





- Tension d'une pile à circuit ouvert
  - Le travail électrique
  - L'enthalpie libre de réaction
- Pile au lithium
  - Détermination des variables de réaction expérimentalement
  - Détermination du travail électrique dans un système non-adiabatique
- L'accumulateur au plomb
- La pile à combustible

Thermodynamique

Hi, my name is Michael. I am a professor of physical chemistry at the Federal Polytechnic of Lausanne and I teach thermodynamics. So this link will deal with the conversion of chemical energy into electrical work. And so there will be several chapters that we have discussed. First of all, there is the conversion that takes place when we discharge a battery, an electric cell. And there are two types of batteries that we have to discuss lithium batteries, lead batteries and others not. There is also the fuel cell which follows the same principle. And so we will treat at the end the conversion of the chemical energy into an electric train by a fuel cell.

Notes

Summary



0m 04s

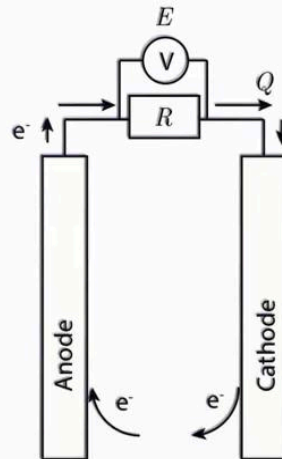


So, seeing on this video the battery a primary battery, we call it discharges once and then it must be thrown away. And then on the left, there is the voltmeter which is used to measure the voltage, thus the electromotive force of the battery. And here, as I said, this voltmeter has a very high internal resistance, so that when we measure the voltage there is no current flowing in the external circuit. This allows us to apply the condition of reversibility to then derive our thermodynamic equations.

Notes

Summary





$$d\omega_{el} = -E \cdot dQ$$

- $dQ \geq 0$  par convention
- $d\omega_{el} \leq 0$  car le système fourni du travail (électrique) à l'environnement, d'où le signe négatif.

$d\omega_{el}$  : travail électrique fourni par l'accumulateur lors de la décharge

Thermodynamique

And so there is already a first very important relationship between this electromotive force and the electrical work which can be released as required to discharge the battery. The equation is shown in differential form. The differential electrical work is therefore the voltage of the battery which is called electromotive force the battery At the same time the load which flows thus when one discharges the battery. And there is a negative signal. This is to respect the conventions, because the work provided by the stack, so it, it by the battery, it must have a negative value while both magnitude and  $dQ$  are positive by convention. And so it is now a matter of developing a relationship between this electrical work, so the quantities that we will try in the basic equation and therefore the chemistry behind when we charge or discharge a battery. And so here the image of the stack shows us in detail what is happening. There is the anode which by definition is the electrode where there is an oxidation which is and therefore there are electrons that are close to the system which comes out of another and the other part is the cathode. By definition, this is where it makes a reduction.

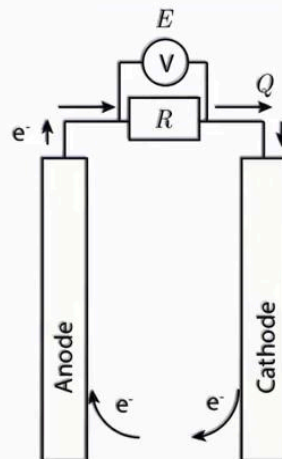
Notes

Summary



1m 37s





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Thermodynamique

So there are the electrons that enter and reduce the substance that is practically active. So now we'll look again at how to find this key relationship and this is the purpose of our first reflection. This key relationship that links electrical work to the chemical variable of reaction, which are thus the free enthalpy in particular of the reaction.

Notes

Summary



3m 14s

$$d\omega_{el} = -E \cdot dQ$$

$$dQ = F d\mu_{e^-} = F \nu_e d\xi$$

$$d\omega_{el} = -E \cdot F \nu_e d\xi$$

- Lorsque la pile débite du courant, les électrons sont consommés à la cathode et générés à l'anode de la pile. La réaction est appelée Faradayique.

- $F$  : Constante de Faraday
- $d\xi$  : degré d'avancement

de la réaction

$$d\xi = \frac{dn_e}{\nu_e} \quad (\text{par définition})$$

- $dn_e$  : nombre de moles d'électrons participant à la réaction Faradayique
- $\nu_e$  : nombre d'électrons impliqués

Thermodynamique

The goal is to start from this elementary equation and derive a second one that links these electrical parameters to the chemistry that takes place in the system when charging a battery or a fuel cell. So we start by expressing the charge that in coulombs by the number of electrons that flows through the system as the battery is discharged. It's a very simple equation I can create. This quantity increases the load tenfold as product of the Faraday constant and the number of electrons. And the number of electrons. I can express in its turn by the stoichiometric quotient of the electrons. It is therefore the number of electrons that pass between the electrode and the battery solution. Not currently. When we translate a molecule, there are three electrons that are exchanged between the electrode and the electrolyte. This figure does not store, but electrons. And then he added the degree of reaction advancement again. And therefore it is still missing to put the CE, this expression in your starting equation. If I do that, I get an electric job. Thus the electromotive force, the Faraday constant. And then DQ expresses itself in these three terms. This is the metric power. Alexis.

Notes

Summary



3m 47s

$$d\omega_{el} = -E \cdot dQ$$

$$dQ = F d\mu_{e^-} = F \nu_e d\xi$$

$$d\omega_{el}^{rev} = -E \cdot F \nu_e d\xi = dG$$

$$\left( \frac{\partial \omega_{el}}{\partial \xi} \right)_{P,T} = -E F \nu_e = \left( \frac{\partial G}{\partial \xi} \right)_{P,T} = \Delta_r G$$

$$\Delta_r G = -E F \nu_e$$

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Thermodynamique

Now there is a key thought. This electrical work is equal provided that the pressure and temperature are and that the transformation is reversible. This electrical work can be equalized or shifted with the change of the G function, thus the free enthalpy of the reaction. I will show you afterwards how to find this quality. And so now, I can divide the degree of advancement of the reaction by two. So I find the differential. Electricity to describe the state of progress of the reaction. And I add again just for us remember when we talk about a reversible condition. So this arrival that is worth. The electromotive force, the electron constant and atwater the derivative of g with respect to which partial because the pressure and temperature are in constant. And that, by definition, is the free enthalpy of the reaction. So I find this way in a rather simple way. In a few lines, I find the relationship between the chemical variable, the reaction which is the free enthalpy of the reaction and the electrical variables which are the electromotive force, the Faraday constant and the stoichiometric number of electrons.

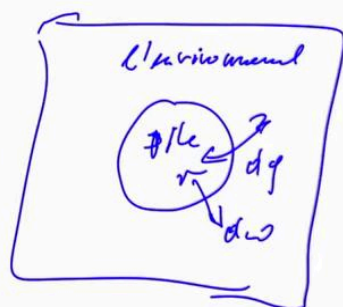
Notes

Summary



5m 47s

# Dérivation de $dG = dW_{el}^{rev}$



$$dU = dq + dw_{rev}$$



Thermodynamique

So it remains to show you that there is actually this correct equality between the reversible electric work and the variation of the free enthalpy of the reaction. And so, to find that equality, I make a little diagram. I. I consider our global system, which has two sub-systems. This is the battery. The electrochemical reaction takes place and there is the environment that serves as a thermostat for the environment. And the amount of work and heat that was done between these two. So if I give a job provided to a worker, a heat to this system, I will increase its internal energy and this first principle of thermodynamics which gives us the relation between these three variables. Is there a heat job that from one side to the other and to the variation of the internal energy? But when I hold the battery open, I slow down the reaction. So the current is very difficult to get through. There is a very high impedance when I put the voltmeter, so that the reaction is good in small steps. And this is a condition called the reversible condition. So if I can, I can afford to write that this heat, when I measure a heat, will therefore be a transformation. The reaction path will be the reversible path.

Notes

Summary



7m 31s



# Dérivation de $dG = dW_{el}^{rev}$

Diagramme schématisant un système thermodynamique (cylindre) avec des variables  $U$ ,  $q$ ,  $w$  et  $V$ .

$$dU = dq + dw_{rev} = TdS - pdV + dW_{elec}$$

$$\frac{dq_{rev}}{T} = dS$$

$$dW_{elec} = dU - TdS + pdV = dG$$

$$G = U + pV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = dU + pdV - TdS$$

Conditions aux limites :  $dp = 0$ ,  $dT = 0$

Thermodynamique

I know, it's two dreams to remind me. And now I will use the definition of entropy which is a D that surfs on CDS. So it represents the variation of the TDS entropy. And for the work by the reversible volume work. CDB PDV. And I still have the electrical work done. This work consists of two contributions. So there is electrical work. There is the volume work. And there I expressed this volume work which is easy to do when we have a reversible transformation. So, we are interested in getting the electrical work out of this equation. So I created an electric one at the beginning. TDS. POS. And this is equal to the variation of the free enthalpy. This equality is very easy to find because the definition of the free enthalpy of H+ can ts. So that's one definition auxiliary variable which is a derivative of the internal energy of entropy. And so by definition we have. We have this thermodynamic relation. And then if I do the differential now, I find u's and u's. I was. TDS. And imposes on him an ISO condition by. Under these conditions, it appears at the end of the collateral effects of collaterals. And like that, we have enough land that falls. So I find and I get. Bus and TDF TV.

Notes

Summary



9m 27s

# Dérivation de $dG = dW_{el}^{rev}$

Diagramme de l'Univers (universe diagram) showing a system (circle) and surroundings (rectangle). Arrows indicate energy flows:  $dq$  (heat),  $dW$  (work), and  $dU$  (internal energy).

$$dU = dq + dW_{rev} = TdS - pdV + dW_{rev}$$

$$\frac{dq_{rev}}{T} = dS$$

$$dW_{rev} = dU - TdS + pdV = dG$$

$$G = U + pV - TS$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = dU + pdV - TdS$$

Conditions:  $dP = 0$ ,  $dT = 0$

Thermodynamique

So with this? Choral singing in. This equation is therefore. We see that it is indeed  $dG$  that we will count three of the equation. So, I have provided you with the proof that these two variables are effectively bound by a simplicity of equality.

Notes

Summary



# Conclusion



- Equation fondamentale de la tension d'une pile:

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

Thermodynamique

So, in conclusion, we have found an extremely important relationship that links a chemical parameter, i.e. a chemical reaction variable, the RG parameter. At a battery voltage. So it allows you to do two things that we measure the voltage of a battery and we will find the value of this variable thermodynamic key which is used for many things in thermodynamics. Or if I'm interested in predicting, the voltage is a battery. I'm writing an equation, so a battery stack, so the reaction that happens of which we will see two or three other examples. We will see three examples. And then we can download the value. We can therefore predict the voltage of the green circuit battery. So it's just like with lead paste, we know that this voltage is about two volts. It is immediately made to say that it is the delta RG. The reaction that takes place in that battery, so that's really a key equation. It can then be further derived with respect to the temperature, we will find other variables of the reaction. So it opens a door to link these two areas that seem completely different, i.e. electricity and chemistry. So there is a very strong link given by this equation.

Notes

Summary



12m 14s