-- or maybe let's say, refine-- with an important little detail the simple system model, namely, the model that applies when we have many particles, both large and-- many. remember this slide which tells us how strong the chemical bonds may be. And yet as a result of collisions, these chemical bonds can be broken to form more stable ones. Or in fact, also, the collisions of these more stable ones, sometimes, if the collision is strong enough, can produce the breakup into products that are less stable.

And actually, at equilibrium, the mechanism that goes in one direction equilibrates-- the rate at which things go in one direction equilibrates the rate in the opposite direction. So this slide-- you can read it later on-- but simply wants to talk about collisions. I actually added this photograph this morning because I was passing in the fourth-floor corridor in building 10, where you probably have gone and seen these photographs by Doc Edgerton.

And you see how a collision between a golf club and the golf ball can deform the ball, which, if you take it in your hands, you know it's kind of hard. It looks like a very hard-- almost a hard sphere. Yet the photograph shows that, even in, I think-- yeah, it says 6 milliseconds. I think it takes 6 milliseconds or less to, during that impact, which is very short, the particle gets deformed so much.

So it-- since it is elastic, it absorbs the kinetic energy that comes from the club. And it becomes deformation energy like a spring. And then that energy stored in the spring will be released very quickly. So in the case of the golf ball, it will hit it at a very long distance. In the case of molecules, it may generate the breaking of some of the weaker bonds and the formation of other, more stable bonds.

There is also this other video in YouTube, which shows you, again, the impact of a golf club-- of a golf ball into a really rigid wall. You see how it-- it's impressive how it deforms. It becomes almost flat, and then it begins to oscillate as it goes away. Very impressive. So this is-- collisions are-- play an important role in chemical reactions.

Let's introduce now this concept that we will call the activated complex. As a result of a collision between molecules, typically, as you know, by thermal agitation, molecules move around and have many collisions per second, billions. And as a result of these collisions, they get deformed. They do what we just said.

Sometimes the combined kinetic energy of the colliding atoms or molecules are enough to form an unstable compound, which we will call activated complex and call it with the star on top. And this compound is momentary. It's momentary. It's very short-lived, and it's unstable.

And this is where, if it decays the proper way-- in other words, if the elastic energy, the vibrational energies, get moved to the right bonds so as to break them and to-- so that the atoms are free to recombine in a different way, then you will have an effective collision that will transform your reactants in products.

Of course, this is contour plot of a diagram that wants to represent here the most stable potential-- the configuration that represents the potential energy of, say, AB plus C is the products. And here, this bottom of this other valley, you have the potential energy combined of the reactants. So typically, if you are at 0 temperature, particles don't move, no collisions, no chance to reach enough energy to overcome, because you see, this is like two valleys.

And this is a saddle point that connects the two valleys. And this one, which is this dashed line, represents the bottom-- let's say, the steepest ascent and steepest descent path from the reactant valley to the product valley of the potential energy. So if energy is only potential, you are at 0 temperature, and the particles will like to stay in the bottoms.

But as soon as the temperature increases, the collisions-- the kinetic energy allows for collisions. And the collisions allows particles to put energy together. And therefore, they can move around in these valleys and find themselves in configurations that are not the most stable.

But momentarily, they can live also in very unstable situations along the sides of the valley. And sometimes they can even reach the saddle point, perhaps also with additional energy than just what is barely enough to be there. So this plot represents, along this dashed line, potential energy. And here, we are assuming that the reactant valley is deeper than the product valley.

What is important for the moment-- then we will-- when we do kinetics next time, we will also talk about how to model the rates at which this climbing of the valley to the saddle point happens. But for the moment, all that we need to know is that this activated complex can be treated, can be-- it's literally a new compound, so a super molecule in which all the atoms that are in play are very close to one another, and they share a lot of elastic energy, exactly like the golf ball is deformed.

And then it only depends-- and then, once you're there, that thing could decay in one direction, or it could decay in the other direction. So there is a chance that you are up here, and you came down this valley, or you can decay the other valley. After all, this is an unstable point.

So in principle-- you see, in principle, if you have a box in which you have only, say-- suppose you have just two hydrogen atoms. So this is-- and now, as a result-- so this is at time, say, t1. At a later time, as a result of collisions, they find themselves in a highly deformed situation like this, very close to one another. This is the activated complex.

And as a result of the collision, you could have two possibilities-- maybe I should do this-- that the thing breaks back to having two hydrogen atoms. So maybe these ones were moving this way. They collide here. They form this activated complex. Let me put that just to say, well, it has a lot of stored elastic energy in it.

So one way is that elastic energy makes it explode into two other atoms that will move that far away. Or it could also-- if the angles of the collisions are appropriate and so on, you can also form just a single molecule that would move away this way. Of course, you have to conserve, also, momentum. So this molecule will have the same momentum that the sum of the two momentum.

So this would be an effective, chemically effective, collision that produces the chemical reaction. And this is an ineffective chemical-- collision, just-- these kind of collisions, the ineffective ones, are the ones that are also responsible-- if you don't have to-- you don't have to go to this kind of extreme, they are responsible for redistributing the energy between the various atoms in your system. And if you have enough particles, that will give you-- produce the Maxwellian distribution, Maxwell-Boltzmann distribution of velocities.

Now, you see here that, for a system in which there are only few particles, like two, literally two particles, here we have those two particles have disappeared at this moment in time. In order to describe the dynamics of this system or the properties as a function of time, we need to know, also, the properties of this activated complex because, for some time, it's the only thing in our box. So if we want to describe properties, we have to know what the structure of this molecule is and what's the specific heats and so on.

So we treat this activated complex as a molecule in itself. However, yeah-- OK, let's do the formal discussion about this. So essentially, what this says is that we can split the reaction mechanism into two parts, a forward half-reaction that takes the reactants and forms, as a result of a collision between the reactants, forms the activated complex. And the backward half-reaction, which is a result of collisions between product molecules, also gives rise to this.

So you notice that we can write our original overall reaction in this way. And by our rule, since we have put the positive stoichiometric coefficients for the products and negative for the reactants, if you want to start from the products and form the activated complex, you have to put this-- you put them this way. And so the net stoichiometric coefficient of the original reaction is given by nu minus minus nu plus, the stoichiometric coefficient of the backward reaction, minus the stoichiometric coefficient of the forward reaction.

So now we have two reactions instead of one. And that's going to be very important, as we see here, in order to describe the possibility for the reaction to occur. So these activated complexes are fundamental. You have to go through the saddle point in order to go from one valley to the other valley. You can also go through higher than the saddle point or any path that takes you from one valley to the other. But the most probable is going through the saddle point.

So each reaction-- for each reaction, we have defined properties like the enthalpy of the reaction. So the enthalpy of the overall reaction, if you remember the other time, is the weighted sum on the stoichiometric-- weighted on the stoichiometric coefficients of the pure-component property at standard pressure in this kind-- in this instance and the generic temperature T. Well, we can also apply this definition to these reactions, the half-reactions.

In order to do that, I have to make the half-reaction with all the components to the left according to our rules. So, if you take this to the left, you see this-- the product is A star, and the reactants are the Ai with the stoichiometric coefficients A plus-- I mean, nu plus. So in this summation, I have to take with the plus 1 coefficient the enthalpy of the activated complex at standard pressure and temperature T and then put the stoichiometric coefficient, therefore minus these things. OK, so that defines the property of the forward half-reaction. And this is the enthalpy of the forward-- I mean, backward half-reaction.

In order to define them, you need to know your-- you have to characterize your activated complex because you need to know its enthalpy at standard conditions, treating it as a molecule. So in a sense, because people don't really do this, this is just a sort of a hypothetical. It's a way of looking at it which will allow, nevertheless, to define a lot of useful things that people do use.

So in spite of the fact that we have just said that the activated complex is fundamental in order for the reactions to occur, next, we are going to neglect them. But it is not a contradiction. We're going to the neglect to neglect them for just one aspect, namely for calculating the properties of our reacting mixtures and only in a limit in which we have many particles.

So this is an addendum to the simple system model. It amounts to saying the following. Yes, if I have a situation in which I have only two particles, this-- passing through this is fundamental. And also, when I take a photograph at this instant of time, the 100% of the scenario is made up of the activated complex. There's only it.

But if I have many particles, it's true that there are many collisions. But they do not occur all at once. So that means that if I have many particles in this box, in addition to the two particles that are going to collide and form these, there are also a large amount of other particles that are not colliding in that moment.

And since they form the majority, the mole fraction of the activated complex is so small that we can neglect its contribution to the properties of the mixture. So in that sense, we say, for many particles-- and when we are dealing with just looking at the properties for making energy and entropy balances, so properties like the entropy, the enthalpy, and the energy, or the volume, we compute them by neglecting the minute amounts of activated complexes that are there.

So essentially, what we are saying is that neglecting the activated complex is like neglecting the existence of the chemical reaction for the purpose of computing the properties. In other words, we assume-- when computing properties of mixtures that are reacting, we assume that they have the properties of the mixture with the reactions, so to speak, turned off. If I turn off the reactions, I stop the formation of activated complex. So there is no activated complex in play, and I'm in the usual situation in which I have only my original particles.

Although, we're not actually turning reactions off, but it's as if you could. Although, the reaction is occurring. And also, what we are assuming is that the-- you see, with the reactions-- If I have this situation here, and I turn off the reactions, and I still have an activated complex that was already there because it was just being formed, that complex sometimes will break up, like explode.

So that explosion delivers kinetic energy locally, so produces a non-equilibrium situation. That amount of kinetic energy, which is concentrated here in these bullets that go away from the explosion, and they have a velocity which is much higher than the typical velocities, it will take a while for other collisions, not of the chemical kind, to redistribute that excess in kinetic energy due to the chemical reaction and redistribute it to the other molecules around. OK?

Well, we will-- we also assume that the-- that this non-chemical collision redistribution mechanism is very fast, so fast that, as soon as we turn off the reactions, or as soon as the activated complexes decayed into fragments of the decay, that energy gets almost immediately redistributed among all the other molecules so that they reach, immediately, this stable equilibrium state with the frozen composition that they are in at that moment. These are all the concepts that go into the idea that then we are going to model the properties of our system with chemical reactions as if they were not reacting, but in stable chemical-- I'm sorry, in stable equilibrium for the instantaneous composition.

Talking in terms of characteristic times, the chemical reactions, we think-- we consider them much slower than the redistribution mechanism by collision, chemically ineffective collisions, which, instead, are very fast. And therefore, the chemical reactions change the composition, according to the proportionality relation. So the reaction coordinate does advance in time.

But we assume that, each instant of time, the system immediately redistributes the energy caused-- the local excesses or defects of the energies produced by the chemical reactions and the activated complex and so on and therefore keeps the state almost close to what it would be, a stable equilibrium if you didn't have chemical reactions. So that's the scenario. And, of course, this formula is going, now, to be our-- head of the game because for example, we can define-- we can compute the equilibrium composition by maximizing, because the maximum entropy principle does apply.

In fact, that same expression here is written more even more formally, saying that this is the S of the off system with an n that is now variable. And it depends on that initial amount of the chemical reactions that are in play and on the reaction coordinate. So if you look at it this way, it's going to be easy to do the partial derivatives that we have to do, for example, here, because for example, we like to-- we are interested in taking the derivative of the entropy with respect to the advancement-- to the reaction coordinate of one reaction because that derivative is going to be called the affinity of the reaction, the De Donder affinity of the reaction. So we have to do that derivative.

But before we do that, here's the graphical representation of what we're doing here. For if you fix the value of the composition, so fix an epsilon, say epsilon 1, you have fixed the composition. And this blue curve represents the stable equilibrium state of a mixture with that composition. Now you change the composition, and here you have another stable equilibrium state curve and another yet.

These curves, they do not represent all the states of your system. They represent this family of states, frozen equilibrium, stable equilibrium states that we have chosen to describe the properties. But this family is rich enough that it can span, essentially, all the allowed region of the energy versus entropy diagram for the reacting system. And certainly, these are allowed states.

So when we want, now, to apply the maximum entropy principle, the maximum entropy principle says, well I fix the value of the energy, I fix the values of the volume, the initial amounts and the stoichiometric coefficients. And the stable equilibrium state of the chemical reacting system is the one that has the highest entropy. So you see, along this line, this black line crosses many of these blue curves until it reaches one, beyond which there is nothing. And if you do the same at another level of energy, you're going to highlight this other equilibrium state and, again, this one.

So the envelope, the red curve, the envelope of these blue curves represents the stable equilibrium states, the maximum entropy-- so those are the stable equilibrium states of the chemical reacting system. So that dotted red curve is the fundamental relation for the stable equilibrium, stable chemical equilibrium, states. Whereas, these blue ones represent stable equilibrium only if the reactions are frozen.

So this derivative is the affinity. And now let's go into a little more details of the same. Same graph, same definition of affinity. What's new here is only a more explicit expression for this red curve, which is a stable equilibrium state fundamental relation with a C in front, which stands for chemical, chemical stable equilibrium states.

You see, at each level of energy, there is one particular epsilon, which we call epsilon 0, that corresponds to the composition at chemical equilibrium. And that's the one that appears here-- so the entropy of the red curve, the entropy of the stable equilibrium with chemical included has this-- shows, for example, the dependence on energy is not only from the original dependence of the frozen equilibrium mixture, but it's also through the epsilon 0, because as you change the energy, epsilon 0 changes. And so energy influences the maximum entropy not only through the properties, regardless the chemical reactions, but also through the composition at chemical equilibrium.

So that means that, when we need to compute derivatives-- for example, the temperature-- you remember the temperature is the derivative-- or actually, the inverse of the temperature is derivative of fundamental relation with respect to energy. Well, if I have to take this derivative with respect to energy, I have the contribution from here. But I have contributions also from here.

So the first one is what would be the temperature if the reactions were off. And these other contribution is a summation because these are vectors. And so this is a summation of all the chemical reactions from j-- that goes-- for J that goes from 1 to z of the derivative of S off with respect to epsilon in here-- you could also do it with respect to n and then with respect to epsilon-- times the derivative of epsilon with respect to U.

However, since at chemical equilibrium, the entropy is maximum-- so if the entropy is maximum, it means that its derivative with respect to these variables here must be 0, including this derivative, the affinities. That is what we call the condition for chemical equilibrium. The affinities must be equal to 0. And in these summations, this derivative is precisely that one. So it's the affinity. And at maximum, it's equal to 0.

So this summation is a bunch of 0's. And it turns out, therefore, that the temperature-- so the derivative of the red curve is equal to the derivative of the blue curve. In other words, they have a contact of first degree. They not only they touch, but also they touch with the same tangent. And this is true not only for temperature, but also for pressure and for the chemical potentials.

So we have, essentially, already said what the condition, necessary condition, for chemical equilibrium is, is that the affinities must be equal to 0. So now let's compute those affinities. Again, that's the derivative we're talking about. And here is a summary of what we just said.

Now, the derivative of S of the off system, of the off fundamental relation with respect to n, is the chemical potential divided by the temperature with the negative sign in front. So when I do this derivative, the result is a weighted sum of the stoichiometric coefficients because here, we are taking the derivative with respect to the epsilon of one reaction. j is the label of the reactions, and i is the label of the components.

So these are the stoichiometric coefficients of the jth reaction for the ith component. And so it's a weighted sum of the chemical potential divided by the temperature. That's the affinity of reaction j.

Now we can use the tools that we have already developed in order to describe chemical potentials of mixtures, because we spent half of the course on this. For example, assume an ideal Gibbs Dalton mixture of ideal gases. Off-- so these are-- the off allows us to use anything that we know of the system without chemical reactions.

If we-- remember, it's like the chemical potential of the pure component at T and p plus RT log of y, y being the mole fraction of that component. If we want the reference to the standard pressure p0, then here we have to put that integral from p0 to p of the partial of mu with respect to p, which is the specific volume. And for the case of a gas, this gives the logarithmic contribution. So we have seen this several times.

Let's substitute it up here. So if you put it up there, you will end up with a summation of stoichiometric coefficients times these mu double i's. And this summation you may recognize is the Gibbs free energy of that reaction because you remember that the chemical potentials of the pure components are equal to the Gibbs free energies of the pure components. And the delta g0, the 0 here is because we are doing it at standard pressure and as function of temperature. So from this part, from this thing, we obtain a contribution like that.

From this other one, see there is no subscript i here. So it goes off the summation sign. And then the summation sign remains only the summation of the stoichiometric coefficients tout court, which we are going to denote as nu of j. So it's the total stoichiometric coefficients of reaction j.

And the last term, it's RT, but the T goes away with the T in the denominator here. And then it's the summation of stoichiometric times log of y. You can see that you can put the pre-factor of the logarithm inside. It becomes an exponent. So this becomes the summation of log of y to the nu sub i. And then you know that the summation of the logarithms is equal to the logarithm of the product of the arguments of the logarithm. This is simply a property of the logarithms.

So that equation is like that. We now, in order to sort of get rid of the logarithm, we can take the exponential. So if you take the exponential of this expression of y-- actually, take the exponential of y, divide also by R, and change the sign-- so that comes from here. The exponential of the logarithm, they cancel each other. So I'm left with this product of the mole fractions to the power of the corresponding stoichiometric coefficients.

And then I have the exponential of this delta g, which is divided by T and also by R because we divided also by R and changed sign. We call that exponential-- it's actually written here-- the equilibrium constant of the reaction. Yeah, here, I should also correct, it should be-- for precision, it should be K sub j. It's related to the j label of the chemical reaction. So this is the chemical reaction constant, e to the minus the Gibbs free energy over RT.

From this term here, the log of p, the log has gone away, and the coefficient multiplying the log was the total stoichiometric coefficient, which goes inside the logarithm and becomes an exponent. And the product of this pressure-dependent and temperature-dependent is also called the equilibrium constant. So these are really not constants, because they depend on temperature, depend on pressure. What they don't depend on is composition. That's why they're called, traditionally, equilibrium constants.

So far, we have made no other assumption than the modeling assumptions. So this is not yet the equilibrium law of mass action. So we call it the non-equilibrium law of mass action. It relates this, that, and that. But of course, since we know that, at equilibrium, the affinities are equal to 0, and so e to the 0 is 1. So if you cancel this, you have the equilibrium law of mass action.

Here, since we have always worked with mole fractions, the y sub i's, it's written in the most natural way for our treatment so far. Often, in the practice of chemical engineering, instead of mole fraction, one uses the concentrations, the molar concentration, so the number of molecules per unit volume. And sometimes you denote that by c, c sub i, concentration. Sometimes you denote it by this N in square brackets. Of course, they're related. And therefore, if you take this one and do this substitution, you get the law of mass action written in terms of concentrations.

What changes is the constants. So for example, the pressure dependence goes away. The p-- you see the p. The total p disappeared. And so this equilibrium constant based on concentration, the c up there, is there just to distinguish between these equilibrium constants. So you have to be careful when you are in this business to understand which equilibrium constant you're talking about.

There's also this last way of writing it also has an additional difficulty that has to do with the dimensions because whereas the top one is dimensionless because the mole fractions are dimensionless, p over p is dimensionless, and delta g over RT is dimensionless, so everything is dimensionless up here. Down here, it's not, because this is N over V. And so these equilibrium constants depend-- for example, this has a-- this has dimensions of moles per cubic meter.

So if your chemical reaction has stoichiometric coefficients that are equal-- that sum up to 0, then this is dimensionless. But if they don't sum up to 0, then this has dimensions that depend on the sum of the stoichiometric coefficients. So that sometimes is a cause of little errors in computations.

Clearly, you can redo what we've just done, also, for liquids. If you, instead of having a reaction occurring in the gaseous phase, you have it in the liquid phase, and you can assume ideal solution at all compositions for all components-- which is rare, but it's a starting point-- then, of course, you remember that integral when you write the chemical potential. Instead of the RT log of the p over p0, it's simply p minus p0 times the specific volume of the pure component liquid-- of the pure liquid component i.

And then you substitute up there. Then it appears also the weighted sum of the volumes. That's the volume of the reaction. And when you do-- so when you go back here, the non-equilibrium law of mass action, this side has the same format, except that the equilibrium constant is different. It has-- also, it has one contribution which remains, the delta g over RT. That's the equilibrium constant K of j T.

What differs is that the other thing that you could also separate and make it two separate exponentials like this could be the prefactor of the standard equilibrium constant. And you can also write it in terms of concentrations. For a liquid, of course, the concentrations-- the relation between mole fractions and concentrations are written this way.

And again, by setting all the affinities equal to 0, if your system is at equilibrium, chemical equilibrium, all the reactions have 0 affinity at equilibrium. So you can set 0 all these ones. And with this law of mass action, you can compute the equilibrium composition.

If instead of having ideal gas mixtures or solutions, you have real mixtures that you model according to Margules, Van Laar, all those models that we have introduced for the models of non-ideal behavior of mixtures, then you can always put that-- the expression for the chemical potential in this way, in terms of the affinities (I meant, activities), which become-- play the same role as mole fractions for the ideal behavior. Instead of calling it y sub i, you call it a sub i, and it becomes non-ideal. But the mathematical steps are exactly the same, so here is what you obtain.

But then, obviously, you need to know-- to have those Van Laar or Margules or whatever relations that allow you to write the affinities (I meant, activities) in terms of the mole fractions. And then this will be a set of equations that will allow you to compute the mole fractions.

Now, the main part of the equilibrium constant, that exponential of minus delta g over RT is something that we have already encountered at the beginning of last lecture, when we talked about the role of the Gibbs free energy in determining when a reaction is reactant-favored or product-favored, because it turned out that the entropy produced by irreversibility is related to this.

OK, so if I take this expression and take the logarithm and actually take the logarithm in base 10, I can plot that logarithm versus the inverse of the temperature. And we have already proved the last time that this derivative, of this logarithm, with respect to 1 over T, is related to-- it's the negative of the enthalpy of reaction.

So when a reaction is exothermic, the delta h is negative. So that means that this slope is positive for the exothermic reactions. So for example, this reaction is exothermic. This one is endothermic because it goes down with 1 over T.

So you see that the chemical equilibrium constants span over a wide range of-- how do you say? [LAUGHS] Senior moment. Orders of magnitude. OK, thanks. [LAUGHS] So you see-- it can go from very high to very small. And the reaction-- the equilibrium constant is what determines the compositions.

If it is very much-- so if the equilibrium is very much towards the products when the chemical equilibrium is-- if you go back here, if the equilibrium constant is large, it will make prevail the mole fractions that have positive stoichiometric coefficients. So it will make prevail the products, whereas if it is small, it will make prevail the one that are the denominator. So they have negative stoichiometric coefficient.

So how do we compute the equilibrium constants? Yeah, they are defined for each reaction. But since they are related to the Gibbs free energy of reaction, we can use the Hess relation that, you remember, allows you to compute the properties of reaction from the properties of formation of your constituents. So all you need to know is the properties of formation. But you need to know them as a function of temperature. So for each component in principle, you should know-- you should measure it as a function of temperature.

However, there's a simplification-- so based just on that, it turns out that the equilibrium constant for your reaction can be computed as the product of the equilibrium constants, of the reactions of formation of your various constituents that appear in the chemical reaction mechanism to the power of the stoichiometric-- respective stoichiometric coefficients. And this is general.

Now, if we use that derivative that we have done in the previous slide and also earlier to show that this derivative is equal to the minus of the enthalpy of reaction, and then if we notice that the enthalpy of reaction seems to be pretty constant with temperature-- how do I-- why do I say that? Because if you look at these curves here, they look like almost straight lines. So straight lines means that the slope is almost constant.

So if you assume-- if you make that approximation-- if you look closely, they're not literally straight lines. So it is an approximation. But if you make that approximation, it means you can do this integral, assume this is constant. And that integral, therefore, it's like an integral in d of 1 over T. It's like a linear relation between the logarithm of K(T) and 1 over T. This is exactly the equation of those lines of the previous plot.

Then, if you notice that this one is still-- the constant of integration is the equilibrium constant evaluated at standard temperature. And so that's also related to delta g over-- I think there's a T missing here. This should be RT 0. And yeah, I have to correct that.

So if you substitute that up here and remember that delta g is delta h minus T delta s, you finally get this expression, which gives the logarithm of K(T) as a linear relation in 1 over T. And those delta s and delta h are the properties of reaction at standard conditions of temperature and pressure. So essentially, by just knowing the entropies of formation and the enthalpies of formation of your various constituents, this expression gives you the chemical equilibrium constant at any temperature.

And if you want to correct for that minor difference that is due to the fact that those lines are not exactly straight lines, but you want to do the approximation, instead of using those, you can use those from a table which does a least square fit, which does a better job. For example, this table gives you good numbers in a wide range of temperatures from 300 to 5,000 K, which is plenty of what you need for, for example, combustion applications.

So we know the chemical equilibrium constant. Let me give you an example. You've probably seen these kind of things in the previous course 2.452-- I mean, 2.42. In any case, suppose we consider the reaction of dissociation of CO2, which is important in combustion because CO2 is a product of combustion. And at high temperatures, this dissociation may occur. So let's assume the temperature is of the order-- is 3,200 K and that we are at atmospheric p.

Somehow, using the previous table, you can compute the equilibrium constant, which is 0.64. And so in order to do the calculation, we need to apply the law of mass action. And the law of mass action says that the product of a mole fractions to the stoichiometric coefficients, it must be equal to equilibrium constant, the equilibrium constant that depends on temperature and pressure.

Now, in this case, the pressure is equal to p0. So this prefactor is equal to 1. So it cancels out. So you are left with K of T, which is E to the minus delta g over RT. So we know the value of the right-hand side.

Now, for the left-hand side, we need to express-- we need to find the mole fractions. And the mole fractions, they're not all independent of one another, because they are related through the proportionality relations. So mole fraction is n over total n. So n of component i is equal to the initial amount plus the stoichiometric coefficient times the reaction coordinate epsilon.

And the denominator is the sum of the numerators, so to speak. So it's the total n initial, the total stoichiometric coefficient and the reaction coordinate. If we divide by n sub a, denominator and numerator, above, I get the mole fractions, the initial mole fractions. Below, I get 1. And epsilon over n sub a, I call it xi.

So each mole fraction depends on the initial mole fractions and on a single variable, xi. So if I substitute that in the law of mass action, this gives us one equation in the single variable xi. And therefore, I can solve for xi, given the initial compositions. And the initial composition for this problem is given somewhere here. You can look up the details.

So once I know xi, I go back here, and I have the entire composition. So I have the mole fractions of all the various constituents. So that's how you compute chemical equilibrium compositions using mole fraction.

Clearly, if you have more than one reaction in play, you have one law of mass action per reaction. So each reaction brings in a new unknown, which is the reaction coordinate. So if you have three reactions or five, say-- for the example that will follow, we have five reactions.

So you have five unknowns, which are the reaction coordinates, epsilons, or the xi's, which are the per-mole coordinates-- five unknowns. But you have five equations which correspond to setting equal to 0 the five affinities of each of the reactions. So of course, you have to compute five chemical equilibrium constants. But then you have a system of five equations and five unknowns, which gives you all that you need.

This is for example. I think we have seen, already, part of this table when we did the adiabatic flame temperature for an internal combustion engine. So here is that computation that does-- at the same time, it computes the energy balance. That gives you the adiabatic flame temperature in terms-- but also, at the same time, you compute the five equilibrium laws of mass action.

And therefore, as a result, you can compute the compositions of all the various components. Notice that these numbers-- this is in mole, this is in millimoles, and this is in micromoles. It turns out that the first two reactions here, the dissociation reactions, are important in determining the thermal aspects of the combustion.

They will affect the adiabatic flame temperature. If you don't consider them, you overestimate it. Whereas, the last three give you an estimate of the formation of the nitrogen oxides that are pollutants, as you know, of combustion products. That corresponds to various ways in which nitrogen and oxygen, the molecules can collide, at high temperatures and combine to form these various oxides.

Now, I told you that life is not that simple. I remember a collaborator of Professor Keck downstairs who used to say that what I just told you so far is Disneyland with respect to the real world because even for the simplest hydrocarbon, which is hydrogen, in order to describe the chemical reactions in play and these activated complexes and so on, you need-- this is the official scheme-- 24 reactions and eight species. And these are the parameters that allow you to compute the reaction rates.

This is a diagram which shows, for various hydrocarbons. For example, isooctane, which is like gasoline, say, you are here. Methane is here. And it gives you, in a log scale, the number of species that you need to consider and the number of reactions.

Turns out that the number of reactions is about 5 times. This straight line is an equation. It says that I need 5 times the number of species. Hydrogen is really a bit of an exception because 5 by 8 is not 24. But in any case, hydrogen would be here in this scheme.

And you see, for example, for methane, I think you need-- yeah, 50-something species-- we could read it here-- and the 350 reactions. At least this is true for kinetics, whereas, for equilibrium, we can avoid this kind of complication. But for the kinetics, it's not so simple.

Actually, if you look up even-- this is not a settled issue, because people are still working on determining these detailed mechanisms for new fuels, but also for old fuels. And now there is a lot of-- the artificial intelligence is playing a game also here because developing these schemes with so many reactions is, first of all, complicated. Second, it makes life very difficult because you-- how do you know?

First of all, if I have 5,000 reactions to be considered, how do I know that the 5,000 parameters that define the reaction rates are correct? And what if-- are they all important? So, in fact, many people are working on-- and artificial intelligence may help-- in model reduction schemes.

So you say you start with the complete scheme, but then you try to cut out at least for ranges of conditions and do a simplified model that allows you to do a good job anyway. So a lot of-- and again, I mentioned Professor Keck because he was one great contributor to this issue through the rate controlled constrained equilibrium method that you might-- if you're interested, you should read about.

Now, so the affinities at equilibrium are equal to 0. Here is another way of saying it, which gives us a chance-- I don't know if I should say again or first chance to use the method of Lagrange multipliers for maximizing functions subject to constraints, because after all, the chemical equilibrium condition comes as a condition from the maximization of the entropy-- of the entropy of our system with the chemical reactions. So therefore, this is the-- we adopt this model for describing its entropy where the n, the amounts, can be varied, but only in a constrained way, constrained by the proportionality relations.

So we consider maximize this function, subject to keeping energy, volume, initial amounts, stoichiometric coefficients fixed and varying the constituents only according to these equations. So this is a constrained maximization problem. And as you may know-- I'm sure you've seen it somewhere else-- the method of Lagrange multipliers consists in taking the function we want to maximize and subtracting the constraints, each one multiplied by its own undetermined parameter lambda.

And so I write the constraint by putting everything on one side and setting it equal to 0. And that thing on the one side is the thing that is multiplied by the Lagrange multiplier. So now I have a function in which I have the Lagrange multipliers. I have the n. I have the epsilons. And I want to maximize this function.

So essentially, I need to take the derivative with respect-- and set it equal to 0 with respect to those-- the derivative with respect to those variables that are undetermined, so the n and the epsilon. So I take the derivative of L with respect to n. I get one contribution from S, from the entropy. The derivative of S with respect to n. This is equal to the minus of the chemical potential over the temperature.

And then, when I take the derivative with respect to n, I also have a contribution from here because this is an n, which is minus lambda. And that's this minus lambda here. This has to be set to be equal to 0 for this Lagrangian function to be an unconstrained maximum. So when we apply the rules of maximizing functions, so you set the derivative is equal to 0.

So this says, ah, OK, the Lagrange multiplier must be equal to the chemical potential over T. Fine. Then I take the derivative of L with respect to epsilon. I pick up nothing from here, because the epsilon doesn't appear here. Epsilon is only there.

So it's with a plus because there's two minuses here. And the epsilon j picks up the stoichiometric coefficients of the jth reaction multiplied by the Lagrange multipliers. So this is what you get.

But since the Lagrange multipliers is minus mu over T, we can substitute. And that is the expression of what we call the affinity of the reaction. And taking the derivative equal to 0 therefore imposes the affinity to be equal to 0. So just another way of deriving the chemical equilibrium conditions.

However, this is useful also to introduce another possibility. Precisely because we have so many chemical reactions and chemical species in play, maybe we can also work, and people do work in fact, in all the simulation softwares, commercial softwares, that have properties for computing equilibrium, they are based on this concept of complete chemical equilibrium. What is it?

The idea is, all right, why should I list such a large number of reactions? Couldn't I just say that all reactions are possible, all conceivable reactions? So instead of listing the reactions, let's assume that all conceivable reactions are possible in order to compute chemical equilibrium.

So what would be the only constraint in chemical reactions? Chemical reactions-- the only thing that they cannot do is to change the nuclei. So the inventory of nuclei in your mixture is fixed. So the constraints here is count the number of nuclei in your mixture, initially. You must be sure that they remain what they were. Otherwise, you would be doing nuclear equilibrium.

So the idea is you want to maximize, as usually, the entropy because we are applying the maximum entropy principle. Now the constraint is that I want to constrain this c sub k. c is the number of nuclei of a given type. And they are given, initially, this way and at a generic composition this way.

So what are these coefficients a sub i k? Let me explain it with this table here. a sub i k represents for each-- for the molecule, for example, i, say, methane, it gives you the number of nuclei of each type.

So the first type is a carbon. Yes, in methane, there is one carbon. So I put a 1 here. There are four hydrogens, so I put a 4. There are no oxygens, no nitrogens. So these are the matrix of-- nuclear composition of your various constituents. So you list the constituents, and you, for each one of them, you put how many nuclei of each kind there is.

And it turns out that, for a very large number of organic molecules, the number of nuclei is very small. Carbon, hydrogen, oxygen, nitrogen, what else? Yeah, maybe argon because it's present in air. But-- OK? So that means, since the index that runs here-- so the number of constraints is that you have is the count of the nuclei in these columns. So you have few constraints, just as many kinds of atoms that are around.

So with the initial composition n sub a-- sub i a, and with this table, you compute how many you have initially. And you have to make sure by this maximization, constrained maximization, that, also at equilibrium, you have that same number of nuclei. Everything else is allowed. So that means you assume that there will be some chemical reactions that will do that change, will take you to that equilibrium because everything is allowed, provided nuclei conservation is done, is satisfied.

So again, to proceed, we assign a Lagrange multiplier to each constraint. And the constraint here is written by taking on the same side here, these two. So it's ni minus initial ni times a summation. And then you multiply each one by the Lagrange multiplier.

And now you take-- you impose that this function be maximal. So you impose the derivative equal to 0 with respect to the only variable, which is the n's, the n sub i's. So you do that, and of course, this one still gives you the chemical potential over the temperature. And this here, n, gives you the summation over k of lambda k times a ik.

Now, for example, let's assume ideal gas mixture or ideal behavior like this. The chemical potential goes with the logarithm of y. So you substitute it up there. And so you obtain an equation. Since this must be equal to 0, you get an equation that gives you the log of y in terms of this chemical potential of the pure component and this summation of the Lagrange multipliers times these coefficients of the matrix.

So this is the-- this gives you the composition. But it is in terms of Lagrange multipliers. So you need, in this case, four Lagrange multipliers. How do I determine the Lagrange multipliers? As typically, in the method-- you have to substitute the solution back into the constraints, and that will give you an equation that allows you to compute the multipliers.

So I take this expression and put it here in order to compute the amount of nuclei that it implies. So this is the n's. Then the n's can be-- n sub i's can be computed as n times the mole fractions.

So this is an equation-- or actually, it's a system of four equations-- because I know the initial amounts of nuclei. So I know the left-hand side. And the only unknowns are the Lagrange multipliers. So I can solve this system of four equations and four unknowns and get the Lagrange multipliers as a function of the initial composition. I plug it back here, and then I have the mole fractions.

And notice that it's very interesting because we didn't put any limit to the number of chemical compounds that you can consider. So this list can be as long as you please. You could take the entire Janaf tables. Or you can just consider the ones that you want. And this expression will give you the mole fractions of anything that you're interested in.

This method was implemented by Gordon and McBride in the '50s, I believe. And it is still the method used in almost all softwares. I know it very well because when I started-- when I did my master's with Professor Keck, I worked for one year. And at those times, we didn't have easy computers. The computer building was like a building near the nuclear engineering department.

And he gave me-- this computer program was a set of cards, like 1,000 or 2,000 cards in a box for the program-- something that today I think stays in like maybe 28k, kilobytes-- and another box with the properties of the various constituents. And he asked me to implement his model reduction method, constraint equilibrium method, into that software, which was a very nice start here.

And now, I notice also that there is something I have to correct here because is it plus or is it minus. I'll figure it out, and let you know. OK, so I think we are done for today.