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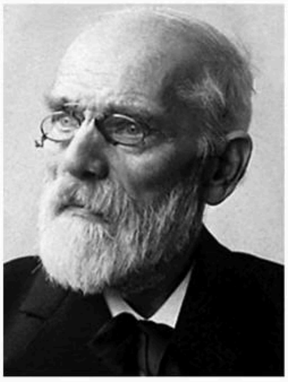
Thermodynamique

Transitions de phase: Critères de stabilité



Johannes van der Waals, 1837-1923

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Video

EPFL

Transitions de phase: Critères de stabilité

- En thermodynamique, le mot phase traduit l'état d'un système homogène ou d'une partie homogène d'un système
- Une phase est également présentée comme étant un domaine de stabilité dans l'espace de coordonnées thermodynamiques
- Une transition de phase est un processus par lequel un système ou une partie d'un système se transforme d'une phase à une autre
- La transition de phase a lieu lorsque l'équilibre devient instable

Thermodynamique

Welcome to the thermodynamics course, reef coordinated by the Swiss Federal Institute of Technology in Lausanne. I am Dr. Boillot, my alma mater, a teacher of thermodynamics at the École National Polytechnic School of Yaoundé, Cameroon. In this course, I will talk about sentence transitions. The word sentences translates the state of a system or a homogeneous part of a system. We also define a phase as a stability domain in the space of thermodynamic coordinates. The phase transition is the passage from one phase to another. This transition is caused by by an external parameter which creates an instability in the medium.

Notes

Summary

0m 05s

This lesson. Has been divided into three parts. The first part establishes criteria of stability as a function of the entropy variables. Internal energy or as a function of thermodynamic potentials. The second part deals with the current phase transition, also called phase transition from the first to the second, and the third and last part studies the liquid-vapor transition using the 20 phase model. Today, we will establish the criteria for stability. In turn. We will write the stability with respect to the entropy. Stability in relation to energy and finally the stability with respect to the thermodynamic potential functions.

Notes

Summary

1m 02s

Let's start with the study of stability over entropy. Consider an isolated homogeneous system consisting of two identical subsets one and two. The initial entropy of this system is two s. Let us also consider that spontaneously, the system evolves towards an instability.

Notes

Summary

2m 09s

Stabilité et entropie

$$S_i(U,V) = 2S(U,V)$$

$$S_f(U,V) = S(U-\Delta U,V) + S(U+\Delta U,V)$$

$$\Delta S = S(U-\Delta U,V) + S(U+\Delta U,V) - 2S(U,V)$$

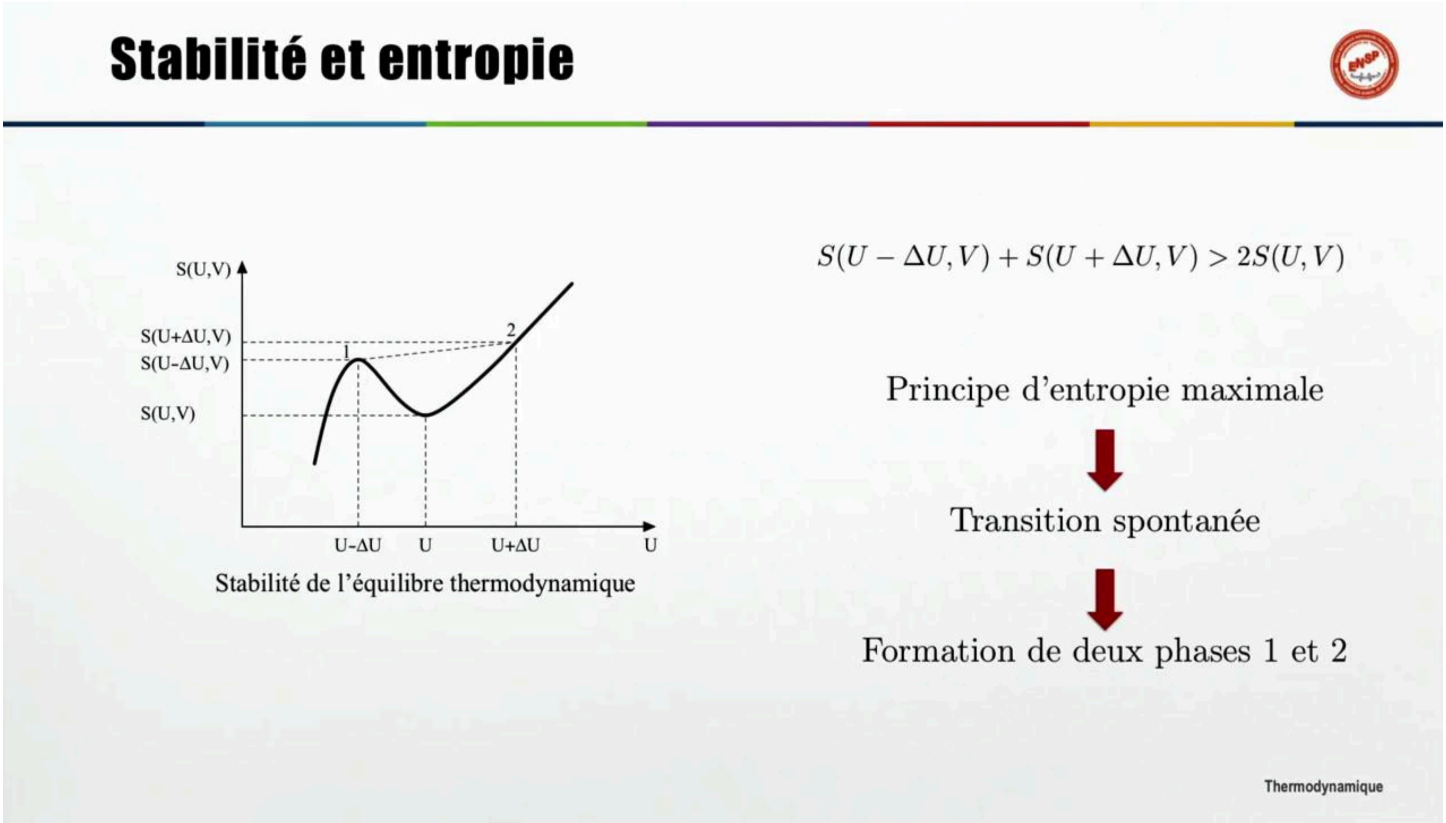
Thermodynamique

the Energy of the part becomes U, delta U and that of the part two U plus. Delta U. The final entropy here is U Delta U plus S de plus Delta U, which leads to the entropy variation. If after.

Notes

Summary

2m 40s

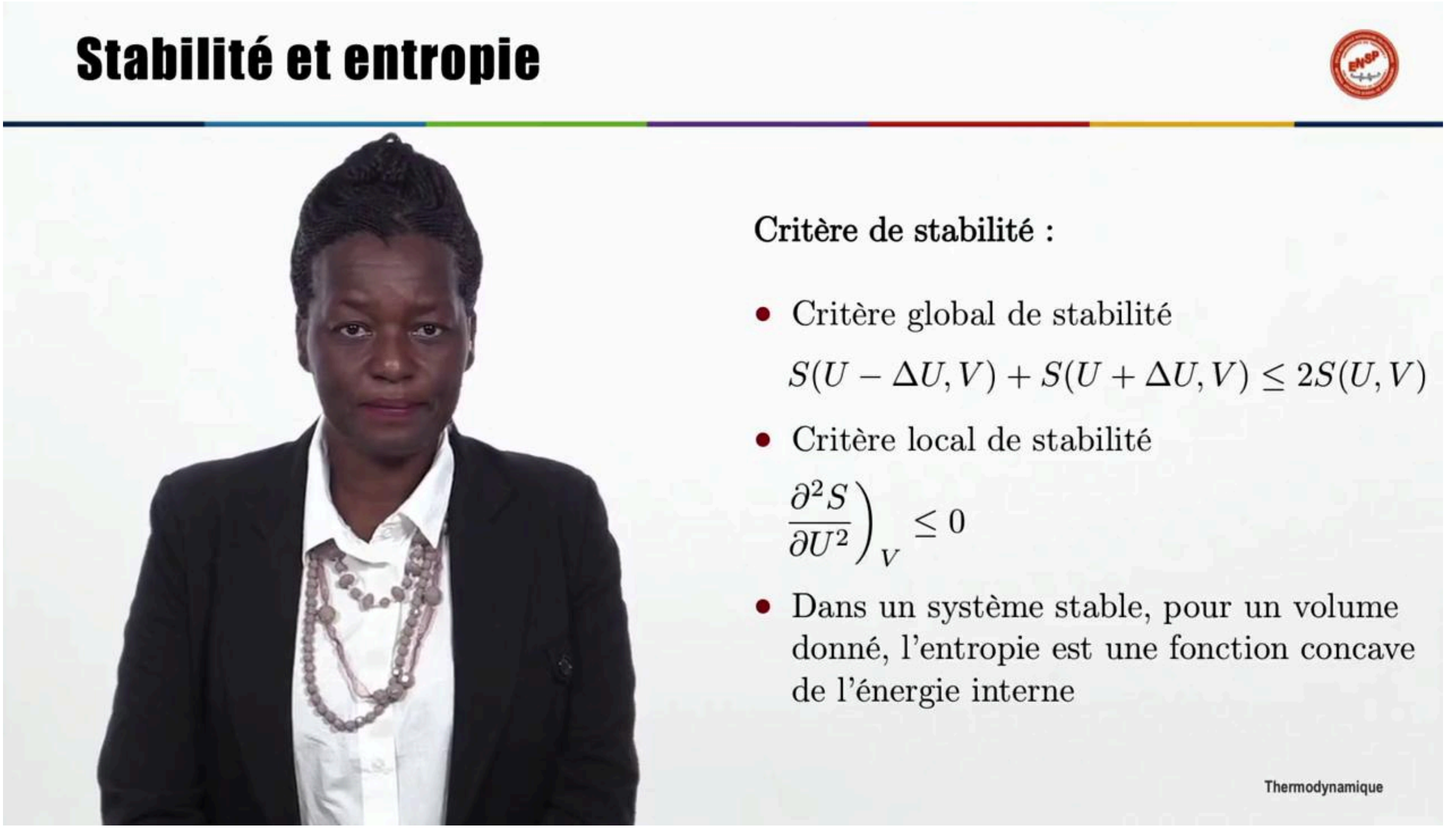


If the entropy profile is convex, as indicated above, the final entropy is higher than the initial one. The principle of maximum entropy implies that the transition considered will be spontaneous and that it will form two phases one and two.

Notes

Summary

3m 02s



System stability is that the profile of the pi tax is concave, namely that the final copy is less than the tax pi. Initial. Moving on to the differences infinitesimal, we obtain the local stability criterion. Squares of s on squares and smaller than zero in a stable system. Entropy is a function concave internal energy for a fixed internal energy.

Notes

Summary

3m 29s

Stabilité et entropie

- Pour une énergie interne fixée:
  - Critère global de stabilité $S(U, V - \Delta V) + S(U, V + \Delta V) \leq 2S(U, V)$
  - Critère local de stabilité $\left.\frac{\partial^2 S}{\partial V^2}\right)_U \leq 0$
- Dans un système stable, pour une énergie interne donnée, l'entropie est une fonction concave du volume

Thermodynamique

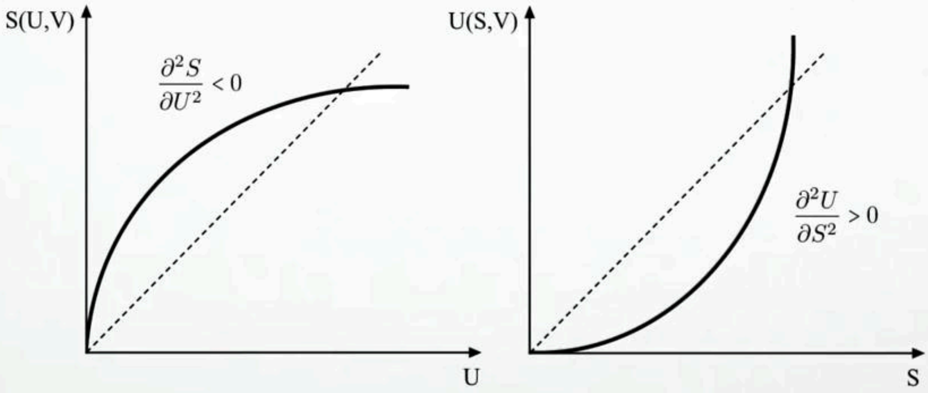
In a similar way, we show that the entropy in a stable system is a concave function of the volume.

Notes

Summary

4m 12s

Stabilité et énergie interne



Symétrie de S et U par rapport à l'axe $\frac{\partial S}{\partial U} = 1$

- Dans un système stable l'énergie interne est une fonction convexe de l'entropie

Thermodynamique

Let's take a look at the following the stability criterion with respect to the internal energy at constant volume. Internal energy and entropy are reciprocal functions. Therefore, their curves are symmetrical about the first bisector. We have established that S is a concave function of U. In a stable system, we deduce from the symmetry of the reciprocal functions with respect to at the first bisector that u is a convex function of the entropy S. In conclusion. In a stable system, the internal energy is a convex function of the entropy.

Notes

Summary

4m 22s

Stabilité et énergie interne

- **Stabilité locale:** $\left.\frac{\partial^2 U}{\partial S^2}\right)_V \geq 0$
- **Stabilité globale:** $U(S-\Delta S, V) + U(S+\Delta S, V) \geq 2U(S,U)$

Thermodynamique

When the volume is fixed, the stability criterion that follows of the convexity of the internal energy is that the second derivative of u with respect to s at constant volume and greater than or equal to zero. The overall stability criterion is u s delta s plus u de delta s is greater than desus of s u.

Notes

Summary

5m 17s

Stabilité et énergie interne

$$dS = \frac{dU}{T} + \frac{P\,dV}{T}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -T\left(\frac{\partial S}{\partial V}\right)_U \longrightarrow \frac{\partial^2 U}{\partial V^2} \geq 0$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = -T\left(\frac{\partial^2 S}{\partial V^2}\right)_U$$

$$\left(\frac{\partial^2 S}{\partial V^2}\right)_U \leq 0$$

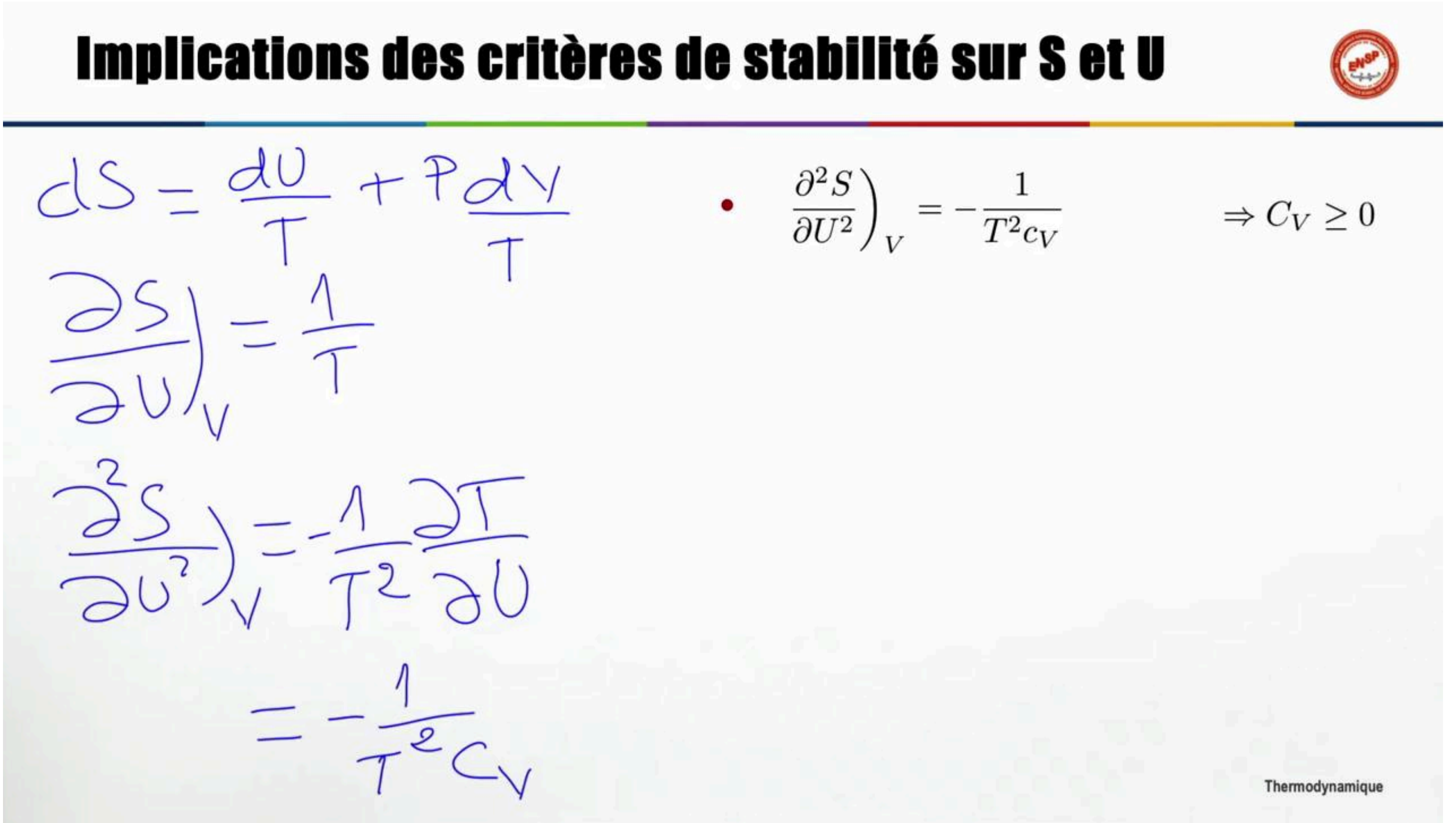
Thermodynamique

Now showing that the internal energy and a convex function of the volume in a stable system. Starting from the fundamental equation. DS. Equal to. Supporters. More. P. dV. Safety. From this relationship, we deduce that. U on DVD to a constant spinner is equal. A. Not as bad. And that. DS on estimate with constant internal energy. Is equal to a safety p. Let that be. D on DVD. At constant entropy is equal to less. T. DS on DVD. With constant internal energy. By passing to the second derivative of this expression. We get. From South Korea's Victory with constant entropy. Equal to. Mounting welded hedge squares becomes constant internal energy square. The second term on the right in DS on DVD cancels out because the entropy is maximal at equilibrium. So they come here. Since squares of welded S of V square with constant internal energy is less than or equal to zero. In a stable system. It is therefore established that the southern squares of the old square. And greater than or equal to zero. In an SAB system, the internal energy is a convex function of the volume.

Notes

Summary

5m 51s



We will now. Write the implications of the criteria of stability on entropy and internal energy. First, we will establish that squares of is sud uk at constant volume is equal to -1 on squares multiplied by cv. This will allow. Assume that the constant cv is greater than or equal to zero. To do this, we start with the basic equation. DS. Is equal to a start drop more p. To deviate, to fall. From this relationship, we deduce ds on start a constant volume is equal to one in ten, either by passing to the second derivative. Squares of s on two squares had. Equal to -1 on offset. Started on eggshells. Equal at last to less insulting Carey. These lives. We use here the fact that. D of DDT is equal to. Sevit. Since we have shown that the second derivative of S with respect to UK at constant volume is less than or equal to zero. We deduce that cv is greater than or equal to zero.

Notes

Summary

8m 32s

Implications des critères de stabilité sur S et U

- $\left.\frac{\partial^2 S}{\partial U^2}\right)_V = -\frac{1}{T^2 c_V} \quad \Rightarrow C_V \geq 0$
- Principe de Chatelier-Braun: $C_P \geq C_V$

$\Rightarrow C_P \geq 0$

- $\left.\frac{\partial^2 U}{\partial S^2}\right)_V = \frac{\partial T}{\partial S} \geq 0$

$$\left.\frac{\partial U}{\partial S}\right)_V = T$$

$$\left.\frac{\partial^2 U}{\partial S^2}\right)_V = \left.\frac{\partial T}{\partial S}\right)_V$$

$$\Rightarrow \left.\frac{\partial T}{\partial S}\right)_V \geq 0$$

Thermodynamique

The second implication follows from Chatelier's principle which says that the specific heat at constant pressure is greater than or equal to the specific heat at constant volume. This implies that CP is greater than or equal to zero. The third implication. Shows that temperature and entropy evolve in the same direction. Indeed, we have shown that. U on DS. A constant volume is equal to, a ? T. If we turn to the second derivative of the squares of U on D of squares, a constant volume is equal to DDP on d of S. A constant volume. Given that the internal energy in a stable system. And a convex function of entropy. It will have been shown that southern deputies of the S. At constant volume and greater than or equal to zero.

Notes

Summary

10m 34s

Implications des critères de stabilité sur S et U

- $\left.\frac{\partial^2 S}{\partial U^2}\right)_V = -\frac{1}{T^2 c_V} \quad \Rightarrow C_V \geq 0$
- Principe de Chatelier-Braun: $C_P \geq C_V$

$\Rightarrow C_P \geq 0$

- $\left.\frac{\partial^2 U}{\partial S^2}\right)_V = \frac{\partial T}{\partial S} \geq 0$
- $\left.\frac{\partial^2 U}{\partial V^2}\right)_S = -\left.\frac{\partial P}{\partial V}\right)_S = \frac{1}{V K_S} \Rightarrow K_S \geq 0$

$$K_T = -\left.\frac{1}{V}\frac{\partial V}{\partial P}\right)_T \geq 0$$

Thermodynamique

The fourth implication of U cadets on square lifts in constant top is equal to less of the two pc's of constant spinning life comes from the relation d of U welded to V. At a constant rate p. Switching to the second derivative, we have Judean squares. Drink Paris is constant, equal to minus d of p over d of V. At a constant rate. This expression is. Greater than or equal to zero because the internal energy is a convex function of the volume. In a stable system, we therefore deduce that less d of p welded to V a rate p constant which is equal to one on V on k s is greater than or equal to zero. Then we have the coefficient of compressibility at constant entropy, noted KS. Is written -1 V. Quotations on a constant spinning top. From the above, we arrive at. Quant s. Greater than or equal to zero. Similarly, we show that the coefficient of compressibility iso tm kt is greater than or equal to zero. In a stable system.

Notes

Summary

12m 00s

Stabilité et potentiels thermodynamiques

- T, V constants ⇒ Energie libre F
- S, P constants ⇒ Enthalpie
- T, P constants ⇒ Enthalpie libre

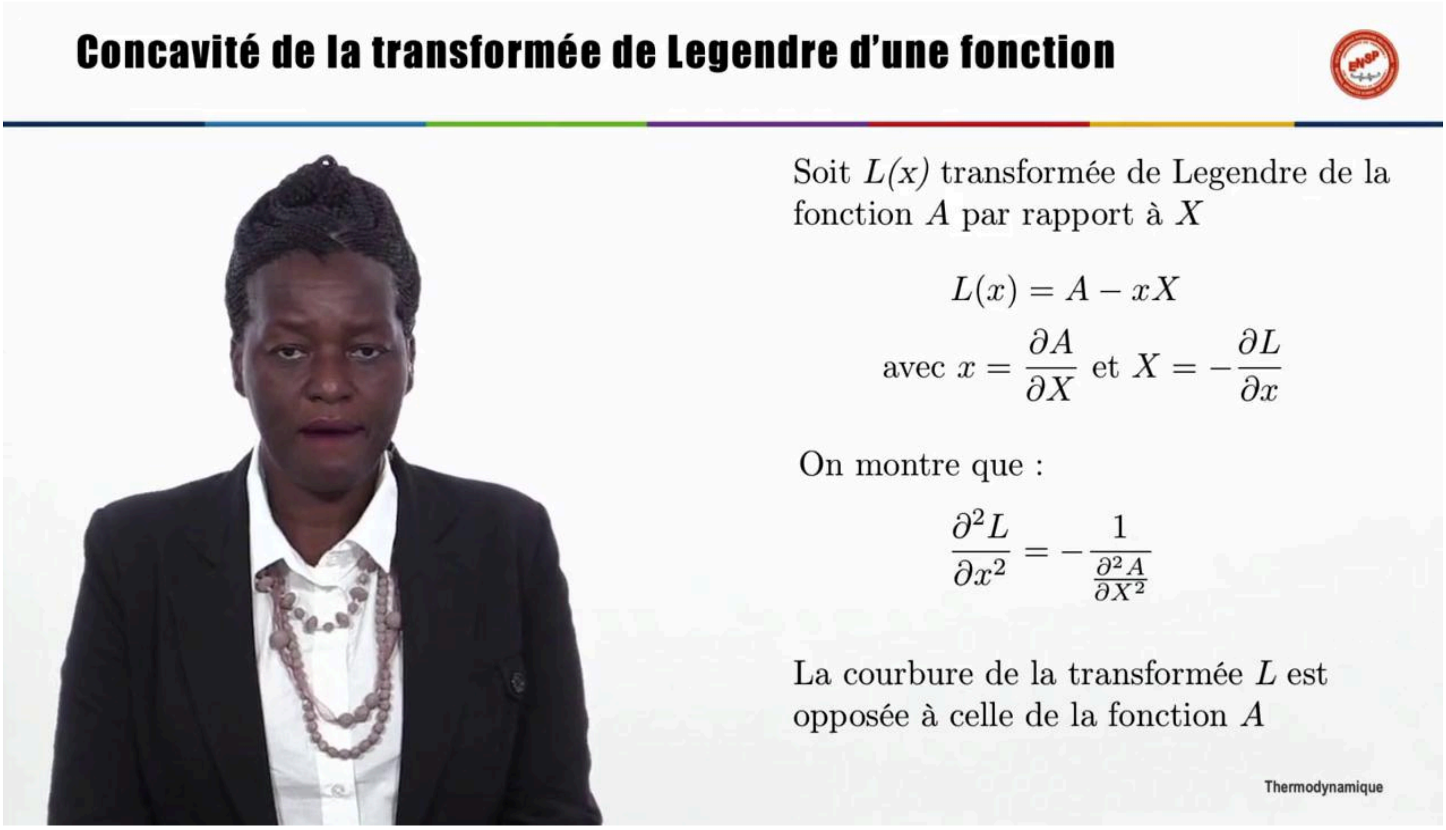
Thermodynamique

We move on to the third and final part of this module on stability criteria. We will write criteria based on thermodynamic potentials. The thermodynamic potential functions have been constructed to adapt to the evolution of systems at constant temperature and volume. The adapted thermodynamic function is the free energy, noted F. At constant entropy and pressure. The thermodynamic function indicated is the enthalpy. At constant temperature and pressure, the thermodynamic function indicated is the free enthalpy. The functions in thermodynamic potential are transforms of legends.

Notes

Summary

13m 53s



Let them be of small X. The legend transform of the function A with respect to large scale of small X is equal to minus small x times large X with small x equal to derivative of A with respect to large X and large x equal to minus d of l over d of small X. We show that the second derivative of l with respect to small x is equal to one on the second derivative of the function a with respect to x. The curvature of the transform is opposite to that of the function at.

Notes

Summary

14m 51s

Stabilité et potentiels thermodynamiques F, H, G

- $F(S) = U - S \left.\frac{\partial U}{\partial S}\right)_V = U - TS \qquad \Rightarrow \frac{\partial^2 F}{\partial T^2} = -\frac{1}{\frac{\partial^2 U}{\partial S^2}} \leq 0$
- $H(V) = U - V \left.\frac{\partial U}{\partial V}\right)_S = U + PV \qquad \Rightarrow \frac{\partial^2 H}{\partial P^2} = -\frac{1}{\frac{\partial^2 U}{\partial V^2}} \leq 0$
- $G(S) = H - S \left.\frac{\partial H}{\partial S}\right)_P = H - TS \qquad \Rightarrow \frac{\partial^2 G}{\partial T^2} = -\frac{1}{\frac{\partial^2 H}{\partial S^2}} = -\frac{1}{\frac{\partial T}{\partial S}} \leq 0$

F,H,G, fonctions concaves des variables intensives

Thermodynamique

From the above, we write that the free energy is the transformation of the internal energy with respect to the entropy. We write f equal to u ts. From the above, we deduce that the free energy function is a concave function of the temperature. The enthalpy function H is the legend transform of the internal energy with respect to the volume. We write H equal to u plus PV and we deduce that the enthalpy is a concave function of the pressure. The free enthalpy function G is transformed from enthalpy to entropy function. We write G and h minus ts and we deduce that the enthalpy function in a stable system is a concave function of the temperature. We find that the functions f, g and h are concave functions, intensive variables.

Notes

Summary

15m 45s

Implications des critères de stabilité sur les potentiels

- $$\frac{\partial^2 F}{\partial T^2} = -\frac{\partial S}{\partial T} = -\frac{c_V}{T} \rightarrow C_V \geq 0$$
- $$\frac{\partial^2 H}{\partial P^2} = \frac{\partial V}{\partial P} = -K_S V \rightarrow K_S \geq 0$$
- $$\frac{\partial^2 G}{\partial T^2} = -\frac{\partial S}{\partial T} = -\frac{c_P}{T} \rightarrow C_P \geq 0$$
- $$\frac{\partial^2 F}{\partial V^2} = -\frac{\partial P}{\partial V} = \frac{1}{K_T V} \geq 0$$
- $$\frac{\partial^2 H}{\partial S^2} = \frac{\partial T}{\partial S} = \frac{T}{c_P} \rightarrow C_P \geq 0$$

Les fonctions F,H sont des fonctions convexes de leurs variables extensives

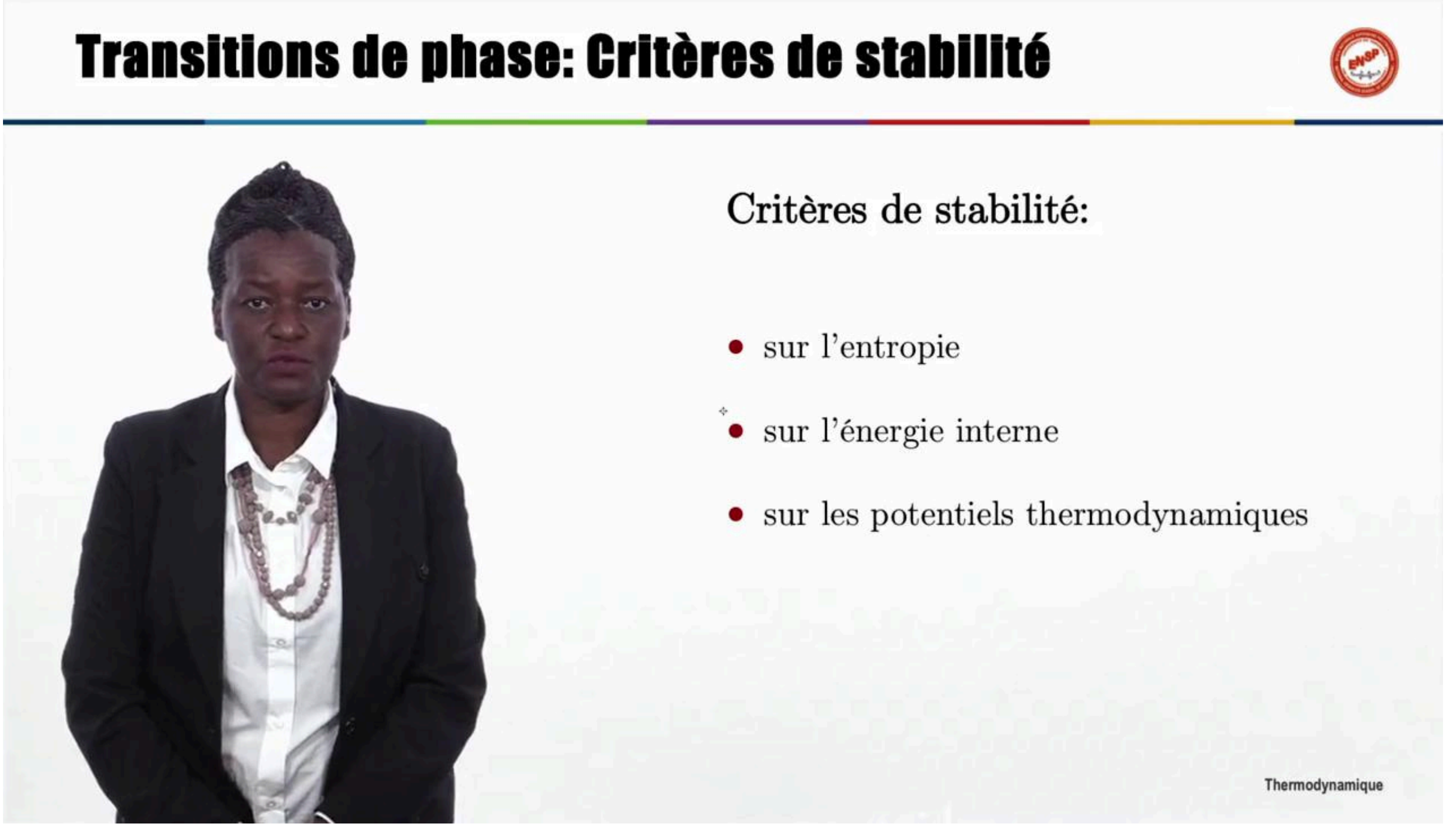
Thermodynamique

Let's move on to the implications stability criteria on the thermodynamic potential of the expression. DF is equal to minus pdv minus s dt. We establish that the second derivative of f with respect to t is equal to less derivative of s with respect to t equal to cv on p. We find the implication cv greater than or equal to zero. The second implication is obtained from the expression DH equal to TDS plus v dp. We arrive at the property obtained previously, namely that the coefficient of compressibility at constant entropy is greater than or equal to zero. The third property is obtained starting from a DG expression equal to v dp s dt. It leads to the property that CP is greater than or equal to zero. The fourth property is obtained from the expression DF equal to minus PDV minus s of. It leads to the fact that the coefficient of compressibility iso tm is greater than or equal to zero. The fifth and final implication establishes here. Comes from the expression. DH equals TDS plus life since. It leads to the results that CP is greater than or equal to zero. It can be seen that the energy functions, free and enthalpy are convex functions of their extensive variables.

Notes

Summary

17m 13s



We have throughout this presentation, writes the stability criteria for a rate. In relation to the entropy function. In relation to the internal energy function and finally with respect to the thermodynamic potential functions. In the next session, we will study phase two transitions. Other. Thank you for your attention.

Notes

Summary

19m 26s