[SQUEAKING]

[RUSTLING]

[CLICKING]

GIAN PAOLO BERETTA: OK, good morning. So we started talking about multi-component systems, mixtures. And our program is that at the beginning, we try to see when it is possible to infer the properties of a mixture as much as possible from the properties of the pure components. And so we are in the process of defining some ideal situations in which this is possible, which as we said, is a good start in our modeling efforts. It's like a reference sample situation in which we do not need to add experimental data to model our mixtures.

But then we will find that in practice, the ideal situation is really only a limiting situation, which is not fulfilled by any real mixture, except in some limits. Nevertheless, we gain a lot of information by just looking at ideal situations. So we have defined these partial properties that are derivatives or functions of the chemical potentials.

For example, the partial entropy of the constituent in the mixture, which is a function of t, p, and y. We will have to be careful in distinguishing well between the partial entropy of the constituent in the mixture and the s double i tp, which is going to be-- which is the specific property, the specific entropy, of pure component i when at the same temperature and pressure of the mixture.

We will see that they are somehow related and the difference is measurable. So we have to pay a lot of attention to the subscripts. Like, so a single subscript is a partial property for the mixture. Double subscript is specific property of the pure component. And then we define the partial volume, which is another derivative of the chemical potential once we know the chemical potentials as a function of temperature, pressure, and composition.

We define the partial energy. And also, we define the partial enthalpy. And let me just stress this one. If you have the expression for the chemical potential and you divide it by the temperature, and take the derivative not with respect to t, but with respect to the inverse of the temperature, then you get the partial enthalpy.

This formula will come out a while often. And also, this one, which I better write here on the board, we can write it this way. OK, so we can say that-- we can see that from this relation here, we can see that the chemical potential can be-- of the component in the mixture can be written as this linear combination, enthalpy minus ts, which essentially is also equal to the Gibbs free energy. So this is also equal to the partial Gibbs free energy.

And in fact, the derivative of g with respect to ni, with respect fixed t and p, and the other constituents, that's the definition of the chemical potential in terms of the Gibbs free energy. But it's also-- you could also call it by analogy with these definitions, the partial Gibbs free energy of the constituent in the mixture. So in other words, we're saying that the chemical potential can be interpreted itself as a partial property. It's the partial Gibbs free energy of the constituent in the mixture.

And the reason why we call these properties partial is because they contribute to building up the property of the mixture by simple multiplication with their amounts. And each-- and you can do this for entropy, volume, energy, the free energies, the enthalpy. They are all-- they all have the same structure.

Of course, now, we are-- we forget the small systems, and we focus on large systems. So this is the right-hand side, the highlighted formulas, because for small systems, we will have also to some contributions that correct this expression in terms of the Euler free energy.

OK, so how do we measure these partial properties? And here's the setup. We take a mixture with a given composition, in stable equilibrium of course. I know I'm not repeating it often enough, but we are concentrating our attention now on the stable equilibrium state. And so we take a mixture with some given composition at a stable equilibrium state, the temperature and pressure p.

And we put it in mutual equilibrium with a thermal reservoir of the kind that can exchange also volume. So you have also the pressure equality as a condition for mutual equilibrium between your mixture and the reservoir. Then we take a little bit of pure component i, and we add it to the mixture. And we wait until the mixture goes again to mutual equilibrium with that thermal reservoir.

OK, so this is a mixing process in which we add a small amount of one of the components. And then since we can measure properties of systems, for example, let me take the enthalpy. And so let me measure the difference between the enthalpy of the mixture in this final state and the enthalpy of the composite system of the mixture plus the pure component in the initial state. OK, so this is for the mixture in the final state. The amounts are the same, but the amount for the constituent i is n plus dn.

This is the initial where in the mixture, I just have ni and the dni is separate from the mixture. So it contributes with its own-- to the enthalpy of the pure constituent through its specific property of the pure component. And notice that usually, as I said several times, enthalpy is not an additive property. But if you're looking at systems that are at the same temp-- pressure, then enthalpy is additive. And therefore, the enthalpy of the composite of these two subsystems is equal to the sum of the two enthalpies, like we do here, the sum of the enthalpy of the mixture, plus the enthalpy of the pure component.

OK, now if we take this and divide it by the amount of constituent i that we have added to the mixture, that defines the change in the enthalpy due to the addition of that amount of a small amount of that component. And of course, the n is supposed to be small. So we're taking the limit of this, which is-- which can be viewed as an incremental product, at least the part with the capital H. It's a partial derivative of capital H with respect to ni.

And then there is this additional contribution of the separate pure component that we have added, which since I divided-- I'm dividing by dni adds, but with the minus sign, a contribution here. Now, we recognize that this derivative is exactly what we defined as the partial enthalpy of the constituent in the mixture in the previous slide.

So here, we have the difference between the partial enthalpy and the specific enthalpy of pure component at the same [INAUDIBLE] of the mixture. This is what we call the enthalpy of isothermobaric mixing. Tp stands for isothermal and isobaric because we are doing this in a fixed T and p imposed by the reservoir. This can be measured. Enthalpy in a process like this is essentially, if you make the energy balance, this is essentially the heat exchanged with the thermal reservoir.

So you measure it with a calorimeter. So that means that since you can measure this with a calorimeter and you know the properties of pure substances, then you have measured the partial enthalpy of the component in the mixture. And this doesn't require any particular assumptions about the mixture being ideal or non-ideal. We actually haven't even defined yet what ideal means.

It's simply a tool, a method, with which people measure properties of mixtures. And what we have done here for the enthalpy can be repeated the same way. So I'm not repeating it here, but to define the volume of mixing, so it's the difference between the partial volume and the specific volume at the same t and p, the energy of mixing and the entropy of mixing. And these are all things that you can measure by energy and entropy balances. So these are ways in which you can characterize.

OK, this is a-- oops, sorry. Yeah, there is an extra character there. OK. All right. So now, let's use that equation, which I've written up there on the board and substitute the expression of the partial enthalpy as a hii. So the specific enthalpy of the pure component times the enthalpy of mixing. And the same for the entropy, s partial. We can write it as s specific of the pure component times the entropy of isothermobaric mixing.

All right, so then, we recognize that also for the pure substance, h minus ts is the chemical potential. So this gives us a relation for the chemical potential, the component in the mixture in terms of the chemical potential of the pure component at the same temperature and pressure of the mixture, plus the enthalpy of mixing minus t times the entropy of mixing.

And at this stage, we should also remember that by the definition of partial pressures of components in a mixture. You recall that that is defined by the condition of mutual equilibrium across a membrane, permeable only, to constituent i. So at that mutual equilibrium across the membrane, you have equality of chemical potentials. So the chemical potential of a constituent in the mixture is also equal to the chemical potential. And here, there is also another mistake. This should be a double i. This is the chemical potential of a pure component on the other side of the semi-permeable membrane.

And therefore, yes. At the same temperature of the mixture, but at a pressure which is what we call the partial pressure. So again, here, I cut and paste, makes errors propagate. So this should be double i and double i. OK, so the-- we are now taking this last equality and putting in evidence the difference. And so taking essentially this term to the right-hand side. So I have the chemical potential difference evaluated between the pressure-- the partial pressure and the pressure of the mixture, pii minus p.

Now here, we have already proved in a previous slide, maybe we can just remind ourselves of how they got here, that-- so we are having that new double i pii-- I'm sorry, at t and pii minus [INAUDIBLE] double i tp. OK, you see, I'm-- if I have a function of x, And the difference of a function evaluated at two different points, I can always write by the integral calculus equation that this is equal to the integral from x2 to x1 of the derivative of that function. Let's call it--

And this x double prime is a dummy variable of integration. OK, so these, you can write for any function. So here, we apply this theorem. So this x2 is p, x1 is p1ii, and the derivative we have to put here is the partial derivative with respect to p of what? Of the chemical potential of the pure component while the other variables are tp-- I'm sorry, t. And this is to be evaluated at the value of the dummy variable, so at p double prime, and integrated over the dummy variable.

But if you look up the many equations that we have derived also for the pure substance, this derivative is the specific volume. So this becomes the specific volume of the pure component evaluated at temperature t and at the dummy pressure p of integration p double prime.

OK, all right. So that explains this integral here. But above, we've seen that this difference in chemical potentials is equal to the delta h mix minus ts delta s mix. OK, now look at this volume. If I have an ideal gas, and if I can-- my substance i behaves according to the ideal gas relation, the specific volume can be written as rt over p. And the pressure that we should evaluate is p that is here. So it's p double prime.

And so when I do this integral, rt goes outside because I'm integrating over p, p double prime. And the integral of 1 over p is the logarithm. So that gives me the formula rt log of pii over p. And that's for the gas. If instead I have a liquid and I can use the incompressible liquid model for which the specific volume vii is approximately constant, meaning independent of temperature and pressure, well, if it is a constant, it goes out of the integral. And then this becomes the specific volume times pii minus p.

And here in the slide, I just switch because the pressure is usually greater than the partial pressure. So I put this difference in parentheses and then I pick up a minus sign on the other side. OK, so this formula will be useful in a moment. And again, we see that there is a relation between the partial pressures, very explicit relations in terms of the enthalpy and the entropy of isothermobaric mixing.

So this is a way in which you can measure partial pressures because you can measure the properties of isothermobaric mixing. For example, here, I want to sort of point you to a couple of references, which if you go and take a look, and they'll-- a huge literature, so a huge community that over many decades, or perhaps over more than a century, have been measuring properties this way.

And they're still doing it because the applications are growing. For example, this is an experimental paper where they collect-- they measure the enthalpy of isothermobaric mixing of liquids. And these liquids are molten salts that, as you may know, are used in various applications, including solar thermal applications in those collectors with mirrors that want to achieve high temperatures. The molten salts allow stable also at very high temperatures.

And therefore, using these fluids, you can collect solar energy at high temperatures up to maybe 600 Celsius. But of course, molten salts are used also in nuclear engineering and in processing industries for producing materials that are useful for all sorts of applications, from electronics to magnets.

OK, so this is for-- so this is a reference in which you can see how people measure and then try to correlate. So there is also a number of correlations, which go under the names of the inventors of the correlations, that do good jobs in determining these effects.

You see, here, the gray molecule, cesium ion, is sort of the solvent. It's like the prevailing, or the common substance of these mixtures. And then they keep changing the other substance. So it's actually not only for dilute, it's for over the full range of compositions from 0 to 1. And you can see that you have a behavior in which the enthalpy of mixing is negative.

OK, so meaning that the substance that when you mix the substance, you have an exothermic reaction. It's not really a reaction, but it's a physical chemical effect, which releases heat. So in other words, you have to-- if you want to return to mutual equilibrium with the reservoir, you have to cool down after the mixing. You have to cool down by this amount.

And that cooling measures is exactly-- so we-- that's how with the calorimeter, you can measure that cooling, and therefore this delta H. You can also do similar measurements for the volume of mixing. And here, I sketched the-- yeah, I think this line should be long a little lower here to the 0 level.

And I sketched-- this is just to show that it's the volume of mixing is not always positive. It can be positive, it can be negative, it can be positive in one range and become negative in the other range, depending on the composition. And it all depends on what kind of molecules you have, and how the molecules interact with each other. And as you can see, these two references where you may want to take a look to see experimental data, and how they're treated, date back to at least 40 years ago.

OK, now, this slide is also just a parenthetical. It just says, all right. So we have seen that in practice, with those measurements, we can infer the values of the chemical potentials, and therefore the partial properties. So the question that we address in this slide is, can we-- is the meaning of partial that we use in partial properties the same as the meaning of partial as we use in partial pressures?

And the answer is no because the definition is different. However, you can somehow relate partial properties in terms of partial pressures. And here, here is the way of doing it. It's just a matter of writing the chemical potential, as we see here. Again, as a function, as it is of the partial pressure. So if you take the differential of this relation here, which defines the partial pressure, and then remember that the derivatives of the partial-- of the chemical potential are the partial properties, then that is where that relation comes about.

And here are the details. So if you like to take derivatives, this is how you can practice it. So I'm not going to explain the details here. At this stage, we need to recall something about what happens when molecules come close to one another. And the Lennard-Jones model gives you the potential energy of the interaction between two molecules. So suppose I have one molecule and I stay in-- and I sit on that molecule on the reference frame that moves with that molecule, and I see another molecule approaching.

The Lennard-Jones model is a pair-interaction kind of model. It looks just what happens between one molecule and the other, not the fact-- it doesn't apply well if you have to consider also the fact that this molecule may also, at the same time, be interacting with a third and maybe a fourth molecule, which of course, is important in liquids.

But OK, so here's the idea. I'm sitting on that molecule, and I see another molecule approaching. Now, because of the electronic structure of atoms and molecules, the electrons that are negatively charged, yes, are attracted by the nucleus or the nuclei of the molecule, or the atom. But as they approach other molecules, they are also a bit attracted by the nucleus of the other atom.

And that produces these so-called van der Waals attractive forces. So the potential going negative-- so if this is the potential, remember that I can calculate the force by taking the derivative of the potential with respect to distance minus sine. So this force is a vector. And ir is the vector that points in the direction outward, so further from the molecule I am sitting on.

So it's like on this axis, isobar is the unit vector in the r direction, in the right direction. All right. So the usefulness of having a potential is that then, you can calculate forces by taking the derivative of the potential. And as you see, here is the force-- if the force is negative. it means that the-- its direction is in the opposite sign of the unit vector in the r direction. So it points left. So it's attractive.

So and up to this point, which is about here, the derivative is-- the derivative of v is positive. So the force is negative. And yeah. Yeah, OK, up to this point, where it is 0, we get to the minimum, it's attractive. And from this point on, it becomes repulsive. The force becomes positive. That repulsion is due to the fact that now, the nuclei, which are positively charged, begin to fill the positive charge of the nuclei of the particle I'm sitting on. And therefore, that repels.

OK, so most of the times, molecules are running around in their Brownian motion. So in which they have some kinetic energy due to the velocity they have. And they have also this potential energy. Some of that kinetic energy gets transformed in potential energy. Or actually when the molecule approaches and gets an attractive force, it gains kinetic energy. So it's accelerated towards the particles. So if the molecule is coming from the right and it's approaching, it's accelerated towards the molecules I'm sitting in.

But then, all of a sudden, it finds also a repulsive force. So that's decelerating. Of course, if the kinetic-- if the kinetic energy is enough, this molecule can go and hit. So make a collision. Eventually, it will make a collision because the force is going to become very large. And the repulsive force becomes very large. And therefore, the particle is pushed away back. That's a collision. It's like a soft collision, but it's a collision.

An even simpler model of this would be the so-called hard sphere model, in which the potential is-- would be like-- OK. OK, will be like this. A function, so v, is a function which goes to infinite, to its infinite at this point, which is 1. It's the distance-- 1 is because we're normalizing these to the diameter of these molecules, of these spheres, assuming they're equal. Otherwise, it would be like the-- have to normalize to the average-- it's the sum of the radii of the two molecules.

And it's 0 here. So the hard sphere model assumes no attractive force until the sphere hits like in a billiard ball situation. It hits the other molecule and it gets repelled by some elastic condition-- elastic collision. OK, let's return to this case here and now consider two important regimes.

One regime is the ideal gas, the gas regime. So it's true that the molecules of the gas very often, billions of collisions per second, we-- maybe we'll have a slide later on that does that calculation, do have experienced collisions. So these molecules do get to feel this potential when they approach the other molecules and have a collision. That happens very often.

But if you look up, if you make an average, a time average, of how much time this molecule spends in this area, where the Lennard-Jones potential is negative, is very small. Most of the times, on average, the particles are far apart. And therefore, on average, they feel zero potential.

See, this is why when you try to measure the properties, you're actually measuring the properties on average, because remember that somehow, the state of your system is the probability distribution of things. For example, here is the probability distribution of finding the particle at these various distances. And that probability for a gas is-- has this very small tail here, and it peaks away. So most of the times, the particles are far away from each other even though they experience a lot of collisions.

But that means that when you're calculating the stable equilibrium properties, therefore, the average time average properties, this potential is irrelevant. And that is what allows you to, for example, use the hard sphere model because that's totally equivalent if the particles live far away on average and the details of the potential of their interaction when they are close is not important, well, those details, you can forget. They don't enter into determining the properties of the mixtures.

So much that in the ideal gas, and also, we will hopefully have a slide also on this, the ideal gas, this relation here that the volume is rt over p, you can derive for a particle, a single particle, in a box, which is a nice illustration also of that's why I will have a slide on this.

But in other words, this-- here in this context is just to say that the properties of an ideal gas, so the origin of this ideal gas equation of state comes from the single particle because the properties of stable equilibrium in this regime are those of particles that leave on average by themselves. They don't feel the effects of the other particles.

There is another case also, which is the liquid case. We will return to the liquid in a while, maybe today. But what's important is that instead, the liquid particles live very close to one another. They live near this minimum. So for them, this potential is more important. This-- the Lennard-Jones potential formula can be written-- is written in two different ways here.

One is in terms of the actual distance, and one is in terms of the distance normalized to this minimum to the distance at which the minimum occurs. Sigma, as I already said, is-- r is normalized here to sigma. So it's 1 at the distance where it is equal to the diameter of the two particles. So where the particles are colliding. And here, we also in the plot normalized the potential to epsilon. And epsilon is the depth of this well here. So it goes to minus 1.

So stronger interactions will have-- would be characterized by stronger values of this epsilon. OK, so with this introduction, let's consider a first ideal behavior, which we will call Gibbs-Dalton ideal behavior, and which will be a very good approximation for gases in the gas phase, because in practice, we will assume that not only particles of the same kind like you would have in a pure substance, but also particles of different kind like we have in a mixture, they also live on average far away from one another. And therefore, we can neglect the effect of their intermolecular interactions.

OK, all right. Formally, this is how the story goes. We will first define ideal behavior. And just so this will be our-- this will be the final result of this slide. And the motivation is that of this definition that we are going to do here is that we will find that under this approximation, or in this limit on this-- when these assumptions are valid, then we obtain a famous result, which is the Dalton law of additive partial pressures.

So the pressure of the mixture is going to be equal to the sum of the partial pressures of the constituents of the mixture. But in general, that is not true. Not-- I mean, this is not true for a non-ideal mixture. So the derivation goes as follows. We start from the Euler relation written for the mixture. We write also the Euler relation for the pure components. And when-- and here, I'm going to write it for the pure components at just on the other side of the semi-permeable membrane so they are in at the same temperature of the mixture, but at the partial pressure.

OK, so this uii here, I'm not writing the explicit dependence, but I'm doing it here, are to be evaluated at t and partial pressure. Then I take these individual pure constituent Euler relations, we multiply-- I multiply them by the amount ni with which that constituent is present in the mixture and sum over all components. And then I take this summation, subtract it from the Euler relation for the mixture, and here is the result.

So you can still identify here the Euler relation for the mixture is given by this term. This ts minus pv plus mu i ni. And what I subtracted is the summation of the ni's with which that are the amounts in the mixture times the single component, pure component, Euler relation. uii minus tsii plus pii vii and plus the mus.

Actually, there's a mistake here because there shouldn't be a summation here. This is, again, a cut-and-paste problem. This should be-- I hope I'll remember all these things to correct in the view graphs. Yeah, so for the pure component, there's only one. And so there is no summation.

OK, now, look at these elements of the last summation. They are identically 0 because of the condition for mutual equilibrium that the chemical potential of component i in the mixture is equal to the chemical potential of the pure component when evaluated at the partial pressure. So these are 0. And then I get a relation here, which contains the pressure and contains the partial pressures, because after all, what we wanted to see here is, is there a relation between pressure and partial pressures?

And here is the result. So I put in evidence, I solve this expression for the total pressure, and here is how it depends on the partial pressures. That's all over. However, if I make these three assumptions, you see this? The first assumption kills these terms in parentheses. The second assumption kills this other term. The third assumption, and note here that this is not a mistake, here, there is no summation sign.

So if this holds, then we'll discuss what it means. But if this holds, it means that inside this summation, every time I see ni times vii, I can put capital V, which doesn't depend on i. It doesn't have a subscript. So it goes outside of the summation and it cancels with the V in the denominator. And then what I'm left with in the summation is just the partial pressure. So I finally get that the pressure, if these three assumptions are together, all holding, the pressure is equal to the sum of the partial pressures. And this is Dalton's law.

Let's see how we could interpret those conditions that define the ideal Gibbs-Dalton behavior. Essentially, it says that I can see the mixture, or at least I can model the properties of the mixture, as the model, as the properties of a composite system in which I have the pure components leaving each one in the same volume of the mixture, so boxes of the same size, at the same temperature and at the partial pressure.

OK, then in these conditions, this is the specific-- they have a specific energy since they are pure. For example, this is component, say, component i as a specific energy, which is u double i evaluated at the t and p because here it is at the partial pressure. The same for the entropy. And now, if I use the fact that energy and entropy are additive properties, the energy of this one is n1 times u11.

And so I sum up ni times uii. And that gives me the properties, the property of the mixture. So sum of ni times uii. So that's-- this last equation is the defining equation for ideal Gibbs-Dalton behavior. The first one here I have added also the general expression, which is valid always, which gives the property in terms of the partial properties. It's the same for the entropy. So it's additive. So I can view this.

And instead-- and here, I've used the fact that each-- you see here, I could also write the specific volume of the constituent, the partial pressure. And the fact that it-- that in the same amount of the mixture, it occupies, the same volume of the mixture is the sort of interpretation of this formula here.

It also goes together with the idea that in the gas limit, when molecules live far apart from one another in either this or the Lennard-Jones kind of potential, if they're on average, they live here. Essentially, they stay and they occupy the volume of the mixture if-- as if they were by themselves, each molecule by itself. And that's why we have-- they obey the ideal gas law, which is valid for the single molecule in a box even if I have many box-- many particles In that box.

But it is as if each one uses the box by itself. It doesn't recognize on average, the presence of the other, even though it does continuously collide with the other. But the time that it takes-- that the collision-- and so that-- it lasts. The time that the collision lasts is very short with respect to the rest of the time that the particle moves freely in space before encountering the other molecule for the next collision.

So that's the ideal Gibbs-Dalton behavior. And if we apply it now, we haven't assumed yet the ideal gas. So now, if we in addition to those, we also assume that each pure substance behaves as an ideal gas, so it obeys the equation of state of an ideal gas in the full range of pressures from the partial pressure to the total pressure of the mixture, I shouldn't call it total, to the pressure of the mixture. So I can write the equation of state for the gas pv equals rt both at partial pressure and at the pressure of the mixture.

Then you see from assumption three, which is this, I substitute this, obtain this result. So I obtain the partial pressure written this way. Now, I'm using what we proved in the Gibbs-Dalton theorem, about the Dalton law that the pressure of the mixture is the sum of the partial pressures. So take the sum of these ones, see rt and v do not have subscripts, so they go out of the summation. I'm left with the sum of the n's, which is just the total n of the particles in the mixture.

So here, what do I got? What do I get? That pv equals nrt. So it means that also, the mixture behaves as an ideal gas. So what this proves is that an ideal Gibbs-Dalton mixture of ideal gases obeys the equation of state of an ideal gas. So it is an ideal gas itself. And the other important result is that if you extract rt over v from here, you see that you can write it as partial pressure over the amount. And rt over v from here, it's the pressure over the total amount.

So that's essentially you combine these two and you obtain that the ratio of the partial pressure to the total pressure is equal to the ratio of the individual amount with the total amount, which is the mole fraction. In other words, the partial pressure is given by the mole fraction of that constituents times the pressure of the mixture.

And this relation, if we put it in this relation that we have derived before, so pii over p becomes in the limit of a Gibbs-Dalton mixture. That is the mole fraction. So this is rt, the logarithm of the mole fraction. And this is a very important relation. It gives the chemical potential of one constituent in the mixture. In terms of the chemical potential that it has, when it is a pure substance, at the same temperature and pressure of the mixture.

Plus rt, the log of its mole fraction, of the mole fraction with which it appears in the mixture. So it doesn't depend on other things of the mixture. For example, what are the other components, or how many they are except that all we need is to know what fraction our component is occupies in the mixture. OK, the first few lines of this slide are just a cut and paste from the previous.

But here, we add some other items. For example, we compute the entropy-- the partial entropy of the component in the mixture, which as you remember, is this derivative. It is equal to the pure component entropy plus a term that in-- when we define the entropy of mixing at the beginning today, this is delta si mix.

But if we-- since now, for this ideal gas mixture of ideal gases, we have the expression for the chemical potential in terms of explicitly here, taking the derivative with respect to t, we see leaves just r times the log of y. And since there is a minus sign here, this is minus r log of y. So essentially, these and we'll return to this in a later, but this says that the entropy of isothermal-- isothermobaric mixing of that molecule is-- of that molecule is equal to minus r log of y.

And this is also equal to the pure component entropy evaluated at pii. This is because you remember for a gas, for an ideal gas, if I evaluate the difference in the entropy a different temperature and pressure, OK, this is equal to-- and this is the perfect-- let's suppose it's a perfect gas. It's t2 over t1 minus r log p2 over p1. So in this relation here, we have s evaluated at p. p, all right, let's say p. pii minus s evaluated at p.

Same temperature. So this doesn't give any contribution. So I'm left with minus r log of pii over p. But that's in our limit of ideal mixture is the mole fraction. So hopefully, what I've written on the board is this relation here. That's to justify this equal sign.

We can also compute the partial volume, taking the derivative of this with respect to p and you see that since this last term doesn't have pressure, I just pick up something from the derivative of the chemical potential of the pure component. And that's the specific volume. So here, we see that there is no volume of mixing. There is no iso-- the delta-- essentially, we are proving that delta vi mix for a Gibbs-Dalton mixture of ideal gases and so on is equal to 0.

Up here, we prove that this is equal to delta si mix for a Gibbs-Dalton mixture of ideal gases. I should write it because otherwise-- OK, the same for the enthalpy. Remember that derivative that I emphasized this morning earlier, if I take the expression for the chemical potential divided by t and take the derivative with respect to t to 1 over t, OK, well, if I divide this by t, it becomes independent of temperature.

So when I take the derivative with respect to any function of temperature, it doesn't contribute anything. So that means that the enthalpy-- the partial enthalpy is related just to the specific enthalpy of the gas, which here also, I removed the temperature, the pressure dependence, because for an ideal gas, the enthalpy depends only on temperature.

And similarly for the-- so that also proves that also delta h mix equals 0. And remember what these properties are. These are the things that I measure when I add a little bit of a substance to my mixture. If I do it with an ideal mixture of ideal gases, those are 0. We can also prove for a gas for this kind of mixture, the so-called Amagat law of additive volumes, which can be interpreted this way.

Suppose I take my pure components that you remember from when we interpreted the mixture before, if they are at the partial pressure, they occupy the entire volume of the mixture. But if I squeeze them from the partial pressure to the pressure of the mixture, they are going to occupy a volume, which is called the proper volume, v prime, which see, this is not--

So this is the volume they occupy at the same temperature and pressure of the mixture when pure. And I do the same for all of them. So they are all squeezed at the same pressure of the mixture. Well, it turns out that the sum of these volumes is equal to the volume of the mixture. OK, and that is Amagat's law of additive volumes.

OK, so now, let's apply for example, for an important example, what we have seen. So we want to compute the so-called-- this bottom line here is the formula that we call the entropy of spontaneous mixing, which is actually going to be an isothermobaric mix. So the idea here is that we start with a container, which is isolated so it doesn't experience any-- there is no heat bath, no thermal reservoir, no contact with thermal reservoirs. It's just isolated.

And I have my r constituents all in mutual equilibrium at the same temperature and pressure because these partitions that separate them are movable, and therefore allow exchanges of volume and energy. So the conditions for mutual equilibrium is equality of temperature and equality of pressure. Then, I make those partitions, those moving partitions, disappear. As you know, since we are within the simple system model, taking the partition away doesn't change the properties of any of the properties.

And the moment I do that removal, the particles are still separated. So the particles, it's which start from here. And my system is the system with the partitions. When I remove the partitions, the stable equilibrium state, and the new system because I've changed the internal structure, it has a new curve for the stable equilibrium states. And the moment I have removed the partitions and the properties haven't changed, this state here, which is-- which was a stable equilibrium state with the partitions, becomes a non-equilibrium state with respect to the system without partitions.

And the system will tend to evolve spontaneously towards a new equilibrium, which is going to be the mixture. The particles will mix. And each one of them, if you think in terms of the single particle contribution, each particle here was squeezed to a small volume. And now, it sees the entire volume available. So it expands. And the same for the particles here, and the same for particles there. So each one experiences a spontaneous expansion.

It's like if you take the single particle view, so say particle one, and here, I have vacuum, OK, I remove the partition and the particle now fills the entire volume and fills the entire volume. There is no more vacuum, because at the beginning, I had zero probability of finding my particles here, and probability 1 of finding it there. When I remove the partition, the particle is still one. But now, I have an even probability of finding it everywhere.

OK, so for the moment, we want to describe that spontaneous process. And so we want to analyze our process here. We have a final state and an initial state. And the tools are, as usual, the energy balance and the entropy balance. Plus the auxiliary balances that are balanced for the volume balance for the amounts of the constituents. So I need to write the various ingredients of those balance equations, which are the expressions for the energy, the volume, and the entropy in the initial state, and in the final state.

I've called this final state b prime. And I call that final temperature t prime and pressure p prime. For the initial state, things are easy because the components are separate. So these are-- this is just a composite of separate substances. We know how to compute properties of pure substances. And here in particular, they are ideal gases, even simpler.

And so we simply have to use additivity for energy, for volume, and for entropy and sum up the energy of each one of them. Since u is the specific energy, the energy of this system is obtained by the specific energy times the amount. And then I sum, and that's the additivity. And the same for volume, the same for entropy. In the final state, in the final state, things are not as simple because it's a mixture.

So we have to take a model for mixture behavior. So here, we are going to adopt the Gibbs-Dalton-- ideal Gibbs-Dalton mixture model for this state. Therefore, the energy for the mixture is equal to the sum weighted by the amounts of the specific properties of the pure components evaluated at the temperature and the partial pressure. So here in principle, I should have written comma pii. But I didn't because I remember that for an ideal gas, the energy is a function only of temperature.

So that dependence isn't there because if you remember, the u is equal to cvdt. And for an ideal gas, there is nothing, no pressure dependence. And here, we are talking about something that holds for each of the pure substances. Then, we can use the relation for-- this is Amagat's relation, or you can use, in any case, the equation of state. And we already proved that v is equal to that the mixture of ideal gases under the Gibbs-Dalton model behaves itself as an ideal gas.

So there is the relation, equation of state pv equals nrt for the entire mixture here. And that's what we use here. And then for the entropy, the entropy is the sum of the entropies of the specific entropies evaluated at the partial pressures. Now, the entropy does depend on pressure. So I did leave the partial pressure that the components have in the final state.

So these are just the ingredients of the balance equations. Now, I make the balanced equation. So the balanced equation, when the system is completely isolated is that the energy is conserved. So u final minus u initial is equal to 0. So I have u final, I have u initial, I subtract them. I can put this under the same summation. Then, I remember this equation here. And so for each of the constituents, I can write that the integrate from t to t prime, this difference, so this is the integral from t to t prime of cv.

And here, there should be a cvii. OK, OK. So this integral has to be equal to 0. Now, when can that be equal to 0? Now, here, we have to remember a few things, that for each pure substance, the specific heats are non-negative, are greater than 0. We proved it because they are related to the second derivative of the fundamental relations. They are related to this concavity here. So we have an integral of positive quantities, of a positive function, weighted and then multiplied by positive numbers because the amounts can only be positive, of course.

It cannot be a negative amount. So you can view this as an integral of a function, an integral from, say, x1 to x2 of a function that has to be equal to 0, while this function is positive. So here is a function, positive, and the integral is equal to this area from x1 to x2. So if the function is positive and I want the integral to be 0, the only way is that the interval of integration must be 0.

So that implies that this integral is equal to 0 only when x_2 is equal to x_1. So that proves that the final temperature must be equal to the initial temperature. We've no need to make any assumptions of what these functions are, whether they are functions of whether they are constant or not. They can be functions, arbitrary functions of temperature, still get the same result.

Then, if I make the volume balance equation, here is another mistake, this is a v, not a u. So the final volume, since we are in the same overall box, final volume is equal to initial volume. So v-- these two are equal. If I look at this relation here, it says that if I put them equal, it says that t over p is equal to t prime over p prime. So that means that if we just prove that t prime is equal to t, so the final temperature is equal to the initial, the volume balance implies that also the final pressure is equal to the initial.

So spontaneous mixing with these conditions is isothermobaric. Different story is for the entropy balance. The entropy balance is written here with another little mistake because this should be a capital S. So the final entropy minus the initial entropy. There are no interactions. So there is no entropy transfer. There are no heat interactions. But there can be entropy produced by irreversibility.

So we rewrite this. So S here is equal to SB minus SA. And I have the terms here. So I substitute. Now, I realize that this we can also write-- well, actually, it's this expression here. I have to-- I don't have to re-prove it. It's written here. This difference is equal to minus r log y, which is also is interpreted as the entropy of isothermobaric mixing. And therefore, the-- if I take r, the minus sign, outside of the summation, I take also the total amount out of the summation.

Then, I'm left inside with the mole fraction times the log of the mole fraction. Now, at first, at first sight, one would be worried about the minus sign because we know that the entropy produced by irreversibility cannot be negative, must be positive. But if you look at this function y log y, the function in the interval between 0 and 1, the function y log y does something like that. Versus y. So it's negative.

So minus y log y is positive. And we are safe. That means for any reasonable, in other words, possible values of the mole fractions, which of course can go only between 0 and 1, that function is non-negative. But it also says that there is entropy production. So the process is irreversible as we have anticipated by looking at the energy versus entropy graphs. And this is called the entropy of mixing.

Now, so if I look at that graph, immediately, I also realize that I have-- that I could have done better. In other words, we could have done the mixing reversibly because if I-- if instead of going this way, I go this way, I do not generate entropy. And I extract some work. So this is what we call the adiabatic availability of the state that is achieved the moment I remove the partition. That non-equilibrium state has adiabatic availability if I am quick enough, or smart enough, to do whatever needs to be done.

And we'll see how we could do it in a moment. We could extract some work. So here is the calculation of that, the adiabatic availability. So now, the final state, OK, what we just derived is that if you-- if we mix this way, the final state is the same temperature and pressure.

Clearly, if we go down and we have extracted some energy, the final state here will have a smaller temperature, which we call it t double prime. And how do we measure it? How do we do the computation? Well, we start-- the previous computation, we started from the energy balance setting that final energy is equal to initial energy. That determines the temperature. Now, we start from the entropy balance because for a reversible process because we want to extract the adiabatic availability, so that's a reversible weight process. The entropy stays constant.

We apply equality of final and initial entropy. And so we start from the entropy balance. Yeah, here is the entropy balance. S final minus S initial equals 0. So we write it this way with the double primes. And then this difference here, we can-- yeah, it's evaluated. It's evaluated in this line because, OK, t double prime is the final temperature that we have. p double prime double I is the partial pressure that the components will have in that new final state.

So that partial pressure is going to be equal to the mole fraction. So that partial pressure will be equal to the mole fraction times the final pressure p double prime. But if we remember, if we remember the question of if we look at the volume balance, which is written here, p double prime over t double prime is equal to p over t. So I can think of p double prime, p double prime, as what is it? p over t. As p times t double prime over t.

And that's why I am writing this here. Then I apply the relation for how the entropy depends on temperature and pressure. Here, we also have a temperature dependence. So we also have the cp log contribution of the ratio of temperatures minus r, the log of the ratio of the pressures. OK, then I can split this logarithm as being the logarithm of the product is going to be the sum of the logarithms. So I take the minus r log y here. And then I combine the log of t double prime that appears from this part and with that part. It gets multiplied by cv minus r, but by the Moire relation that's cv.

OK, so we finally have this expression. We can put it in the entropy balance. Now, I see here that I could define an average-specific heat at constant volume of the mixture as being the weighted as being this summation here. And then I recognize this final term, which is very close. I mean, it's exactly what we call the entropy of mixing.

But in any case, by setting-- since this has to be equal to 0 by the entropy balance, this gives me an expression way to calculate t double prime, the final temperature. And this is the result. Now, the fact that these functions are negative, so e to a negative number is less than 1, shows that, of course, as we expected, the final temperature will be less than the initial temperature. And now that we have the final temperature, we can perform the energy balance.

Now, the energy balance here, since the system is not isolated anymore, because we have lifted the weight in a weight process, we have extracted the adiabatic availability. So the energy given to the weight is equal to the difference between the initial and the final energy. So by substituting these ingredients that we calculated up there and using the same-- the specific heat at constant volume, and then the fact that the summation we defined as sort of an average mixing mixture, specific heat at constant volume.

And we substitute t double prime. And you compute the value for the adiabatic availability. So we see that this represents this work. Just to show you how we could actually do it with a picture, so we conclude, we have one minute. How can we do that? Can we actually separate a mixture? Remember, the problem here with the single particle, if I have a single particle there, and I have vacuum, and I have this-- and instead of removing the piston, I can just have it move rightward while connected through a pulley to a weight.

And the pressure of the particle will push it to the right. Therefore, the particle will do work and lift. And similarly, if I have this other particle on the other different particle on the other side, say, suppose I have a particle of different kind that is confined, that's separated, and it's on the other side. Also here, I can do the same and have the pressure of the particle, or the particles. Doesn't really matter because each one acts by itself. So that pulls this this way.

And when you have the presence of both particles, you have to do it more carefully. Instead of having an impermeable piston, you have to use semi-permeable membranes so that when this one moves to the right, it will-- so this one allows the black particles to freely move in and out. And then it fills only the pressure of the gray particles until you move to the right. And this other membrane, instead, is-- allows the gray particles through, and instead, fills the pressure of the black particles.

OK, so when you're done, and if you've done it reversibly, you have extracted this adiabatic availability. So I think we have to stop here today.