[SQUEAKING]

[RUSTLING]

[CLICKING]

GIAN PAOLO BERETTA: OK, good morning. So let me remind you where we were. We are dealing with systems with chemical reactions. We talked about the role of the activated complex in the mechanism of converting reactants into products as a result of collisions. And in order to do that, then we did chemical equilibrium derived from the principle of maximum entropy.

So if you remember, one of the key modeling assumptions that we had to make was to integrate what we call the simple system model, which others call the thermodynamic limit or the many particle model, in which you remember that the idea was that, essentially, we could add or remove partitions in our system without that affecting the properties. Here, we add also the fact that we add and remove or, say, turn on and off-- very conceptual idea-- the chemical reactions.

And that doesn't affect the properties-- of course, it affects the time evolution because it will inhibit or allow chemical reactions to proceed. But for the instantaneous picture that we take when we measure properties of our mixture with chemical reactions, that the reactions are on or off doesn't make a lot of a difference for many particles because the role of the activated complexes is minute, since they are very few, since they are very short-lived, and also because the collisions that produce chemical reactions are much fewer than the collisions that simply redistribute energy among the molecules.

And so as part of our assumption here, that we can model the properties as if it were a stable equilibrium state with the actions turned off, is also the assumption that the non-chemical collisions are much faster, are much more abundant, and therefore equilibrate energy much faster than the effective chemical collisions.

So that all is in order to allow us to essentially represent this family of would-be equilibrium states if you didn't have chemical reactions, the blue curves. And this family has one parameter if you have one chemical reaction or has as many parameters as there are chemical reactions. So you shift from one to the other by changing the reaction coordinate epsilon.

And the envelope of these stable equilibrium state curves is the stable equilibrium state curve for the system with chemical reactions. And that's where the stable equilibrium states are with the reactions on, and that's where we calculate the maximum. We apply the maximum entropy principle. And the maximum entropy principle implies that the derivatives of how the entropy varies with respect to those parameters must be 0. And these derivatives are what we call the affinities. These are the entropic affinities. Some others call affinity this times minus the temperature. That would be the energetic affinity.

And then, by applying the definition, the simple definition of affinity, which is this one, and applying the expressions for the chemical potentials that we have worked out in several cases, we end up with the law of mass action. This is in general, so it's a nonequilibrium law of mass action, which becomes the equilibrium one when you set the affinities equal to 0.

And, as you have seen, we've defined various forms that we all call equilibrium constants. For example, this one is a dimensionless equilibrium constant, which is simply e to the minus the Gibbs free energy of the reaction divided by RT. And this other one is the equilibrium constant. In terms of temperature and also pressure for a gas. This is for the gas. And so this is the pressure dependence. Or you often work with concentrations, the molarity-- so how many moles per volume you have per liter. And so you use this symbol for those concentrations. And then you have this form. So will we proceed using more often now this form here.

And, of course, these various forms of the chemical equilibrium constant are related to one another. As an example, before we proceed, I wanted to just mention this one, which is that which happens in pure water, the fact that water ionizes itself. And so there is an equilibrium between the water molecules and the formation of the hydronium or the hydroxide ions. And as you know, the abundance of these ions defines the scale of acidity of an aqueous solution. In fact, what we call pH is minus the log base 10 of the concentration of the H3O plus ions. And, sometimes, you call also pOH minus the log of this concentration.

Now since this is a concentration, so it is dimensional, it is mole per liter, you have to divide here by the dimension. So this is put under the logarithmic number, which is dimensional. So you have to take the dimensions away or use the convention that you always going to use those dimensions because, usually, logarithms like to have nondimensional numbers as arguments.

And here is how the law of mass action looks when you write it for that equation. See the stoichiometric coefficients are minus 2 for water. So when you get to this exponent here, it's a minus 2. So that's why the concentration of water goes to the denominator. And then plus 1 and plus 1 for the other two molecules/ions so that they go to the numerator with the power 1. So this is the product of those. And that has to be equal to-- at equilibrium has to be equal to the equilibrium constant based on concentrations.

Now in this business, therefore, you need to compute the concentration of pure water. And that's defined by how many molecules you have per liter. You can write it as the density over the molecular weight. And, for example, at 25 degrees C, the density is 997 grams per liter. Molecular weight is 18 gram per mole. And so that concentration is 55.3 moles per liter. You need it squared. So in order not to carry these along in the practice of chemical engineering, often-- almost always-- you find this product of these equilibrium constant times the square of the water concentration-- you find it called the Kw, the equilibrium constant for water.

And then, therefore, this equation rewrites this way that the product of the concentrations of the hydronium and the hydroxide ions is equal to this constant. Which constant is not. Because you remember that the equilibrium constants vary a lot with temperature, and also this constant has dimensions because, for this particular reaction, usually also the equilibrium constant based on concentration is dimensional. It has dimensions of the overall concentration to the power equal to the sum of the stoichiometric coefficients.

Now, for this particular reaction, the sum of the stoichiometric coefficients is 0 because minus 2 plus 1 plus 1 is 0. So this is dimensionless. It coincides with the equilibrium constant K(T) without the c. So this is dimensionless, but this is not. So the Kw has dimensions of mole squared per liter squared. At 25 degrees C, it is almost exactly equal to 10 to the minus 14 in those units.

And if you have a neutral solution in which there is no acid or base dissolved that would capture some of these ions, they would be equally populated, so their concentrations will be equal and, therefore, each one takes 10 to the minus 7. 10 to the minus 7 times 10 to the minus 7 gives 10 to the minus 14. And 10 to the minus 7 put into the log base 10 with the minus in front makes pH equals 7. And that pH equals 7 is, therefore, the notion of a neutral-- like pure water is neutral-- and it has a pH equal to 7.

At 25 C, though, because if you go at different temperatures-- for example, you go here, you see how, for example, at body temperature, which is 37 degrees C, the Kw is not 10 to the minus 14, but it's 3.55 times. And that makes the pH for neutral 6.7-- at 100 degrees, 6.17. Or, at 0 degrees, it's 7.47. So this is one of the applications of equilibrium. Of course, it's just one of the many examples.

So now we already talked about the elements of the model for chemical kinetics, and we want to develop more details. As you see, we are transitioning from the second part of the course to the third part because we've already been talking about nonequilibrium from the first lecture, I believe. But the more we advance in and we get close to our stable equilibrium, which will be the end of the course, we'll talk more and more about nonequilibrium states.

You remember this picture in which we presented the idea of a potential energy surface, and that's what we used to define the activated complex. The potential energy surface represents the energy at 0 temperature of the various configurations with which you can find the reactants or the products. For example, these are the reactants. These are the products. And here, in this scenario, and along the path of steepest ascent here and steepest descent here, or vice versa, you find the saddle point, which is the lowest point that allows you to go from one valley of this landscape to this other valley.

Now that's at 0 temperature. If there is temperature, it means that part of the energy of the molecules is in their degrees of freedom-- translational, rotational, vibrational, electronic. They all are capable of storing energy in the molecules. At low temperatures, most of the energy is stored in the-- let's call them easy degrees of freedom, which is the translational, the rotational. As you increase in temperature, also the vibrational become important. And if you go even higher, also electronic, you can excite the electrons and, therefore, they could jump up and down from the various orbitals that represent the energy levels of the molecule.

So if, therefore, there is a kinetic energy, first of all, we've seen that there are collisions. Molecules, by having kinetic energy, undergo a lot of collisions. And, as a result of these collisions, they put together their kinetic energy, and they form these activated complexes, sometimes. Sometimes, they don't form the activated complex. Sometimes, they just jump on the sides of the valleys, which have higher energy. But then they go back. So they bounce in the valley up in these higher energies. So the result of collision might be the formation of things that look like almost activated complexes, but they're not this particular one or in this area that would allow going from reactants to products and vice versa.

And also, we've seen that, as a result of collision, the kinetic energy gets momentarily transformed into elastic energy, like two springs that collide. So they store the energy for a while, and then they explode back and shoot the fragments of the fission of this activated complex in various directions. These fragments will have a higher energy than the neighbors.

And, therefore, by the other collisions, the nonchemical collisions, that energy will get redistributed and will either heat up if they have higher energies, but sometimes, also, they also have lower energies because some of the energy, if the reaction has been effective, has been retained by the new configuration of the molecule in the form of potential energy, like here.

So if you go from here in this direction, so from left to right here, this much potential energy is stored in the new configuration. So it came from kinetic energy, went up to form this complex, and then, as you go down, you release-- so this difference from here to here will be the kinetic energy that is released by the fragments of the explosion, so to speak, whereas this other difference is not anymore available as kinetic energy because it has become potential energy.

Now the collisions are governed, as you know, by the Maxwell-Boltzmann distribution of velocities. And this distribution-- maybe later on, if I have time, I'll show you how it can be derived from the maximum entropy principle. And so it is the distribution that maximizes the entropy given certain constraints. So that means that these molecules do not all have the same velocity. And also, this nice GIF that I took from Wikipedia shows-- if you look at it carefully, it starts from a nonequilibrium situation in which there are some particles that have higher velocities than others.

So it's a slightly skewed distribution. And it shows how quickly the many collisions will redistribute and return the distribution back to Maxwell-Boltzmann. This is like a pictorial representation of the idea that nonchemical collisions is a fast dynamics because collisions are many and occur many more than chemical ones. And, therefore, you can assume that this distribution is almost immediately-- it returns almost immediately to Maxwellian after each chemical reaction has released or absorbed some local energy.

So now let's go back to this path from the reactants from the bottom of the reactants valley to the activated complex, the saddle point, to the bottom of the products valley. And here, on the side, I have drawn not exactly the Maxwell-Boltzmann distribution, but a distribution that can be obtained from the Maxwell-Boltzmann. And it is a distribution of the kinetic energy that is made available upon collision. Because what we need in order to climb this diagram here, this valley, to go to the saddle point, we need enough energy for the collision-- as a result of the collision. And so this curve, it represents the probability density function not for velocity, but for kinetic energy of particles from the Maxwell-Boltzmann distribution of velocity.

So as a function of kinetic energy, which is plotted this way, that's the PDF. In order for a chemical collision to be effective, we need that it has at least this much kinetic energy so as to climb up here. So all the collisions that have energies above that are good. So if you do this, the area under this probability distribution function, which is the integral from this energy to infinity, that's the overall probability that your collision has a kinetic energy higher than this value delta H. So that's the result of the integral. So on this side, I need that to be-- therefore, the kinetic energy that I need is the enthalpy of the forward reaction or forward half reaction of formation of the activated complex from the reactants.

On the other side, I start lower. I'm in the same box, so-to-speak. So the molecules are in the same mixture, same Maxwellian distribution, same temperature. So this curve is the same as that one, only that it starts below here. Therefore, if I want to form the activated complex from this side, I need this much energy, the enthalpy of reaction of the backward half reaction. And so the probability to have the necessary energy as a result of the collision is this one, this area, which is equal to this exponential formula. And this exponential formula is what is called the Arrhenius law. And, of course, from this side, it's smaller. So there is more probability to get up here from the reactants than from the products in this case because the delta h plus is smaller than the delta h minus.

So this is one of the ingredients in order to formulate a theory or a model for the rate of chemical reactions, for the rate at which chemical reactions proceed. And in our language, therefore, it's for the rate at which the reaction coordinate changes with time, epsilon dot. So the bottom line is here. Epsilon dot will turn out to be the net result of how many-- of the epsilon dot of the forward half reaction and the epsilon dot of the backward half reaction. And these ones are done in here. So this column does the half reaction. This column does the forward and this does the backward.

So we talked about we can view this thing in terms of this in terms of probabilities. So the Arrhenius formula gives us, as we've discussed, the probability to have enough collisions, enough kinetic energy from the collision so that we form the activated complex.

Then we need another probability. Once I have the activated complex, which is that springs that are compressed and short-lived and ready to explode, the question is, will it explode towards the reactant valley or towards the product valley? That depends also on how the molecules have collided. It's not just the kinetic energy. It is also the angles with which they collide that is important because that allows to have the right vibrational modes to be triggered and, therefore, form the new configurations.

So it is complex reasoning about that. It's not simple to make a theory about this part of the probability, and, therefore, you just say, all right, let's call it a probability. And let's call it A. And there is one for the forward and one for the backward.

But then you also need another situation to occur, that it's not enough that the particles have the proper kinetic energy, but you need the right particles to collide. I need, for example, two hydrogens and maybe something else. So it'll be a three-body reaction. So because if I have a collision with the right energy but the wrong molecules, that's useless.

So you remember that the probability to have a molecule in a mixture is the mole fraction, a nice number between 0 and 1, which represents how many you have. And so the chance that you have those molecules is the probability. And the chance that you have several of them-- it's the multiplication of the probabilities. And if I need two molecules of the same kind, then that probability counts twice. So it's the mole fraction to the power 2.

And those amounts are precisely what the stoichiometric coefficients are. So that is why this product is a product of probabilities and the exponents of the stoichiometric coefficients which count properly how many times you need that kind of molecule to be present in a collision. Most of the times, effectively, the most probable collisions are two-body, just two molecules that collide. Already, the three-body reactions are much fewer and going four and so on, it's almost irrelevant. So this is a bit hypothetical. Again, that colleague of mine would call it Disneyland. But for a theory, that's OK.

For the practice, it means that you are never going to work with an overall chemical reaction scheme. But you will split the chemical reaction in many steps. So that is why we need so many reactions, like we will see again in the hydrogen will be 24 reactions just for the oxidation of hydrogen. It's not just one reaction. And those detailed kinetic schemes are mostly done with two-body or three-body reactions.

Well, anyway, these are probabilities. We assume they are independent events so we can multiply the probabilities. And yeah, we can also rewrite the mole fractions because here, we want to write it in terms of the concentration. So the mole fractions can be written in terms of concentrations. So we multiply this, that, and that, and we say, all right. We assume that the rate of change of the forward half reaction is given by the product of these probabilities. And this is the formula. This is the multiplication.

And then the traditional naming is that, yes, you have this product of concentrations to the stoichiometric coefficients that's singled out, the prefactor of that is called the rate constant, which is not really a constant. Again, it's a function of temperature. And it is an Arrhenius factor times a prefactor here.

Clearly, what I've done for the forward I can do also for the backward. So you just change the pluses into minuses, and you get the backward rate. Of course, here is the Arrhenius term that is important for the kinetic energy. And here are the concentrations based on the backward stoichiometric coefficients. So, in the end, the net reaction rate will be the difference between the forward and the backwards. And when we are at equilibrium, they will be equal to 0-- I'm sorry, not equal to 0. They will be equal to one another.

Notice also, here-- just we need to remind it later on-- that the way we have defined the half reactions, these stoichiometric coefficients with the plus and with the minus are positive numbers. And they are related to the overall reaction stoichiometric coefficients in this way, the one of the backward minus the one of the forward, at least according to our convention that puts everything on the left hand side and with a positive stoichiometric coefficients for what we call the products. Of course, you can always switch point of view and call what-- the products, call them reactants, and then you'll change all the signs.

So, for example, here is the rate constants for the set of 24 reactions that we already mentioned that is the most trusted, detailed kinetic scheme for the oxidation of hydrogen in pure oxygen. As you see here, they are listed from number 11 to 24. They are two-body reactions. You see, on both sides, you have two molecules.

So, in order for this reaction to form its activated complex, you have to have a collision of an oxygen atom and a hydrogen molecule. And if it is effective, that will form a hydrogen atom and an OH. And here is the prefactor. Actually, the prefactor-- what we call the A of T now, here it is written as a constant times T to the power b-- this is the power of the temperature. These are experimental values. And the activation energy, so the Arrhenius threshold is listed here.

It is also noteworthy that these three-body reactions, instead, you see on the first 10 reactions require three bodies, three-body collisions on either one side or the other or both-- just one side or the other. And they're represented with zero activation energy. We'll actually have, later on hopefully today, another example in which this list of reactions will be analyzed somehow.

Now let's see what are the consequences of this model that we have developed. So we just said we want to represent reaction rates this way, forward and backward. Notice that all the ingredients are positive because, after all, it's a product of probabilities and you cannot have negative probabilities. So these are both positive epsilon plus and epsilon minus are positive. Remember also that we defined and we just recalled the nonequilibrium law of mass action.

So let's now compute the ratio between the backward and the forward reaction rates. So we substitute from up there. We notice that this product, on the numerator and the denominator, you can also write-- since the argument of the exponent are the same, you can also write it as Ni to the nu minus minus nu plus. That's N to the stoichiometric coefficient of the overall reaction. So you can make this step. And then we can substitute, from the non-equilibrium law of mass action, because this is valid always, and you get this expression here.

Now this expression here is general, at least given this kind of modeling for the kinetics is general. Therefore, it applies also at equilibrium. So also, when the affinity is equal to 0. So when the affinity is equal to 0, this e to the 0 is 1. And also, at equilibrium, the rate of the backward is equal to the rate of the forward. They are not 0, but they are equal to one another. So it's a dynamic equilibrium. So this is one, and also, the left-hand side is one at equilibrium. And so that gives us a relation between the backward forward reaction rate constants and the equilibrium constant.

This is called the principle of detailed balance. It's useful because you don't, as you have seen, for example, we mentioned that-- in the list that I gave for the hydrogen rates, we gave only the k plus, the forward. That's because from the equilibrium constant, which you can compute from the thermodynamic properties, like the Gibbs free energy of the reaction, given the forward rate, you can compute, using this principle, the backward rate. So they're not independent.

That means I can, say-- well, that means that this combination here, this prefactor of the exponent, is equal to 1. And so, in general, I obtain that the ratio of the backward to the forward rates is equal to e to the minus the affinity over the gas constant. If you take the logarithm of that-- or, actually, if you take the logarithm of the inverse of that, so the logarithm of the forward to the negative rate, which by this formula is equal, therefore, to the affinity divided by R, we typically call that the degree of disequilibrium of the reaction.

So, in other words, it's another way of-- we can call it affinity, but you can also call it a degree of disequilibrium. And it's related to this ratio. Clearly, when the ratio is equal to 1 at equilibrium, the logarithm is 0, and the degree of disequilibrium is 0. And the degree of disequilibrium can be positive and negative.

So let's turn, for example, to other results that follow from what we've just seen. Think of the energy balance for a system-- for an isolated box in which there are chemical reactions going on, but there are no exchanges of energy or particles with the outside nor entropy also. So the rate of entropy change is equal only to the rate of entropy produced by irreversibility.

Now the rate of entropy change-- it's the partial of the entropy with respect to time. Now in that scenario, for the model that we have given-- we just reviewed in early slides today the expression for the entropy. In our model, in our simple system model, it's a function of many things, including the epsilons, the reaction coordinates. If the epsilons are the only things that change with time because the energy, the volume, and the everything else is fixed, then the rate of change of the entropy is the partial of S with respect to epsilon times epsilon dot. But the partial of S with respect to epsilon is the affinity. So we have these expressions here.

And since the system is isolated, that also represents the entropy produced by irreversibility. And it better be nonnegative. In fact, if you write epsilon dot like we have written as a dot plus minus dot minus multiplied by the affinity, if you remember that the affinity-- we just defined it as equal to-- I mean, not defined-- we just discovered that it is equal to R times the degree of this equilibrium. We get this expression, which gives us the rate of entropy change, which has to be equal to the rate of entropy produced by irreversibility for the closed system, for the isolated system. And this one, in fact, is a combination of numbers that is always positive. You can find that for any x and y, you have this inequality.

So at least we are happy that we are not violating the principle of entropy non-decrease. And therefore, we accept this model as a reasonable one, otherwise people would not be using it.

We can also look at this expression here. And notice that we could call-- so the contribution of to the entropy change or the entropy production for the closed system or the isolated system has a positive term and a negative term, or at least a term with a plus sign and term with a minus sign.

And, actually, since we said that these epsilon pluses and minuses are always positive, whereas the affinity can be positive or negative. So what we do is, we call these two contributions this way. We call it S plus, S dot plus, and S dot minus. So we rewrite that expression for the entropy change as S dot plus minus S dot minus.

Of course, we notice here that these results in always being positive. But sometimes, it's positive because S plus is greater than S minus. But sometimes, it's positive because S minus is more negative than S plus. In fact, we can-- by this definition, we see that S minus over S plus is also equal to the ratio of (the backward to) the forward. So it's essentially related to the degree of disequilibrium of the overall reaction. Or you could also take it as the ratio of the exponentials of the degrees of the disequilibrium of the half reactions.

Expressions of this sort, have in the recent literature-- let's say, 15 years-- being called fluctuation relations, there are many of this sort. And here, essentially, you see that the degree of disequilibrium governs the probability that these numbers be greater or smaller than 1. Sometimes people push a bit too much the interpretation, they say, this is a process that goes against the second law. This one goes towards the second law. But the net balance never violates. So it's like saying, well, one is more unusual than the other. But for the second law, what counts is the overall net effect.

And here is the list of possibilities if you want that to be greater than 0, which is always. If you have a positive affinity, so a positive degree of disequilibrium, then this is the case in which the S plus is more positive than the S minus. Or, if you have the affinity negative or the degree of disequilibrium negative, this is the case in which the S minus is more negative than the S plus. And, of course, at equilibrium, they are both equal to 0.

There is another way of getting to the same result, to the same kinetic theory-- theory of chemical kinetics. And this is a model based on equilibrium considerations. So let's start from the overall reaction that we are studying, like this one, for which we recall what the definition of the affinity is-- it's the weighted sum of minus nu over T of the various chemical potentials-- and here is the law of mass action, the nonequilibrium law of mass action.

Now let's consider also the half reactions of formation, now here, for compactness, I call them plus and minus. So this represents two reactions, the half forward and the half backward of formation-- so they are also written in that same format with everything to the left of the equal sign. So that's the activated complex.

This being a reaction as any other, I can define its affinities. So I can define the affinity plus or the affinity of the minus reaction. I have to be careful that the stoichiometric coefficients are not only these ones. But also, there is a stoichiometric coefficient equal to 1 in front of the activated complex. So that's this contribution. So I need to know, or at least to theoretically assume that we are able to know the chemical potential of the activated complex.

Whereas these are the usual ones. I mean, those of the reactants and the products. And, clearly, also for this reaction, I can write a nonequilibrium law of mass action exactly like that one, only using properly the stoichiometric coefficients. The concentration of the activated complex goes on top because it has a plus stoichiometric coefficient. In this summation, I put it at the denominator because, otherwise, I would have to put it at the numerator with a minus nu plus minus. And, clearly, I also need to compute an equilibrium constant for the forward and for the backward reaction. So that's pretty general, no assumptions so far.

We can also compute, therefore, the equilibrium. Now here's the trick. We are going to assume partial equilibrium, only either for the forward or for the backward reaction. So we say, suppose the backward reaction is at equilibrium. We set its affinity equal to 0. And from this law of mass action, this becomes 1. And we compute what would be the concentration of the activated complex if it were in equilibrium with the reactants-- I'm sorry, with the products because that's the backward reaction. So only on that side of the valley, there is equilibrium. And that gives me N star minus. I do the same also on the other side, and that would give me another value for the concentration.

The actual concentration of the activated complex is related to those ones through the degrees of disequilibrium of the forward and backward reactions because I can simply recognize that this k and this summation appear up here. So if I substitute these two in here, it brings me this relation.

I also notice that the ratio between what would be the equilibrium concentration of the activated complex for the minus or for the plus, the ratio of the two is equal to, again, the degree of disequilibrium, or the exponential of the degree of disequilibrium. So the degree of disequilibrium equilibrium can be written also, therefore, as the logarithm of those would-be concentrations, meaning that at equilibrium, those concentrations are equal. If they are both-- at overall at equilibrium, so equilibrium for the overall reaction, then also, the forward and the backward are at equilibrium.

So the idea is-- so that means that I have an indicator-- which is this ratio of the unbalance. We can think of this equilibrium concentrations as the rate at which the reactants form the activated complex. And if those rates are unbalanced, there is more formation of activated complex from one side and from the other, and, therefore, there is more chance that the reaction proceeds in order to balance this.

That is why we can assume that the reaction rate, of the forward, is equal to the forward equilibrium of the activated complex times a coefficient, which represents the frequency with which the activated complex decays in the forward direction and, conversely, for the minus. So that is the assumption.

And, with that assumption, we get-- if you substitute this equilibrium expression, you get this formula, which is very similar to-- it has something that depends on temperature, which is still what we call the rate constant. So it's another way of writing the rate constant, essentially, from a different reasoning-- not in terms of probabilities, but in terms of equilibrium.

And, of course, we can apply-- we can do the same as same ratio that we did in order to compute the principle of detailed balance. So this is in general. If you evaluate this at equilibrium, when epsilon minus and plus are equal and they are equal to epsilon 0, so this is equal to 1. The affinity is equal to 0, so e is equal to 1. That implies that k minus must be equal to k plus, so that this frequency of forward and backward decay is equal on both sides-- symmetrical-- which gives us some nice understanding. So we could have used here a single k. And, therefore, you see that this forward and backward reactions are proportional by the same constant to these would-be concentrations of the activated complexes.

Let's return to the rate of entropy production. And this is for the case in which-- we did it before for the case in which we have only one chemical reaction. Most of the times, we have many chemical reactions, like the 24 for hydrogen or the 350 for methane and so on. So we don't have only 1 epsilon. We have many epsilons, and z is the number of reactions. So the rate of change for the entropy, which for the isolated system is also the entropy produced by irreversibility, is a summation of affinities, each multiplied by each rate, which we can write also in this vector form.

Now here, sometimes, we realize that not all reactions are important in the sense that we need to describe their kinetics because some reactions are so fast that regardless of the kinetics, they equilibrate very quickly. So we can save ourself some time or complication if we assume that they are at equilibrium.

So essentially, what we do is to split the set of z reactions into a set of slow and a set of fast reactions. I split the summation into two summations. Of course, the proportionality relation is this one. It's also a summation. So we have split the summation also in here. And slow means that we can assume that this part of the composition is slowly varying as compared to this contribution here of the fast reaction.

And then we assume that the epsilons of the fast reactions, are at any instant of time the equilibrium epsilons. So we use the law of mass action to compute the equilibrium composition only of the subset of fast reactions, assuming that the slow ones are frozen. We temporarily freeze the slow reactions. So that fixes this part of the composition.

And we say, all right, for this-- so this become the initial amounts, like the na's. So for these initial amounts, what would be the equilibrium composition for the stoichiometric coefficients of the fast reactions? And that's what we've been doing. We apply the law of mass action in order to compute compositions, which can be cast as values of the reaction rates (I meant, coordinates), the epsilon 0's.

Of course, this has to be done at every instant of time because slowly, the slow reactions do advance. They also advance. Actually, they are the bottleneck of the mechanism. They are the rate-controlling reactions. The slow ones are the ones that control the rate of the others. When you have a car jam, the slow cars ahead impede the ones behind to go faster, even if they are faster. But as soon as they get there, they get stuck. So, essentially, this is what the fast reaction do. They get stuck in queue of-- they wait for the slow reactions to change something, and then immediately adapt.

So you may say, that's interesting. But if the reactions the fast reactions are at equilibrium, it means that their affinities are equal to 0. So in the expression for the entropy change, the affinities of the fast reactions are, by this model, assumed to be all equal to 0, which is true.

But one might be led to conclude, oh, so the fast reactions don't contribute to the entropy production? Because this sum is equal to 0? No, that would be a wrong conclusion because these assumptions makes the epsilons of the fast reactions appear in the affinities of the slow ones. So here, this says that the affinity of the fast reactions is equal to 0, which is the set of equations that you have to solve in order to compute this epsilon 0 fast. Once you find it, you put it in the expression, the analogous expression, for the slow reactions, which depend on energy volume and the amounts.

Now the amounts are given by the proportionality relation here. With the epsilon, instead of being now a function of time this way, it is a function of time this way. So I substitute this epsilon with the result of the equilibrium computation. And so now you see that the fast reactions advance. So these epsilon 0's advance following the slow ones, and their advance changes-- affects the affinities of the slow reactions. So, essentially, we have moved the effects of this summation, which is actually fast. So it's producing, immediately, the entropy. And we built it in the affinities of the slow reaction.

So with this model, at least, you find that it's useless to know the reaction rate constants-- so the Arrhenius factors and all of that for the reactions that you feel are faster and, therefore, equilibrated. So here is an example of a nozzle expansion. So here, we have, at the entrance before this throat of the nozzle-- this is a supersonic nozzle-- this throat has, on the left-hand side, not drawn here, a combustion chamber in which you have produced the-- you burnt hydrogen in pure oxygen. And so you have the products of combustion, essentially water and a few other things-- the other eight species that are in that scheme that will appear again in the next slide.

So these products of combustion are the adiabatic flame temperature. They are at a certain pressure, about 25 atmospheres. And the throat is so designed so as to achieve the maximum speed that when you have Mach number-- so when the flow is at Mach number equal to 1, that's the maximum speed allowed by the combination of the entropy, momentum, and energy balance, plus the equation of state for the gas. That's fluid mechanics, combined with thermodynamics.

But, in any case, so you have Mach 1, and then as a result of the expansion here, if you have a well-designed nozzle, the fluid will accelerate and become supersonic. For example, here it would exit at Mach 4. Of course, that means that the thermal energy gets transformed into kinetic energy. So the gas cools down, and also the pressure goes down. This occurs pretty quickly because of the high velocities-- this expansion. And the rapidity is important here because the time that the collisions require to re-equilibrate energy is not enough. Given the short residence time, those collisions cannot keep up with equilibrium.

Here, at the entrance of the nozzle, we have chemical equilibrium. So the composition here is that of chemical equilibrium. And this is the temperature. As it expands, you would think that the chemically effective collisions are fast enough to keep up and maintain chemical equilibrium. If they did, you would follow this blue dotted line-- dashed line. In reality, they follow the red line. That's at least according to the 24 reactions, 8 species detailed chemical scheme.

They are not completely frozen, though. Some reactions do occur because if you try to compute, assume that the composition here remains the same all through, you would obtain this result, when you assume all the reactions frozen. So they are not frozen. They are active.

So here are the 24 reactions that we have seen. And now we look at what each one does by looking at the individual degree of this equilibrium that we have defined. And we find something, which is a bit surprising if you don't think a lot about this, that-- what's not surprising is that you have some reactions for which the degree of disequilibrium remains practically 0. So they remain at equilibrium. These are the ones that are pretty fast.

And if you group them here, like 11, 13, 14, 18, 20, 21, 23, it's these ones. They are two-body reactions. They have certain features, these FO minus FV. FO represents the free oxygen and FV the free valence of the molecules. And this difference, turns out-- I frankly don't know why that particular difference. I'm not enough a chemical engineer or a chemist to understand that. I wish Professor Keck was here to tell us.

What's surprising here is that there are other groups of reactions. So the reactions behave like groups. For example, 7, 8, 9, and 10 build up a degree of disequilibrium. So that means that the kinetics cannot keep up and, therefore, you build a-- keep up to reach equilibrium. And, therefore, you build disequilibrium. That's the degree of disequilibrium as you go downstream.

But these four reactions, which are very different from one another, yet they follow the same departure from equilibrium. And notice that this one are three-body reactions. These are reactions that require the collision of three molecules. They are much less frequent. And that is why this doesn't occur fast enough to keep up with equilibrium. But they do not change the difference between free oxygen and free valence.

So, essentially, these reactions are subject to what we would call the same bottleneck, which is the three-body reactions. You need a three-body reaction for them to-- a three-body collision. And those are infrequent. And that is characterized by a change in the overall molecular number because you see go from 3 to 2. So you have collision of three particles, and after the activated complex breaks down, it produces two fragments.

Then we have another set, another group. Which is these ones-- these ones. These are two-body reactions. But their bottleneck is that these reactions change, this magic difference between free oxygen and free valence. They change it by the same amount. This is what they have in common. So they have to face the same bottleneck, changing that. And apparently that requires probably something of the mechanism that is common, even if the molecules are different. And that difference plays a role in the kinetics and it's slow. It slows down. So those cannot keep up.

And then you also-- if you look long enough, you may recognize that this other group follows a curve which is the sum of the curves below. So if you take the sum of this curve and of that curve, you get that. So the degree of disequilibrium of these ones at any instant of time is equal to the sum of the degrees of disequilibrium that has built up for the other two mechanisms. And, in fact, this is the group of reactions here that is subject to both bottlenecks. They require three collisions-- I mean, a three-body collision-- plus they require to change the difference between free oxygen and free valence. And that's why they play double-duty, so-to-speak, and they remain behind by the sum of these degrees of disequilibrium.

So the idea, if you go back one moment, the idea of the rate controlled constrained equilibrium model is to assign-- instead of using all the 24 reaction rates-- and, actually, here, this shows that you get very good results with only rates for four constraints. Two are just the element conservation. And the others are-- one is the number of molecules conservation, which is conserved by the two-body collisions and not by the three-body collisions. And the other is that difference between the free valence and free oxygen.

And that means that you can obtain the exact match of the experimental results. Instead of solving 24 rate equations, you just solve 2 plus 2. So that makes 4 with a big gain, especially if you're doing also computational fluid mechanics. And, therefore, in addition to the chemical kinetics, you have to solve the fluid mechanics of the problem, where if you have to deal with turbulence and so on, it makes the problem already complicated enough that savings in the number of differential equations you have to solve simultaneously makes a lot of a difference.

Now this same idea also applies here. Again, a nozzle-- you take products of combustion of some other fuel so that you obtain, here, a mixture at equilibrium in which you have carbon dioxide, nitrogen, and a little bit of water-- 90% nitrogen, about 10% CO2, and 1% water. Water, I think, acts as a catalyzer of the reactions that we're going to describe here.

Now also in this nozzle, the important effect is that there is a degree of disequilibrium that builds up, like we have seen, only that here, the disequilibrium is not between molecular species or a certain chemical reaction. It's within the molecules-- in particular, the molecules of CO2, which are the key molecules that are interesting in this application. It's the balance in how the energy is distributed between the translational rotational and vibrational levels of the CO2 molecule.

What happens here is that as the rapid expansion occurs, but also here, we have sonic and Mach 4 at the exit. So that's similar to the other problem. What happens is that here, you have a lot of random kinetic energy of the thermal agitation of the molecules, and the nozzle takes that kinetic energy and transforms it into a stream, the kinetic energy of the flow, like a bulk velocity.

And if the collision mechanisms were very effective, as soon as the translational degrees of freedom cooled down because of the expansion, you see the temperature goes from high to low, so that means the thermal kinetic energy goes down. It transforms into flow kinetic energy. You can see that here. This is the flow of kinetic energy. It goes up. And this is the thermal kinetic energy that goes down.

And this is the vibrational energy, the energy in the vibrational modes of the molecules. Those also, if the effectiveness was very high, would lose energy quickly and transfer the vibrational energy into the kinetic and rotation. But this mechanism is relatively slow.

So the degree of disequilibrium builds up in the vibrational levels. For example, this is the lower level. It gets cooled down. But there is an upper level, the upper vibrational level, that remains sort of frozen for a long time downstream. So why is that important for this application?

For this application, what counts is the vibrational levels of the CO2 molecule. And the CO2 molecules, being a molecule aligned this way, can vibrate in various ways. This is a symmetric stretching. This is a bending mode. And this is asymmetric. So it goes distant from one side, while it goes shorter on the other side, and keeps going like that.

Now each of these modes have frequencies. And these frequencies are quantized because we live in a quantum world. And these are like harmonic oscillators, springs. A mass and a spring, according to quantum mechanics, cannot live in a continuous set of levels, but the levels are quantized.

And so the molecule-- if you give more energy to the molecule, you need to give it enough to jump to another level. You cannot give it continuously. And the same is, if you have excited some high level, in order for that to release energy, it has to jump down to another level.

The important one is this level here, which is at this wavelength. Wavelength is a frequency. There is a relation between frequency and wavelength. So the frequency of vibration is related to the wavelength. And here, it is important to look at the wavelength because of photons, because of light, we will see in a moment.

So the important thing that happens here is that this vibrational level, which is a high level, will be, say, up somewhere here, is relatively highly populated in the hot gases before they enter the nozzle because we are at high temperature. Not only-- that level is very close-- I mean, that level for CO_2 is very close to a similar level for nitrogen molecules. So by simple collision, the nitrogen molecules can populate that CO_2 particular level because they are tuned, so-to-speak. They are exactly the same height. So it is a good chance that you transfer the energy of one to the other one. And that's why they chose nitrogen and CO_2.

And this one, when it decays, it decays to this level. Now every time a vibrational level decays to a lower level, it emits a photon. If that happens in just a random situation, those photons would go in all directions randomly. That is called the spontaneous emission. But if that decay happens in a situation in which there are other photons with the same frequency, so other photons that have exactly the same frequency, these other photons stimulate the emission of this decay by producing photons that have exactly the same frequency and direction. This is what happens. This is called stimulated emission.

And this is the objective of this entire construction. Because by doing that-- let's see if have another-- by doing that, this picture shows you the details of how big this is. So the nozzle is about a meter here.

So what they do, essentially, is to put-- I'm sorry, this is the diffuser. The nozzle is here. These are the nozzles, several of them. This is the expansion. And this is the downstream area in which we have that degree of disequilibrium. So in which I have still populated the high levels, this is called inversion of population. It's the inverse of what it would be at equilibrium at the local values of temperature. But with that inversion, it turns out-- if you have an inversion of population it means that this one is more populated and, therefore, the rate at which you produce photons by decay is higher than the typical rate at which photons get absorbed in order to repopulate that one.

So you have a net release of photons. And if you put that between mirrors so that these photons go back and forth and stimulate the emission, then you get the building up of light, coherent light-- photons with the same frequency, same direction. So that's a laser. And this is actually a power laser because, usually, the lasers that you have use for-- a pointer laser for PowerPoint is, I don't know, microwatts or milliwatts. I don't know-- very small power.

But with this one-- and we're talking about 1970s-- the output was continuous output of light of 60 kilowatts, which is a huge amount of power, especially if-- This is that the kind of light with which you can do laser cutting of metals. And this is all due to the fact that you managed to establish a degree of disequilibrium. And I think I would stop here for today.