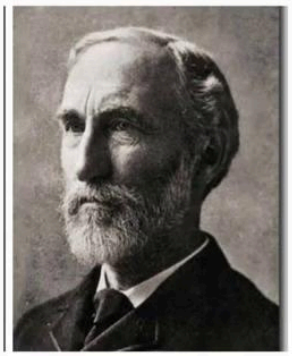
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

RESCIF
Réseau d'excellence des sciences de l'ingénieur de la Francophonie

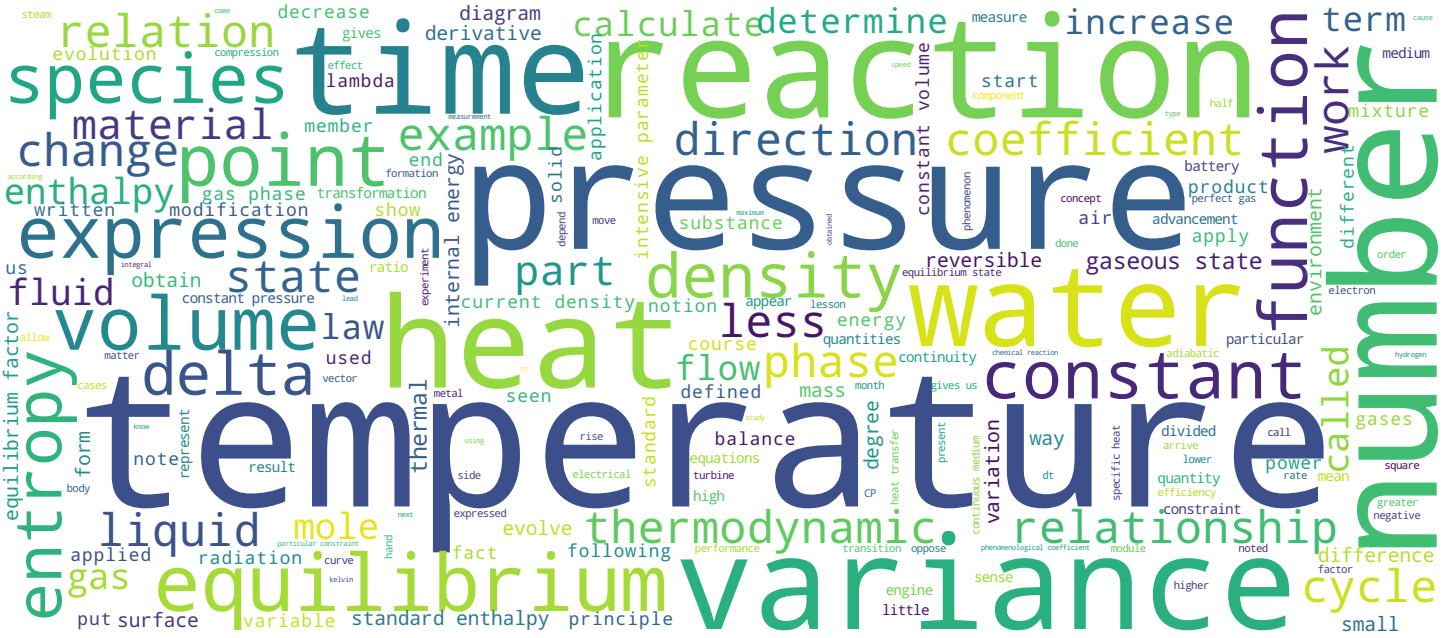
Thermodynamique

VARIANCE OU REGLE DE GIBBS



Josiah Willard Gibbs

Dr. Théophile MBANG



Video

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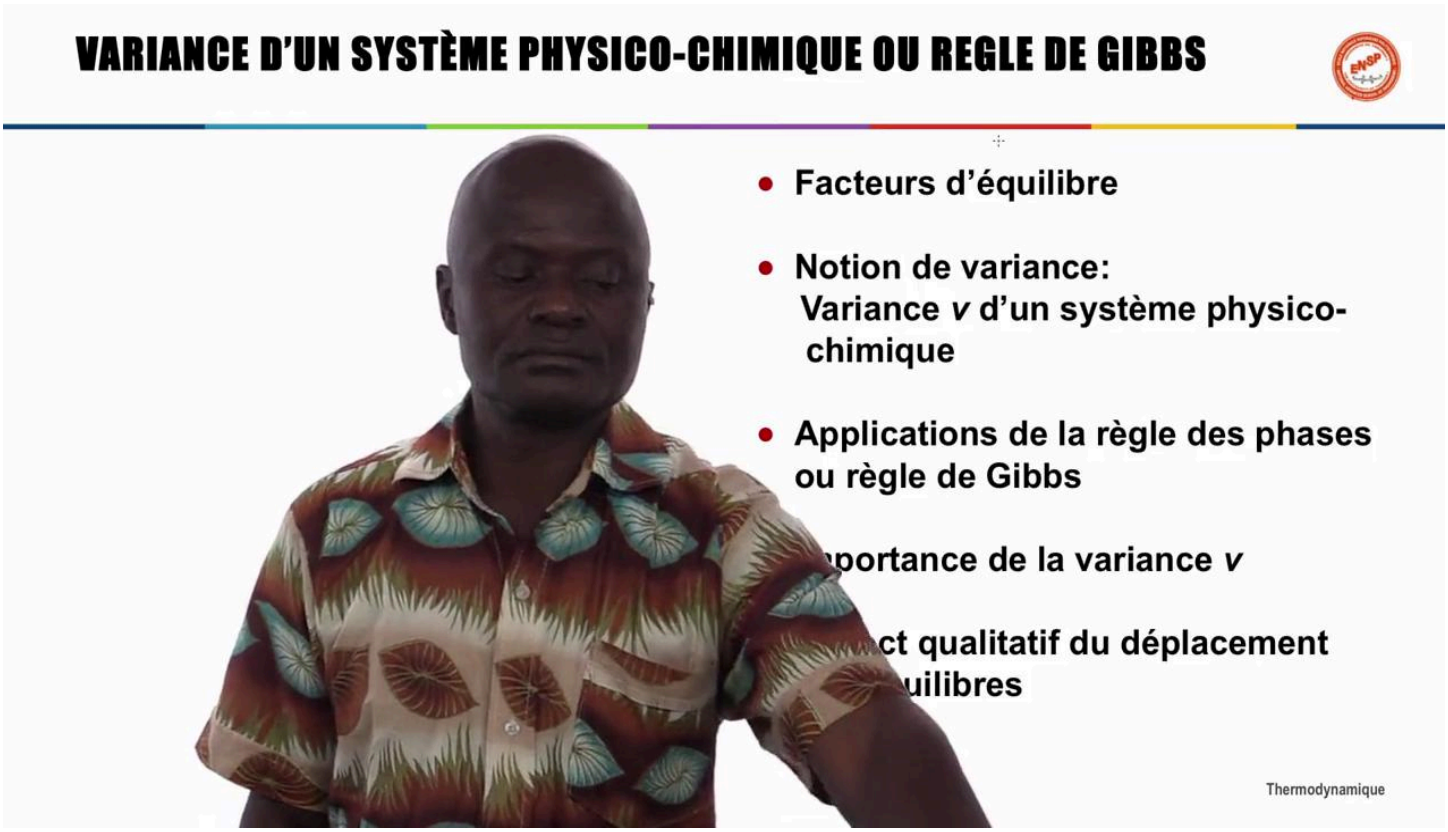


Hello. It is a great pleasure to contribute to the coordinated thermodynamic reef by the École Polytechnique Fédérale de Lausanne and PSL in Switzerland. I am a son of a chemistry teacher at the Ecole nationale supérieure polytechnique. An SP in Yaoundé, Cameroon. We will continue our thermo chemistry course. We will see the notion of variance or rule and jeeps. To do this, we will recall the equilibrium factors that we need for the notion of variance. Define the variance. Apply this concept to different equilibria, i.e. calculate the variance, show its importance and make a qualitative study of the displacement of equilibria. By applying Le Chatelier's law as a function of temperature and pressure, before concluding.

Notes

Summary

0m 04s

FACTEURS D'ÉQUILIBRE ET NOTION DE VARIANCE

- **FACTEURS D'ÉQUILIBRE**

1° Paramètres intensifs physiques: T et P

2° Composition des phases: la pression d'une phase gazeuse idéale B:

$$P_B = \chi_B.P \quad \text{avec} \quad P = \sum_B P_B \text{ et } \chi_B = \frac{n_B}{\sum_B n_B}.$$

χ_B= fraction molaire pour une solution solide, liquide ou gazeuse.

3° Facteurs d'équilibre proprement dits: ce sont des paramètres dont la variation peut entraîner une modification de l'état d'équilibre du système : volume V, P, P_B, T.

Thermodynamique

Equilibrium factors. We have the physical parameters, including temperature and pressure, and see the composition of the phases in the pressure of an ideal gas phase. Grains B is defined as by P, but the partial pressure of B is equal at the molar fraction of B times the total pressure. Of which what happened to me was the mole fraction. For a solid, liquid or gaseous solution. We have the balance factors themselves. These are parameters whose variation can lead to a change in the system balance. Volume. The pressure. The partial pressure. Temperature.

Notes

Summary

1m 14s

Variance V d'un système physico-chimique

- **1° Définitions**

La variance d'un système physico-chimique à l'équilibre correspond au nombre de degrés de liberté de ce système ou au nombre de paramètres intensifs qu'il est nécessaire de fixer pour déterminer l'état d'équilibre d'un système.

- **2° Calcul de la variance**

Ce calcul se fait grâce à la règle des phases proposée par *Josiah Willard Gibbs* en 1878.

For the variance. We will therefore define this notion. The variance of a physical-chemical system at equilibrium corresponds to the number of degrees of freedom or number of intensive parameters. Who is necessary to fix to determine the equilibrium state of a system. How to calculate the variance? This calculation was made using the rule proposed by Josiah Willis Gypse in 1878.

Notes

Summary

2m 10s

APPLICATIONS DE LA RÈGLE DES PHASES OU RÈGLE DE GIBBS

- **1° Equilibres chimiques homogènes**

Synthèse de l'ammoniac:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$$

$V = (3 - 1 - 0) + 2 - 1 = 3 \Rightarrow$ il faut définir trois paramètres intensifs pour déterminer un état d'équilibre.

Cas particulier où l'opérateur utilise un mélange stœchiométrique pour faire la synthèse.

Il s'agit d'une contrainte particulière , la variance devient alors : $V = 2$.

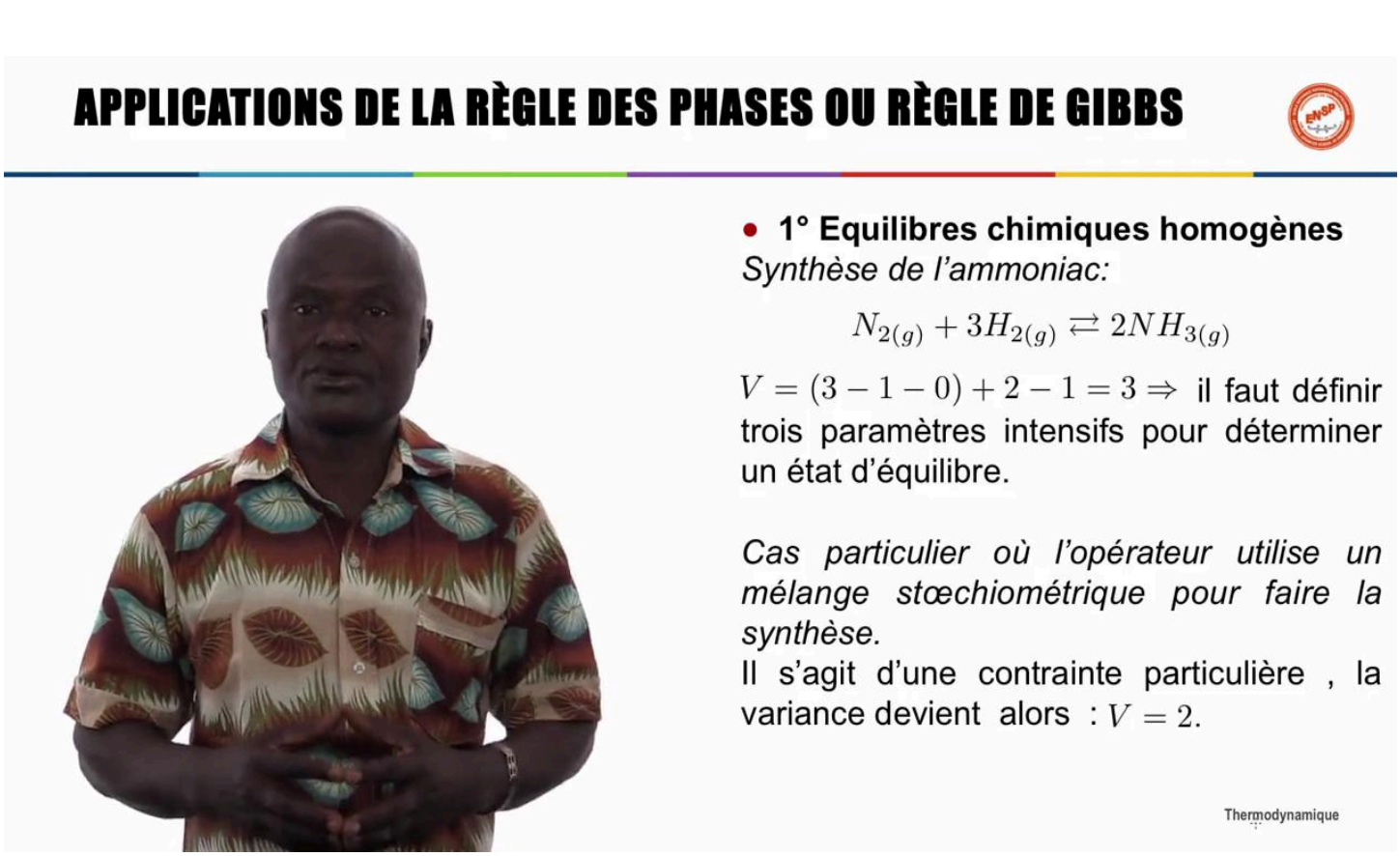
Thermodynamique

So the variance, the variance of a physical-chemical system. As we have seen these calculations thanks to the James rule. The sentence is given by v, which is the variance that is equal to the number of species contained in the reaction medium small n the world of reactions large land area minus the number of specific constraints. P. Plus B if the temperature and pressure are at equilibrium. When the pressure is not strong of equilibrium, we will take more and more thread to the number of phases. We are going towards some application of the rule, phases or chips. We will take here the equilibrium applied to the homogeneous equilibrium. Let's take the case of ammonia synthesis. Nitrogen in the gaseous state and reacts with dihydrogen, the gaseous state to give ammonia. The variance is equal to the number of species of which we have had six times the number of reactions. We have a single reaction, less and less the number. The particular constraints do not have -0 plus two, because pressure and temperature are the equilibrium factors. We have much more moles of gas to the most memorable than to the second member. The number, the phases. We have only one gas phase with equal variance.

Notes

Summary

2m 43s



To what? Three intensive parameters must be defined to determine a steady state. Let's take the particular case where the operator uses a stoichiometric mixture to make the synthesis. This is a particular constraint. There, the variance becomes equal to two. For this, we can cite the number of species, the number and the relationships. Less and less, we mix which is the constraint because the reaction is a bit like it is one constraint, plus variance equal to two.

Notes

Summary

4m 11s

APPLICATIONS DE LA RÈGLE DES PHASES OU RÈGLE DE GIBBS

- **2° Equilibres chimiques hétérogènes**
  - $FeO_{(s)} + H_{2(g)} \rightleftarrows Fe_{(s)} + H_2O_{(g)}$
    $\Rightarrow V = (4 - 1 - 0) + 1 - 3 = 1.$
  - $PbCO_{3(s)} \rightleftarrows PbO_{(s)} + CO_{2(g)}$
    $\Rightarrow V = (3 - 1 - 0) + 2 - 3 = 1.$

Thermodynamique

But let's apply this to the heterogeneous chemical equilibrium where we have several phases the solid liquid phases in gas phase. Let's take the case where the solid iron oxide reacts with the hard dihydrogen gas to give solid iron and water in the gaseous state. The variance equals the number of species. Here we have four species, four selves, the number, the reactions. We have only one reason: the number of specific constraints. We do not have -0 plus one because the pressure is not equilibrium factor, because we have here a mole of gases to the first member and one mole of gases to the second member, minus the number. Phases. We have two phases is solid and a gas phase -3. The variance is equal to one. If we apply the second version well. Solid lead carbonate decomposes as well as solid lead and carbon dioxide gas. The variance is equal to the number of species. Here, it's three months. The number of reactions, there is an average of one month. The number, the zero plus two constraints. So because the temperature and pressure are a factor of balance, minus the number. The phases we have two phases is solid and a gas phase less than three. The variance here is equal to. It can be applied in different equilibria.

Notes

Summary

4m 48s

Aspect qualitatif du déplacement des équilibres

- La modification d'un état d'équilibre obéit au principe de modération ou principe de *Le Châtelier:* « *Lorsqu'un système est en équilibre stable, toute modification d'un facteur d'équilibre provoque une réaction qui tend à s'opposer à cette modification.* »

- **Application de la règle de Le Châtelier:**
  - **Influence de la température:** L'élévation de la température d'un mélange à l'équilibre provoque, à pression ou volume constant, un déplacement de l'équilibre dans le sens où la réaction est endothermique.

Exemple: $SO_{2(g)} + \frac{1}{2}0_{2(g)} \underset{2\leftarrow}{\overset{\rightarrow 1}{}} SO_{3(g)};\ \Delta_r H^\circ = -98,2\ \mathrm{kJ/mol}.$

Si la température augmente, alors il y a évolution de la réaction dans le sens 2.
Si la température diminue, alors l'équilibre se déplace dans le sens 1.

Thermodynamique

But how important is valour? It is the valour is equal to zero. We will say that the system is invariable. All intensive parameters are set. Therefore, any modification, no matter how small, of the value of a parameter leads to a break in the equilibrium. Here the variance. When we calculate the variance one as the variance is equal to one, then the system is mono-variant. In this case, it is sufficient to set the value of an intensive parameter that is a factor of equilibrium for the other intensive parameters to be determined. The modification of these parameters, the others remaining constant, leads to a break of equilibrium in the case. There are also cases where the variance is greater than or equal to two if there are several variants. It is therefore. A modification of an equilibrium factor causes the value of another equilibrium factor to change. The system then evolves towards a new equilibrium state, with no change in the number of species, but not on the qualitative aspect of the displacement of equilibrium, contrary to the equilibrium. How can we make the calculation evolve in one direction or the other? The modification of an equilibrium state obeys the principle of moderation or Le Chatelier principle.

Notes

Summary

6m 19s

Aspect qualitatif du déplacement des équilibres

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Si la température augmente, alors il y a évolution de la réaction dans le sens 2.
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Thermodynamique

When a system and an equilibrium are stable, any change in a factor of equilibrium provokes a reaction which tends to oppose this modification. If, as they say, nature always tends to oppose the cause that gives birth. So application of the Le Chatelier rule. The gifts, the influence of the temperature. The rise in temperature or mixtures at equilibrium causes at constant pressure or volume a shift of the equilibrium in the sense that the reaction is endothermic. Let's take the example of sulfur dioxide. Kazuki reacts with oxygen gas to give rise to several cycles of gaseous sulfur. The standard enthalpy of this reaction is less than 98.2 kilo joules per mole. The reaction is exo thermal. The system loses heat. If the temperature rises and we increase the temperature, then there is an evolution of the reaction in the direction of. If you raise the temperature, the system goes to what? Absorb this temperature, it will evolve in the direction man and in a way to oppose the temperature increase. Now, if we lower the temperature, then the system moves in the direction one as the temperature locus. His will evolve in such a way as to provide us with heat, thus opposing to the decrease of the average temperature, the influence of the pressure.

Notes

Summary

7m 44s

Aspect qualitatif du déplacement des équilibres

- **Influence de la pression**: Une augmentation de la pression provoque une réaction correspondant à la diminution de la quantité de matière gazeuse c'est-à-dire dans le sens où $\sum \nu_{B,gaz}$ est négatif

Exemple: $SO_{2(g)} + \frac{1}{2}0_{2(g)} \underset{2\leftarrow}{\overset{\rightarrow 1}{}} SO_{3(g)}$; $\sum \nu_{B,gaz} = 1 - \frac{1}{2} - 1 = -\frac{1}{2}$

Si la pression augmente, alors la réaction évolue dans le sens 1
Si la pression diminue, il y a évolution dans le sens 2

Si $\sum \nu_{B,gaz} = 0$, alors la pression n'est pas un facteur d'équilibre

Thermodynamique

An increase in pressure causes a reaction corresponding to the decrease of the quantity of gaseous matter, i.e. in the sense that its modulus B gas is negative in the sound of a UV-B of all gas species is negative. Let's apply this to understand what it means. Example. We take the first examples we have seen. Sulfur dioxide in its gaseous state reacts with dioxygen in its gaseous state to give the cycle of sulfur in the gaseous state. If we calculate the sum of the moles gases, we find here the sum of the gases equal to less than half. If the pressure increases, then the reaction evolves in the direction one, which if we increase the pressure, the system will evolve in the sense that there is less. Gaseous. Here, in the first member, we have a molecule, in the second member, a mole. In a sheet, the pressure evolves or there is less soft gas. If the pressure drops. There is an evolution in the ocean, it is two. This will oppose the decrease in pressure. Therefore, the pressure decreases. I want to evolve in a way that gives much more, to ask themselves much more gaseous molds. It evolves in the sense of if the sum of gases equal to zero, then the pressure is not a factor of equilibrium.

Notes

Summary

9m 23s

Aspect qualitatif du déplacement des équilibres

- **Influence de la pression**: Une augmentation de la pression provoque une réaction correspondant à la diminution de la quantité de matière gazeuse c'est-à-dire dans le sens où $\sum \nu_{B,gaz}$ est négatif

Exemple: $SO_{2(g)} + \frac{1}{2}0_{2(g)} \underset{2 \leftarrow}{\overset{\rightarrow 1}{\rightleftharpoons}} SO_{3(g)}$; $\sum \nu_{B,gaz} = 1 - \frac{1}{2} - 1 = -\frac{1}{2}$

Si la pression augmente, alors la réaction évolue dans le sens 1
Si la pression diminue, il y a évolution dans le sens 2

Si $\sum \nu_{B,gaz} = 0$, alors la pression n'est pas un facteur d'équilibre

Thermodynamique

There, even if we increase or decrease, the reaction does not move. Even if you feel pressure, pressure is not a balancing factor. When there are so many gas moles in the first second, that's it.

Notes

Summary

10m 49s

CONCLUSION

- **La variance** est le nombre de degrés de liberté d'un système ou le nombre de paramètres intensifs qu'il est nécessaire de fixer pour déterminer l'état d'équilibre d'un système.
- **Calcul de la variance** V :

$$V = (n - \Re - \Im) + 2 - \varphi$$

Thermodynamique

The other course follows the variance. And what is the variance? The variance is the number of freedom of a system or the number, the intensive parameters that need to be set to determine the equilibrium state of a system. How to calculate the variance we were told just the variance. V is equal to the number of species. The reaction medium small n months the number of planetary reactions, minus the number of particular constraints p plus two. If the temperature and pressure are equilibrium factor, minus the number of phases. In case the pressure is not strong at equilibrium. Instead of the bus, we will put more. Thank you and goodbye.

Notes

Summary

11m 04s