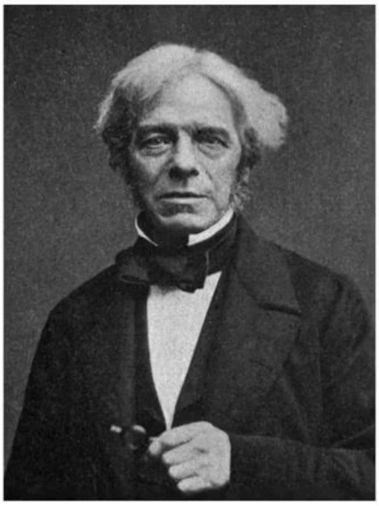
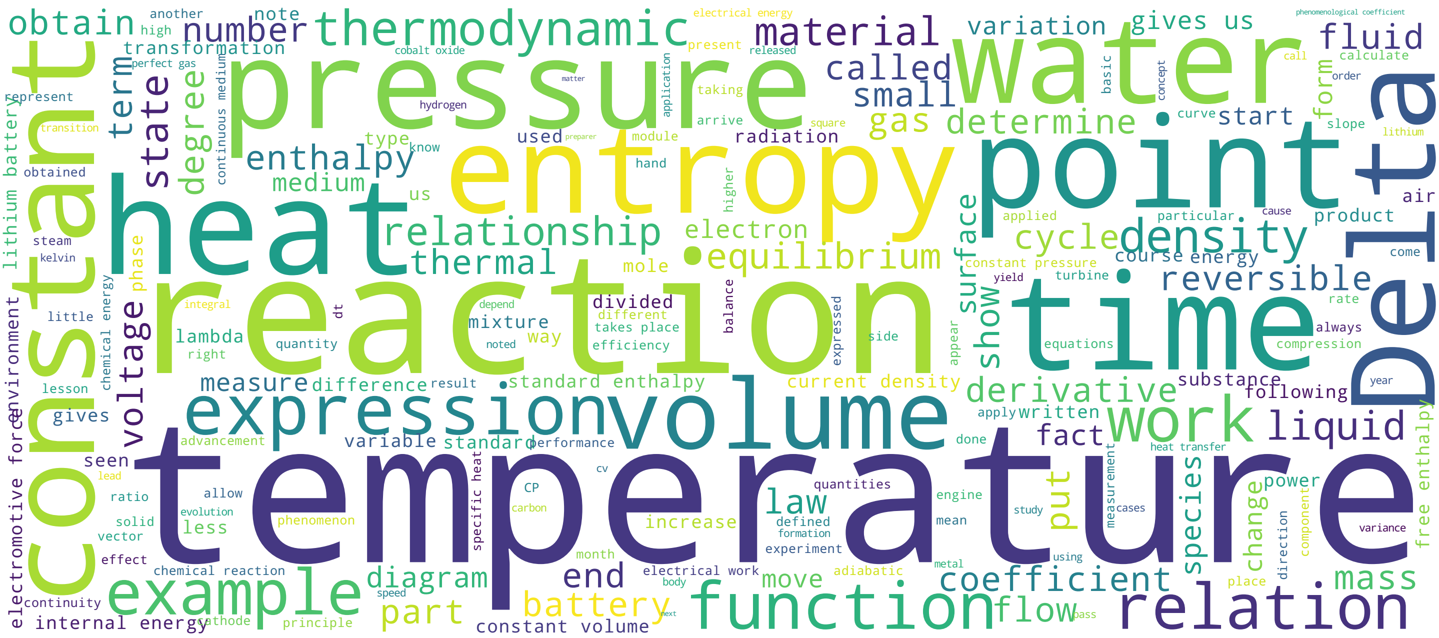
Thermodynamique

La pile au lithium

Prof. Michael Grätzel



Michael Faraday



Video

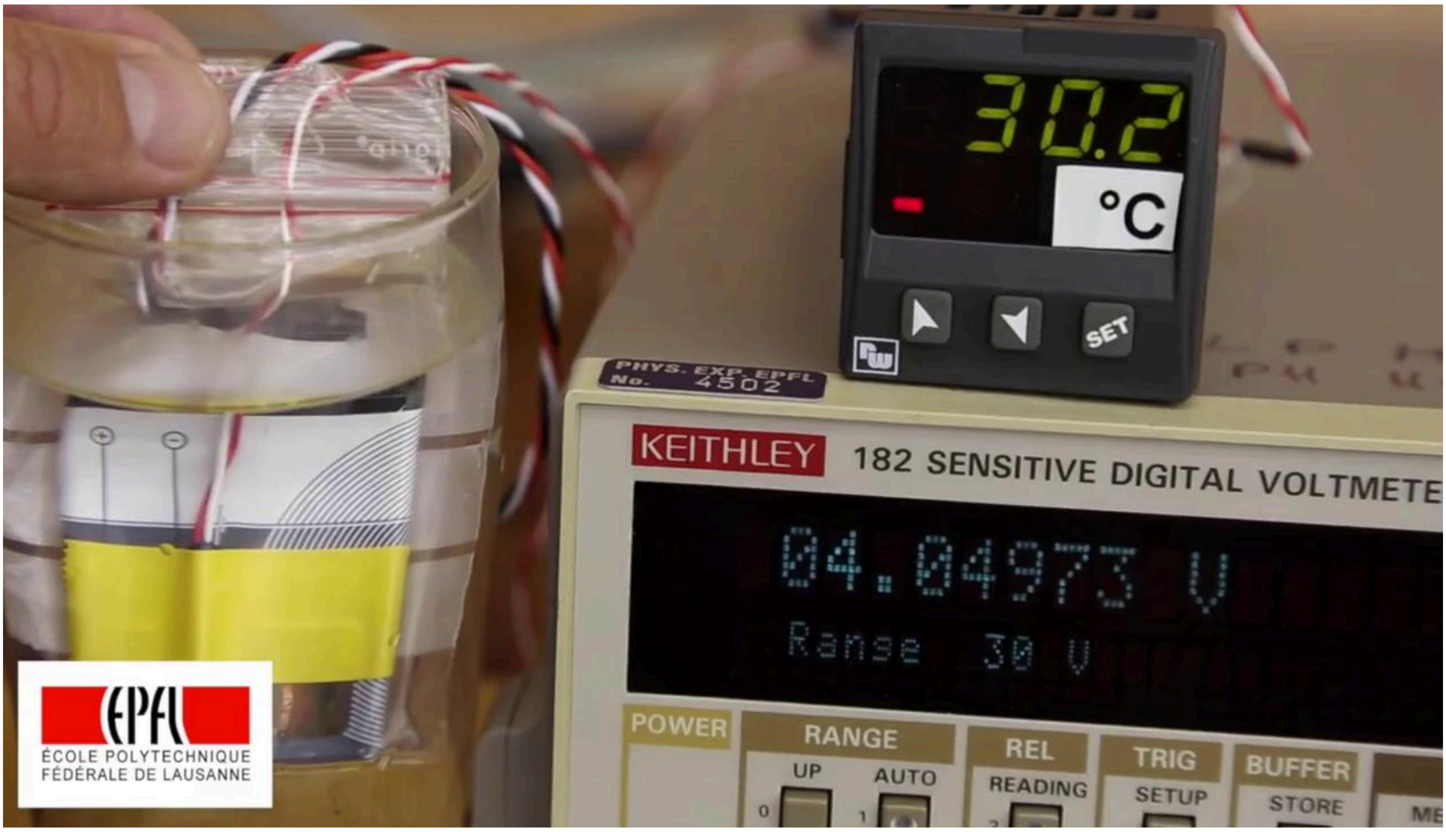
EPFL

That's it. So now we move on to two examples. We will talk about two types of batteries the lithium battery and the lead-acid battery. For these two examples, will show us how to apply what we learned earlier. First of all, we will look at a lithium battery in the picture which shows that the type of battery they have used today to a very large number. For example, in electric cars and in computers. And so there are the two poles. There is the negative side. There, there is the other end, there is the cathode and we are going to look now at the reactions which takes place in such a lithium battery.

Notes

Summary

0m 04s



Here we are in front of a lithium battery. This is the same one you have in your computer and we dive into a bath. The goal is to change the weather and the planet. It was the technician who did the experiment. It varies between a cold and a warm temperature. It measures the voltage as a function of temperature. Then you watch the temperature slowly change. It goes down with the temperature and we see that the tension rises. The effect is weak because we had the entropy of the reaction and is not very big, but it is possible.

Notes

Summary

0m 55s

Détermination des l'enthalpie libre de réaction

$$C_6Li \rightarrow C_6 + Li^+ + e^-$$
$$Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$$
$$LiC_6 + CoO_2 \rightarrow LiCoO_2 + Co$$

- L'enthalpie libre de réaction est donnée par
  $$W_{el} = \Delta_r G = -n \cdot F \cdot E$$
- Où E est la tension mesurée entre les bornes de la pile (force électromotrice)
- Pour les piles à lithium:
  $$E = 3.6V$$
  $$\nu_e = 1$$
- Chaque composé étant solide, leur activité vaut 1.

Thermodynamique

So here I have to explain. So it's half reactions that take place at the cathode and at the anode. We start with the anode. There, there is a release of electrons, there is the oxidation which occurs. And what is oxidized? So there is the lithium that is intercalated in a graphite, in a carbon form. So there's a bed over here. If the carbon atoms and thus it is silicon are released at the same time, there is release of the electron. This is the harmless reaction and the reaction of the other electrode. The counter electrode, so the cathode, is the reduction of the cobalt oxide and the interpellation of lithium in this same oxide. So in fact, what happens globally is that the lithium is transferred from carbon to cobalt oxide and it releases electrical energy. And the chemical energy that is converted in electrical energy, according to the formula that we will thus take again. The reversible electrical work will therefore measure to a measure, to an open circuit the voltage, the battery. And so this simple relationship that we have theorized earlier, which gives us the head of the reaction.

Notes

Summary

1m 41s

Détermination des l'enthalpie libre de réaction

$$C_6Li \rightarrow C_6 + Li^+ + e^-$$

$$Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$$

$$LiC_6 + CoO_2 \rightarrow LiCoO_2 + Co$$

$$\Delta_r G = -\nu_{el} \cdot F \cdot E$$

$$= 1 \cdot 96485.3 \left[\frac{C}{mol}\right] \cdot 3.6\,[V]$$

- L'enthalpie libre de réaction est donnée par

$$W_{el} = \Delta_r G = -n \cdot F \cdot E$$

- Où E est la tension mesurée entre les bornes de la pile (force électromotrice)
- Pour les piles à lithium:

$$E = 3.6V$$

$$\nu_e = 1$$

- Chaque composé étant solide, leur activité vaut 1.

Thermodynamique

And so, for lithium batteries measuring has a voltage of 3.6 volts and by putting this number there and the number of this committee in electrons, that it is a metallic stock that causes the electrons involved in the Faraday reaction. So we get the delta G of the reaction and let's put the numbers in the G. I have aware of those who put the electron at the constant and there the voltage of the battery and so it gives us for the delta of the reaction.

Notes

Summary

3m 16s

Détermination des l'enthalpie libre de réaction

$$C_6Li \rightarrow C_6 + Li^+ + e^-$$
$$Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$$

$$LiC_6 + CoO_2 \rightarrow LiCoO_2 + Co$$

$$\Delta_r G = -\nu_{el} \cdot F \cdot E$$
$$= 1 \cdot 96485.3 \left[\frac{C}{mol}\right] \cdot 3.6\,[V]$$
$$\Delta_r G = \Delta_r G^{\ominus} + RT \cdot lnK$$
$$K = \frac{a_{LiCoO_2} \cdot a_{Co}}{a_{LiC_6} \cdot a_{CoO_2}} = 1$$
$$\Delta_r G = \Delta_r G^{\ominus} = -96500 \cdot 3.6 =$$
$$-347.4 \text{ kJoules mol}^{-1}$$

- L'enthalpie libre de réaction est donnée par
$$W_{el} = \Delta_r G = -n \cdot F \cdot E$$
- Où E est la tension mesurée entre les bornes de la pile (force électromotrice)
- Pour les piles à lithium:
$$E = 3.6V$$
$$\nu_e = 1$$
- Chaque composé étant solide, leur activité vaut 1.

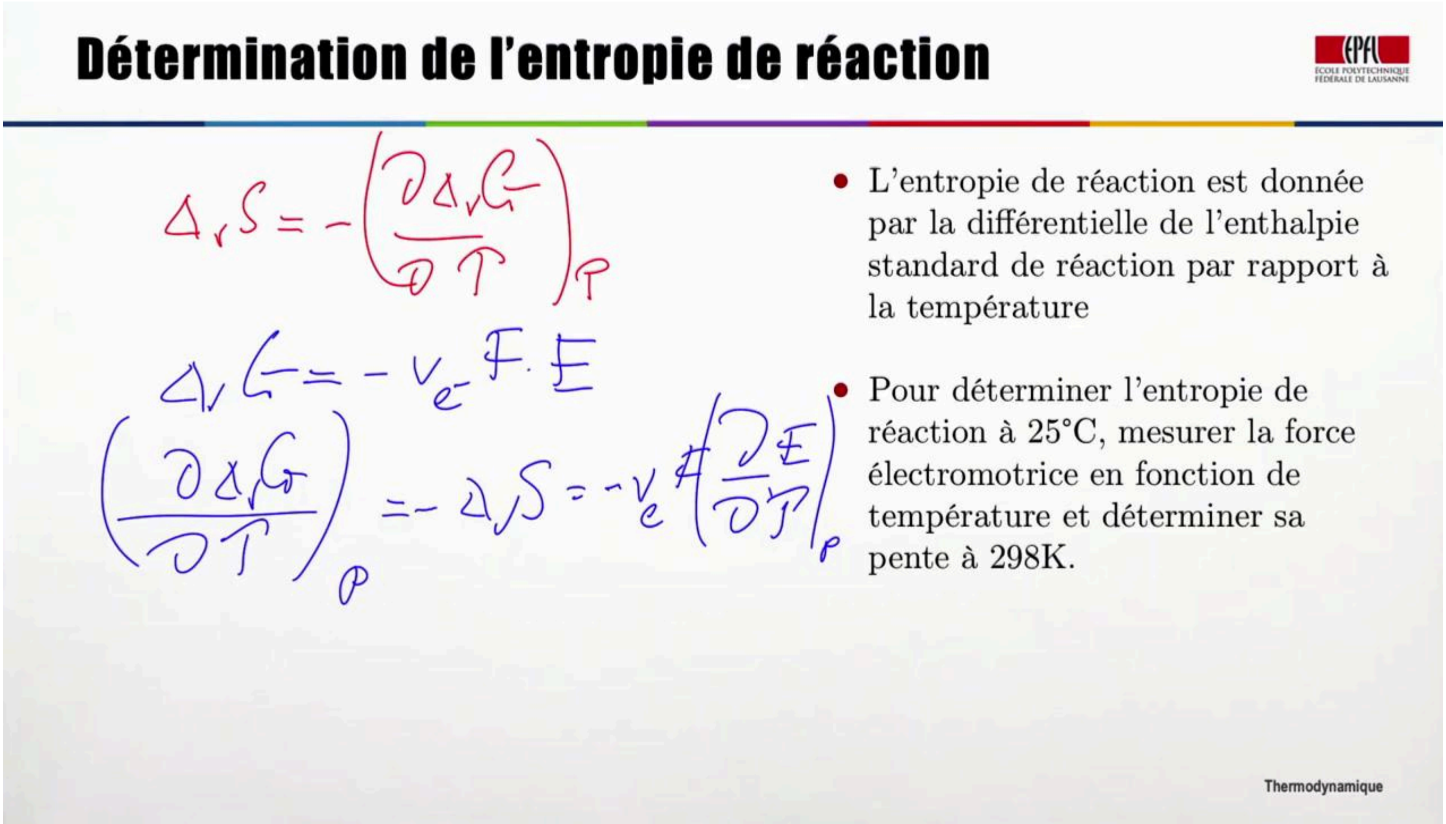
Thermodynamique

It gives us. 347 wants someone who doesn't play badly. I would like to point out that this is also the Standard. That's the reaction that happens in the Alycia stack. She is, she knows how to make pure compounds. And there is lithium, graphite with rings and cobalt oxide. There are no mixtures between the two materials that are formed. There is no electrolyte, there are species that pass that are consumed. So we have only pure compounds which are involved in the reaction and that makes that the equilibrium constant. So we will formulate according to the equation of the law of mass is constant, it is rare and therefore I can in this way equalize the free enthalpy with the standard free enthalpy of the reaction. That's it. So we finally arrive at our one month value at 357 kilos per day per month. It is thus a considerable energy which is released just by transferring the sums from one material to another.

Notes

Summary

4m 06s

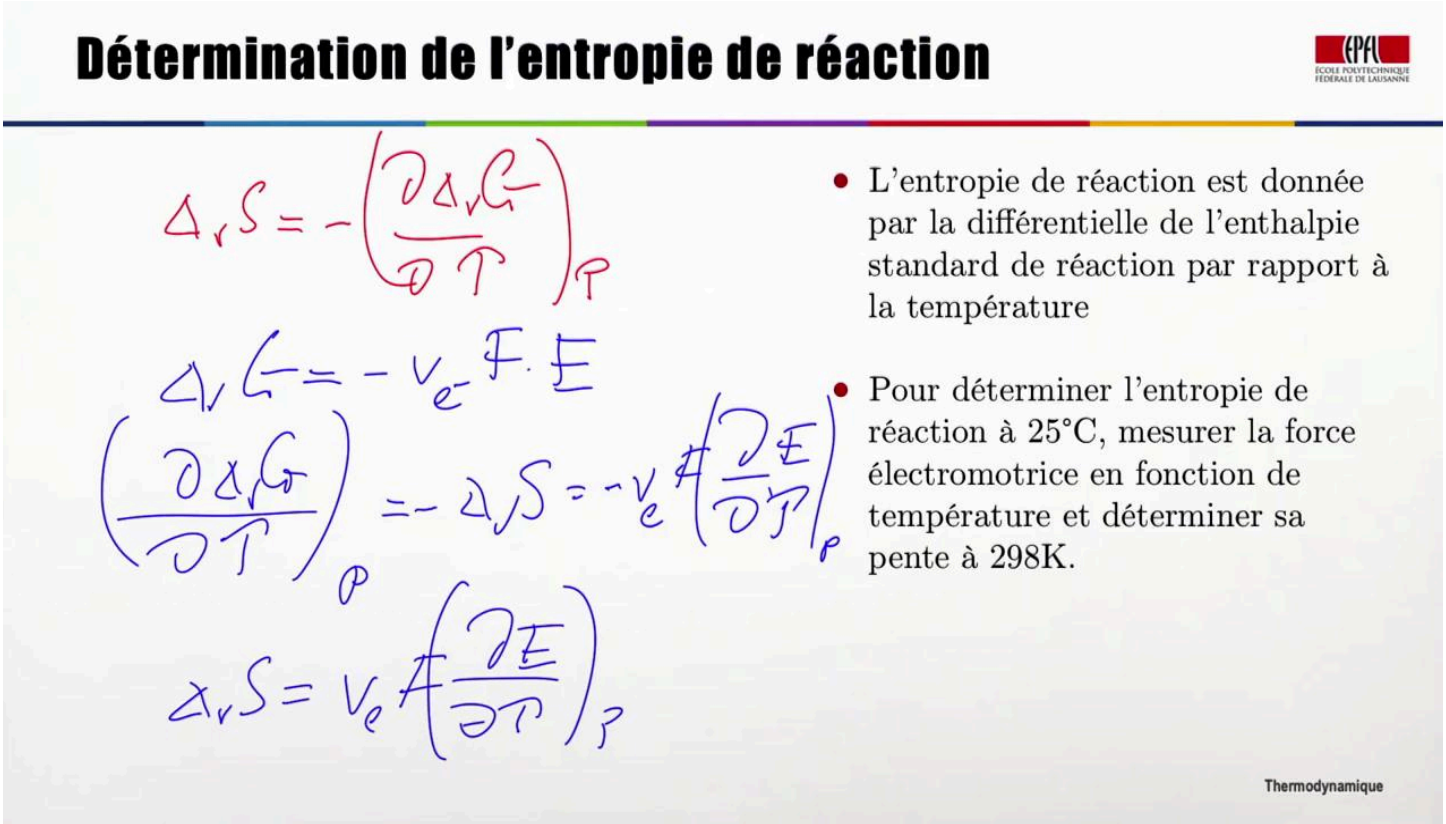


That's it. Let's move on to the second variable that interests us in the company the reaction. How to determine electrically, by electrical measurements, this variable which is also a key variable of thermodynamics? So we already start from the definition of our country. We can find the entropy of the reaction. By taking the derivative of the free enthalpy of the reaction with respect to the temperature. And leaving the pressure constant. That's the way to find out what's wrong with it when it's downloaded. Now, we know that the download is presented by this basic equation. How many times do you discuss nude on screen, at the constant time? So the electromotive force of the reaction is this point? The derivative of this basic equation, which we derived from, leaving. It is therefore the derivative with respect to the temperature at constant pressure. Which gives us the negative of entropy. And down that I have to drift, so right too. So that's two constants, but it is the derivative, the electromotive force in relation to to the temperature leaving the pressure constant. So this temperature quotient of the electromotive force? I can find it. But we will make strong measurements to determine this temperature.

Notes

Summary

5m 26s



So I can then use the equation. I'm writing it again. From what emanates from our basic equation to find the entropy. It is by simple measurement of the electromotive force at different temperatures that I can determine the entropy of reaction of the pile.

Notes

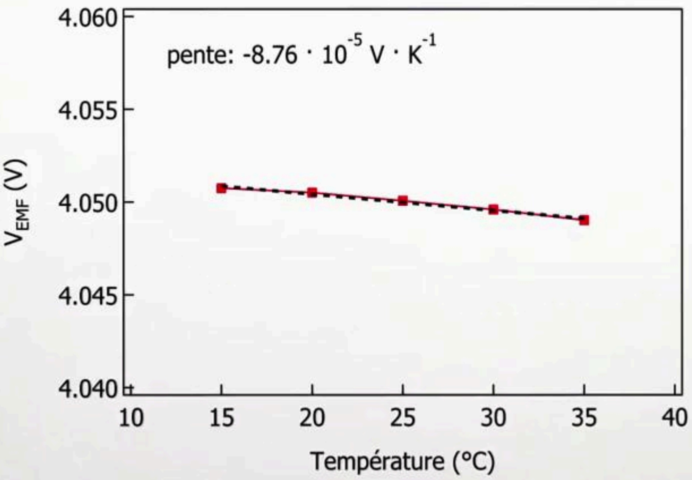
Summary

7m 17s

Détermination de l'entropie de réaction

$$\Delta_r G = \Delta_r H - T \cdot \Delta_r S \qquad \Delta_r G = -\nu_{el} \cdot F \cdot E$$

$$\Delta_r S = -\left(\frac{\partial \Delta_r G}{\partial T}\right)_{p=const} = \nu_e \cdot F \cdot \left(\frac{\partial E}{\partial T}\right)_{p=const}$$



- L'entropie de réaction est donnée par la différentielle de l'enthalpie standard de réaction par rapport à la température
- Pour déterminer l'entropie de réaction à 25°C, mesurer la force électromotrice en fonction de température et déterminer sa pente à 298K.

$$\Delta_r S^{\ominus} = \Delta_r S = \nu_e \cdot F \cdot (-8.76 \cdot 10^{-5})$$
$$= -8.45\, J \cdot K^{-1} \cdot mol^{-1}$$

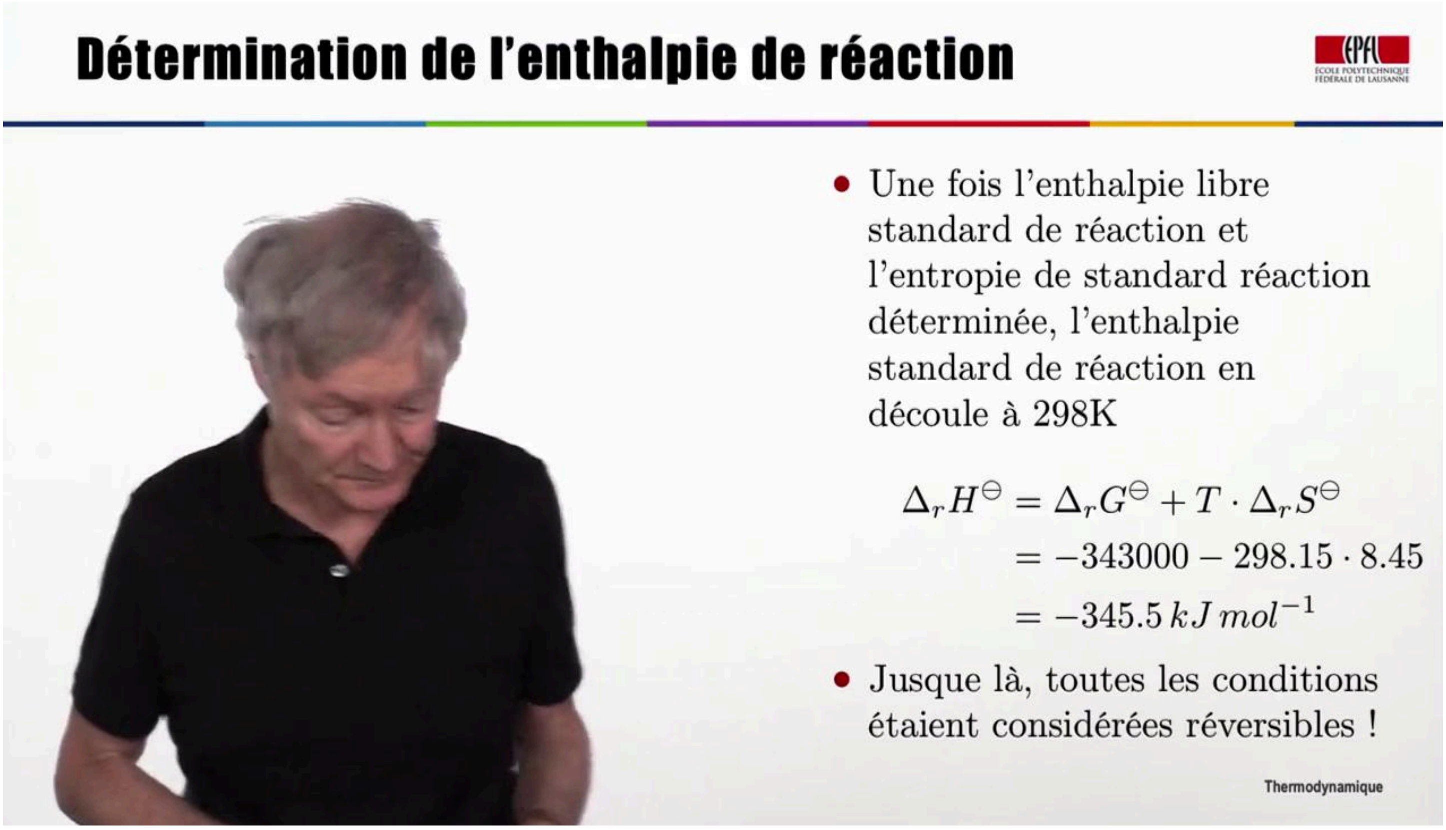
Thermodynamique

And so we go back to that equation that I just came to you with. And I am now presenting you with experimental data. Or we actually took a lithium battery and measured the electromotive force at different temperatures. So you see the graph, there are five points on this four and therefore we will go from 15 to 35. Integrate. What we are interested in is the Slow reaction at standard conditions, i.e. 25 degrees. So I'm going to take the slope here in this point at 25 degrees. And then taking that, I find the value as me. And you can tell that seventy-six times 55 wheelbarrows a year, it shows. The slope of the curve. And then I can turn that slope into a total value. Land and it gives me a wood value. Quickly, 45 cabins per month. So we see that the temperate zone of the negative reaction. So there is less descent in the products than at the beginning. And it comes from the fact that silicon is in carbon. There are six carbons by which therefore more than three can arise. So it gives more possibilities in the lesions than in the cobalt optics and fix it on a point in the crystal. And so we now have this knowledge of the reaction.

Notes

Summary

7m 46s

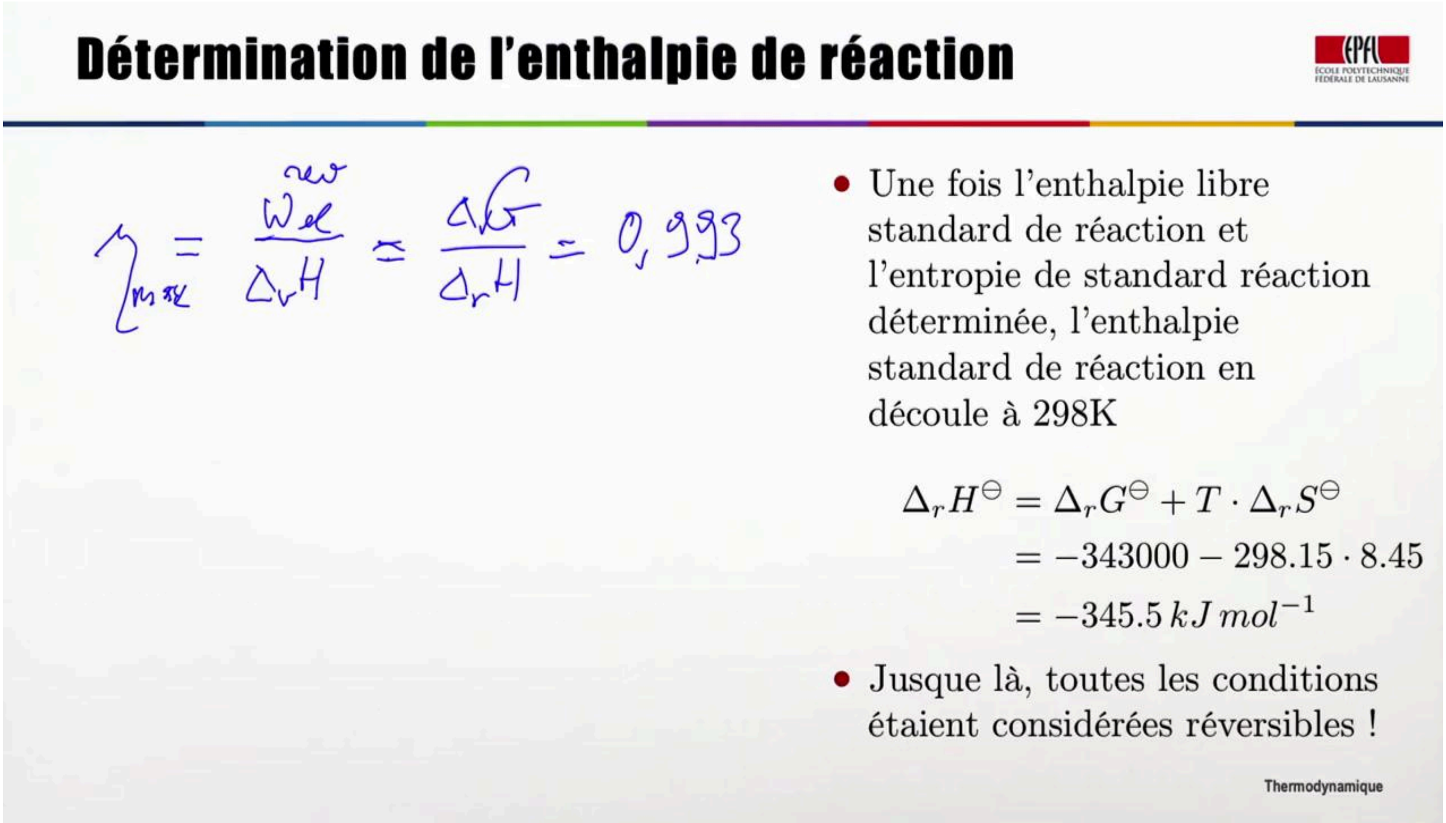


And can we move on to determine the third variable thermodynamic key that is the enthalpy of the reaction? And so we use the so-called famous equation which is given on this case delta h at the top rg delta S.

Notes

Summary

9m 30s



It is the value of Delta 349,9 that it by Mole. And so mix the three key parameters. The reaction at Delta H. I downloaded Delta S and I can even order that conversion yield. What is the effectiveness of the battery by converting the chemical energy into electrical work. And there for any definition of performance, we always have the output that is given as what we want to obtain. So I'm going to get an electrical job. And what we put as energy in the transformation of our chemical energy into HR detergents which invests in the reaction and in this ratio gives the return. And as I take the reversible case, we discussed. The gentlemen did an open circuit. So the values of the working hours are the reversible work and that is the maximum amount of work that can be done. So the reversible conditions give us the most work. So this is also the maximum yield that can be obtained in this way. So now I'm filling in. Delta G reversible electron. And is not divided into Delta HR. This gives a yield of. It's a step backwards, isn't it? Nine three years is very close. It's not quite. So there is a small loss in these conversions, but it is very small.

Notes

Summary

9m 53s

So in summary, we learned two things. First, we learned how the electrical parameters and voltage of a battery, a variable of chemical reaction which takes place in the battery. When it is this relationship of downloading it that for me harms both. France has electromotor, we have drifted. So it allows to calculate the variables chemicals from the end or vice versa. But we learned something else. We have seen that by taking the measurement, the voltage and the temperature, I can easily obtain the entropy of the reaction. So you can take for example an Alycia battery, but you put yourself in a thermostat. You see the temperature, you take the blood pressure. And here we have this second information which is the key information on the entropy of the reaction. So we will now move on to a second example that piles up a plan, therefore an accumulator, a plane where also a chemical reaction takes place. Which is used to store electrical energy.

Notes

Summary

11m 51s