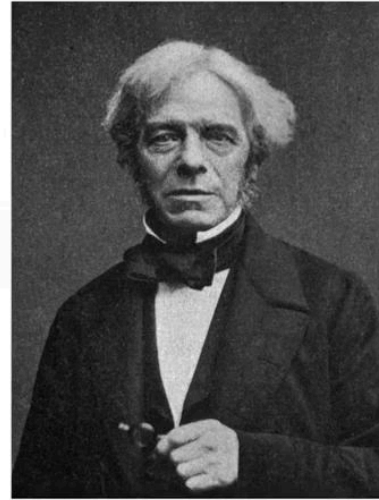


Thermodynamique

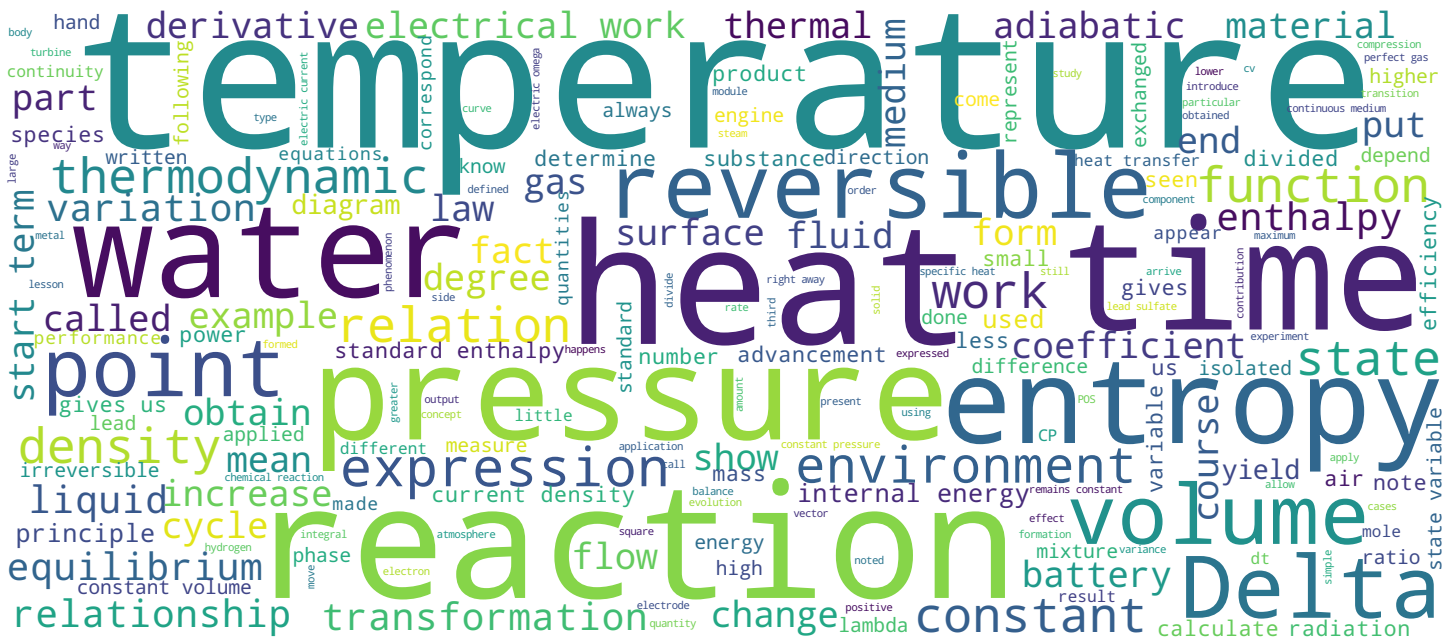
La batterie au plomb



Prof. Michael Grätzel



Michael Faraday



Video





- Les grandeurs chimiques de réaction standard suivantes:

$$\Delta_r H_{298.15K}^\ominus = -315.6 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r S_{298.15K}^\ominus = 263.35 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r G_{298.15K}^\ominus = -394.12 \text{ kJ} \cdot \text{mol}^{-1}$$

Thermodynamique

Here, I will now tell you about a second type of battery that you all know. This is the lead-acid battery that everyone still uses in the cars, for example to start the morning. The engine is still an archaic technology, but it is still widely used because it is cheap. And they are stable, these systems, not very efficient but still very useful from a practical point of view. So the reaction that happens at the pump is very simple there is lead oxide, lead dioxide which reacts with lead. And then lead sulfate is formed. So the reaction noted is the oxidation of lead to lead two. It can be made into two sulfates, one lead. And the cathodic reaction, is the reduction of lead dioxide oxide to lead sulfate. So there are two electrons involved in the Faraday reactions. So the stock metric of reaction two and therefore a battery calling at a voltage typically around two volts. Do you have a car? It was launched and here right in series 1 to 12 of tension and thus the two barrows that corresponds if I measure approximately to standard conditions, it corresponds to these three four that are not bad that I indicated stupidly. And so now we're going to see two scenarios, three scenarios.

Notes

Summary



0m 04s



- Les grandeurs chimiques de réaction standard suivantes:

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Thermodynamique

We will first see what happens to the heat? In fact, the question we ask ourselves is how? How much heat is transferred between the battery and the environment and how I can relate this to or the transformation is done and reversible under iso condition. Term or what is called adiabatic. And in the end we will consider in case irreversible or by short-circuiting the battery. And so there is electrical work that is cleared.

Notes

Summary



1m 54s

Mesure de la tension en V

Mesure de la température en °C



So that's the tension. As much as towards one that one has that made me a plan and would have different temperatures to remind us.

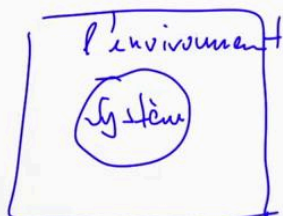
Notes

Summary



2m 32s

La batterie au plomb



$$\Delta S_{\text{global}} = \Delta S$$

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Thermodynamique

The goal is to derive the entropy of the reaction that takes place in this accumulator. So yes, we put this battery in an oven. You don't want to go too high. There, we went up to 45 degrees. And then we go down gently. We measure the potential. We started at twelve, between twelve and thirteen volts. That's six elements in a row. And then it goes down nicely, so weak. Radians, but it can be easily measured. And so, to determine the entropy of the reaction at 25 degrees, we take the slope therefore at 25 degrees and we use the same relation as we have derivative to calculate the entropy of the reaction. So I'm doing my little diagram again here. And then I know this system that is the battery. So the accumulator is called a system. And then there is the environment that surrounds it. And all this is an isolated system which in fact I can write at the entropic level. So the, the entropy, the change of the entropy of the system global global isolated in Chapelle-Anthenaise consists of two contributions only the system and the environment. And for the system, in the system, we have there the chemical reaction. So there is the delta s account place by the system.

Notes

Summary



2m 44s

La batterie au plomb



$$\Delta S_{\text{global}} = \Delta S - \frac{q}{T}$$

$$\Delta_r S = \frac{q_{\text{rev}}}{T}$$

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$$\Delta_r H_{298.15K}^\ominus = -315.6 \text{ kJ} \cdot \text{mol}^{-1}$$

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$$\Delta_r G_{298.15K}^\ominus = -394.12 \text{ kJ} \cdot \text{mol}^{-1}$$

Cas réversible
 $\Delta_r S_{\text{global}} = 0$

$$q_{\text{rev}} = \Delta_r S \cdot T$$

Thermodynamique

And then the environment is heat divided by temperature. So that's our starting equation. And now we will see the reversible case. If the transformation is reversible, the isolated system keeps its entropy, it changes nothing to the entropy. If the transformation is reversible, the global entropy remains constant. In this term becomes. This is the reversible case. We give Delta s global. Equal to zero. In fact, this is a very elegant way to introduce the reversible condition in a time to a demonstration of this kind. So, we can see right away that this reversible case gives us a very simple relation between delta S and the reversible heat this time, which exchanged between. The system. And the atmosphere is there is heat. There is again the work that can be exchanged. And so I find this relationship which gives us for the reversible heat equal to it ten times t. What do I see now? I see that the TV remains the transformation that we watch and positive. So we increase when we transform lead oxide and lead to lead sulfate. The reason for this is that water is formed which has a much higher entropy The temperature of the water is higher than that of sulphuric acid, and therefore there is an increase in entropy.

Notes

Summary



4m 44s

La batterie au plomb



$$\Delta S_{\text{global}} = \Delta S - \frac{q}{T}$$

$$\Delta_v S = \frac{q_{\text{rev}}}{T}$$

- Les grandeurs chimiques de réaction standard suivantes:

$$\Delta_r H_{298.15K}^\ominus = -315.6 \text{ kJ} \cdot \text{mol}^{-1}$$

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cas réversible
 $\Delta_v S_{\text{global}} = 0$

$$q_{\text{rev}} = \Delta_r S \cdot T$$

Thermodynamique

And we see that it is that it makes that this reversible work is positive. What does that mean? It means that, in fact, during the reaction, there is a heat input to the transformation of electrochemical. Which increases the reversible work, transforms the heat of the environment into electrical work according to a situation which you find very favorable because we use the heat by transforming it into electrical work and thus in the end we can Now calculate the yield of the reaction.

Notes

Summary



Conditions réversibles

$$\eta_{\text{rev. max}} = \frac{\Delta w_{\text{el}}^{\text{rev}}}{\Delta_r H} = \frac{\Delta_r G}{\Delta_r H}$$

$$|\Delta_r G| > |\Delta_r H| \quad \eta_{\text{rev}} = 1.25 \quad 125\%$$

Thermodynamique

So the yield of the transformation is in omega. Max. Reversible. Which marks a maximum of performance. And as I explained at the beginning of this letter, you can divide what you want to obtain, that is to say the electrical work. To divide by what we put, it is the chemical anarchy, the reaction. So I want to be reversible again and so it doesn't give. I used no HR. And we see that the debt in this case is greater than Delta Rage. We have a greater danger situation than Delta H in absolute terms. So like this. And so that means that the target backlog is even greater. And in this case 1.25. We have a 100-25% yield. Therefore, it is necessarily reversible. This will come up again when we discuss the fuel cell. We have the reversible flow, so there, the battery discharges the lead-acid battery very slowly thanks to the increase in sales. Then we do not only convert chemical energy. electrical energy, but the battery transforms at the same time the heat of the environment into electrical time, so the environment cools down when the battery is discharged.

Notes

Summary



7m 31s

Conditions adiabatiques



$$dU = \cancel{dq} + dw = dw_{\text{elec}} + dw_{\text{vol}} - p \cdot dv$$

Thermodynamique

In the second case or the consumption is adiabatic, so adiabatic means say that if I draw my little diagram with the system again. The atmosphere. All this forms an isolated system. So now I'm blocking everything. Any heat transfer between the system and its environment. I always have the option of transferring work between these two subsystems. So now I'm going to write the first principle for this case. And there we will have cubes, more omega. And by definition so adiabatic. So it remains that the term omega, so omega electric omega volume. We can see right away that this time, it is the work that is changed. Corresponds to this amount of work corresponds to a variation of a variable, therefore fundamental, and a state variable that depends only on the initial and final state. So the variation of U depends on these two states. So that means that for the moment we don't have to specify the path because for the variation of a state variable, the path does not play a role. So the final initial sizes are fixed. We can go anywhere, we always have the same variation, therefore not necessary to put a so reversible or not. But on the other hand we will put adiabatic because we took an adiabatic condition and for volume work.

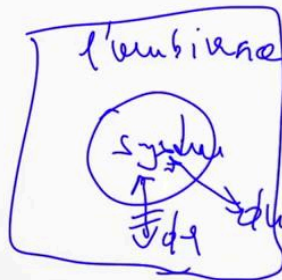
Notes

Summary



9m 27s

Conditions adiabatiques



$$dU = \cancel{dq} + dw = dw_{el}^{ad} + dw_{mech} - p dV$$

$$dU = dw_{el}^{ad} - p dV$$

$$dU + p dV = dw_{el}^{ad} = dH$$

$$dH = dU + p dV$$

$$p = w_{mech}$$

$$H = U + pV$$

$$dH = dU + p dV + V dp$$

$$p = w_{mech}$$

$$dH = dU + p dV$$

$$w_{el}^{adiabatique} = \Delta_r H$$

$$\eta = \frac{w_{el}^{ad}}{\Delta_r H} = \frac{\Delta_r H}{\Delta_r H} = 1$$

Thermodynamique

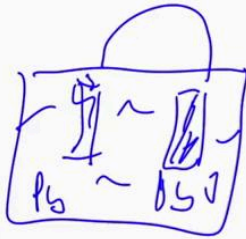
So we'll use the POS term that I'm replacing in this equation. And so with that I find equal to electric omega. Adiabatic. Me. POS. And therefore PDV. I want to put the POS side of the POS. Equal to electric omega. Adiabatic. And this is the change in enthalpy. It can easily show that. So now I've applied a tie. EU plus PDV which is correct. If the pressure remains constant during of the transformation, this can be seen from the definition of the enthalpy h or u v. And so DH. At first, they were swords. And so if the pressure remains constant. I find des. TH. TH equal to u ? US and t? We had to show you. So we have a very simple relationship that gives us now the adiabatic electrical work. And like typing in these people integrates this work, I find that on an advancement of the reaction, I find that the electric work adiabatic. For Delta HR. Reaction. And so that means, This means that the yield, if I go back to the yield CA, can be conversion of chemical energy into electricity. So we have the electrical work. This time it is the adiabatic part. Divide by kilometers h as c of electrical work your delta h is divided by 1 th. So the efficiency is lower for the case of the accumulator. Recall that for the reversible case isotropic or we have an efficiency of 125%, it is only 100%. Now I come again to a third case of figure which is the irreversible case.

Notes

Summary



Conditions de court-circuit



$$dU = dq + \cancel{dW_{elec}} - p dV$$

$$dU = dq - p dV$$

$$dq = dU + p dV = dH$$

$$q_{irr} = \Delta_r H$$

Thermodynamique

So here, I take the lead battery. My home is the two electrodes. The problem. Two There is the electrolyte and they agree. I connect these two electrodes and I recommend not because it gives a terrible spark. All the energy is released for an electric current, so don't do it. But if you do so, you are in an irreversible condition or there is no electrical work and uncheck everything leaves as heat. And so by applying the first principle again. So I was created right away as an electrical job. I'm a POS, so a volume job. So there is the choice now that the work. Electric is null because there is, we do not earn a job therefore. And that means ass, we are looking for the calculated heat, so the heat is. In fact of ? EU. Higher. And this, this new DH. So I integrate. It turns out that Q. Irreversible. Equal to Delta HR. So now we have takes a look at these three different ways of consuming and so we will summarize the reversible case.

Notes

Summary



14m 25s

Rendement de la batterie

- Rendement: énergie sortie (électrique) divisée par énergie investie (chimique)

$$\eta = \frac{W_{el}}{\Delta_r H}$$

$$\eta = \frac{W_{el}}{\Delta_r H} = \frac{\Delta_r G + T_{therm}(S_f - S_i)_{global}}{\Delta_r H^\ominus}$$

$$= 1 - \frac{T\Delta_r S - T_{therm}(S_f - S_i)_{global}}{\Delta_r H}$$

Cas réversible

$$\eta = \frac{\Delta_r G}{\Delta_r H} = 1 - \frac{T \cdot \Delta_r S}{\Delta_r H}$$

$$= 1 - \frac{q_{rev}}{\Delta_r H}$$

$$\eta^\ominus = 1 - \frac{T \cdot \Delta_r S^\ominus}{\Delta_r H^\ominus} = 1.25$$

Cas adiabatique

$$\eta = \frac{\Delta_r H}{\Delta_r H} = 1$$

Court-circuit
Cas irréversible
extrême

$$\eta = \frac{0}{\Delta_r H} = 0$$

$$q = \Delta_r H$$

Thermodynamique

So here we go again that the most favorable case or we have reversible ISO conditions. If I switch to the adiabatic case, the question of reversibility does not arise more because the work corresponds to a change of a state variable. So I get as output actually one. In the adiabatic case. And for the opposite case. Of course, the output is quite rare, but we can say about the heat which is changed, thus the heat, and change q or which is reversible at delta H gives off a lot of heat and this can cause problems, it can cause accidents. This is where we will end up with this analysis on the reaction in a trivial act that accumulates it flat.

Notes

Summary

