ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

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

Thermodynamique

Relations de Maxwell

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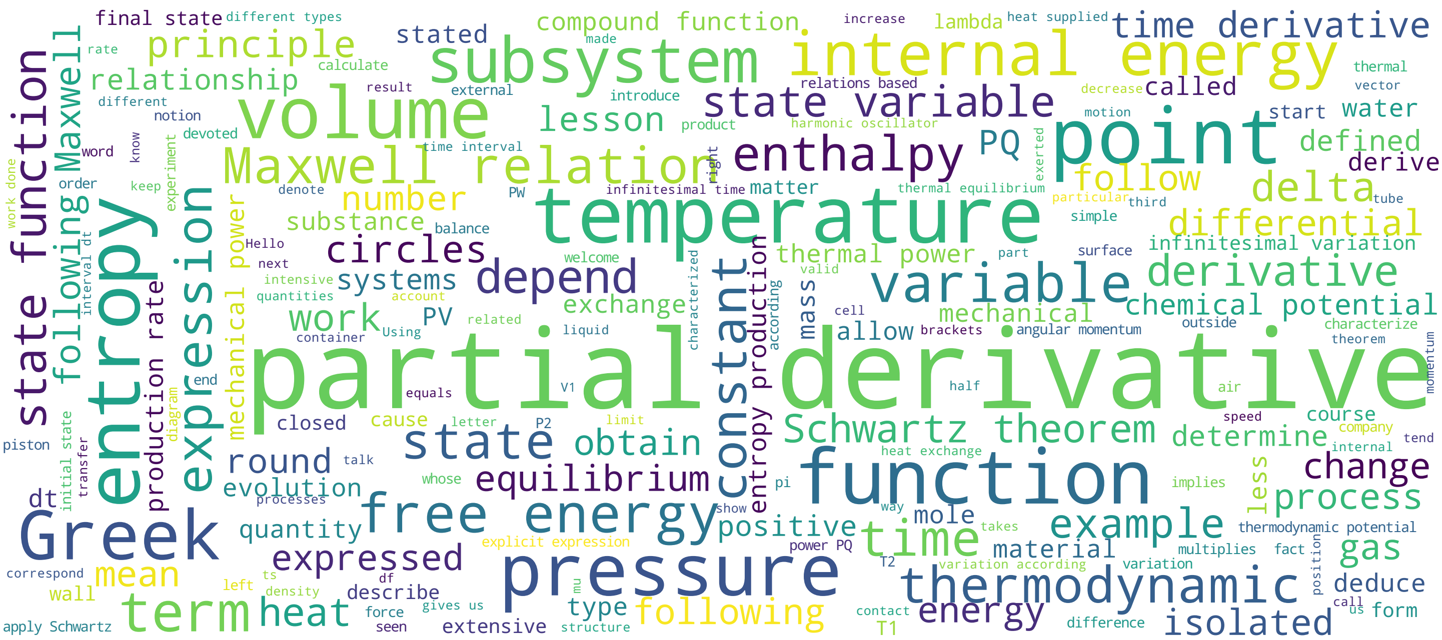
Hermann Ludwig Ferdinand von Helmoltz, 1821 - 1894



Video

EPFL

Hello and welcome to this mode of thermodynamics. This lesson is devoted to Maxwell's relations. First, we will state Schwartz's theorem. And then we will use it to deduce the structure of Maxwell's relations. We will then obtain different types of Maxwell's relations based first on the internal energy. Secondly, on free energy. Thirdly, on the enthalpy and fourth on the free energy of gypsum. And finally, we will define the partial derivatives of a compound function.

Notes

Summary

0m 05s

Relation de Maxwell : énergie interne

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- **Energie interne :**

  $U(S, V)$

- **Dérivées partielles de l'énergie interne :**

$$T(S,V) \equiv \frac{\partial U(S,V)}{\partial S} \qquad \text{et} \qquad p(S,V) \equiv -\frac{\partial U(S,V)}{\partial V}$$

- **Théorème de Schwarz :**

$$\frac{\partial}{\partial S}\left(\frac{\partial U(S,V)}{\partial V}\right) = \frac{\partial}{\partial V}\left(\frac{\partial U(S,V)}{\partial S}\right)$$

- **Relation de Maxwell :**

$$\boxed{-\frac{\partial p(S,V)}{\partial S} = \frac{\partial T(S,V)}{\partial V}}$$

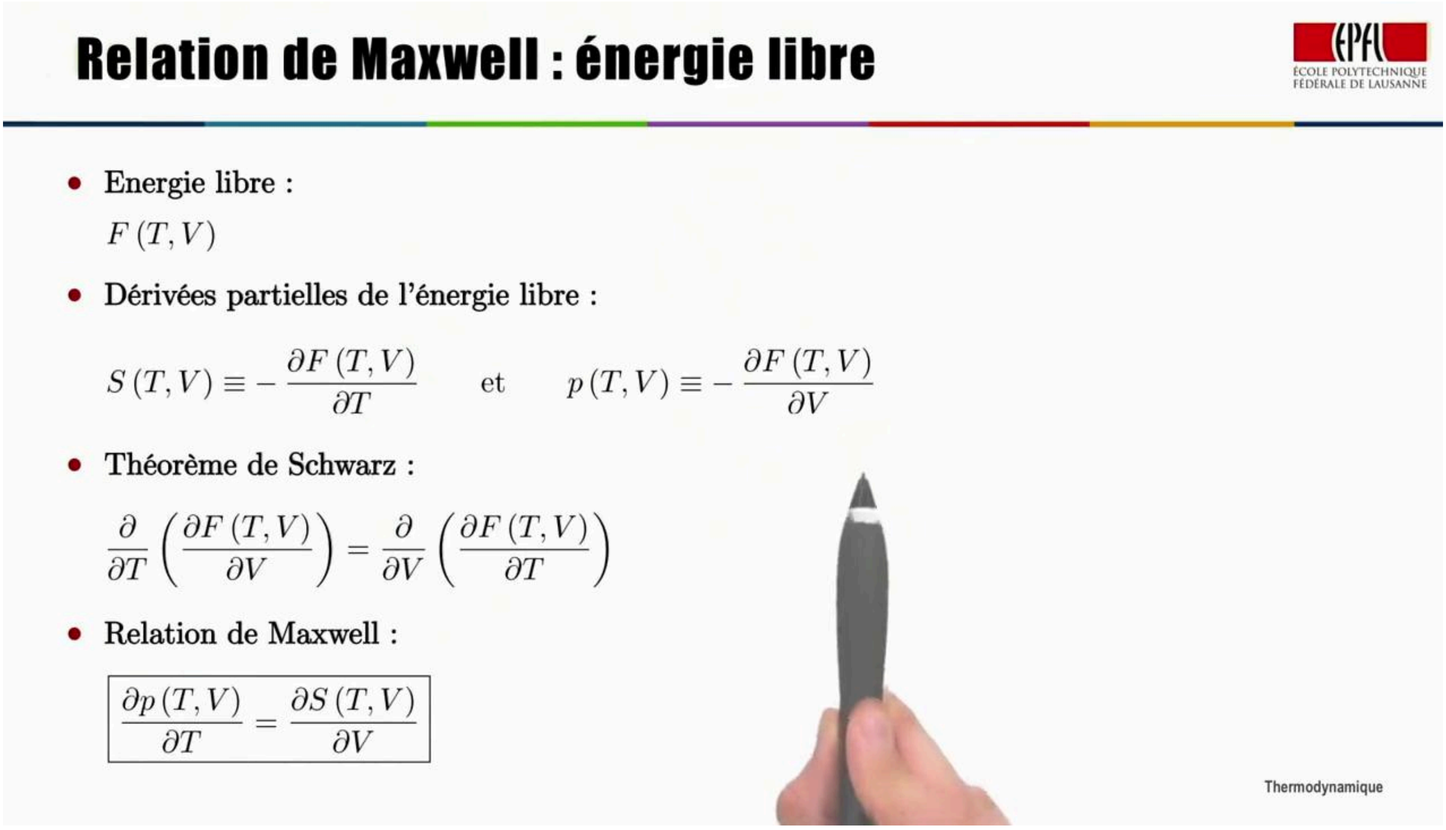
Thermodynamique

Charles' theorem is a theorem for functions in several variables. We will consider here a function of two variables. It is the function f that depends on the variables x and y. We will define the functions G which depends on of x and y Greek which is the partial derivative of f with respect to x and the function h which depends on x and y Greek which is the partial derivative of f with respect to Greek i. Schwartz's theorem essentially says that the order of the partial derivatives of a function does not change the result. In other words, the partial derivative with respect to x of the partial derivative of f with respect to at i Greek is equal to the partial derivative with respect to i Greek of the partial derivative of f with respect to x. Given the definitions of the functions G from X to y Greeks and h from X to y Greeks, we derive the following Maxwell relation. The partial derivative of h of x and y with respect to x is equal to the derivative partial of g from x to y Greek with respect to i Greek. We will now determine the Maxwell relations. Based on the different thermodynamic potentials. First, we will consider the internal energy. the internal energy U is a function of the entropy S and the volume V.

Notes

Summary

0m 41s



Temperature T and pressure P are state functions. They are related to the partial derivatives of the internal energy. T is equal to the partial derivative of u with respect to s and p is equal to minus the partial derivative of u with respect to V. We can now apply explicitly Schwartz's theorem to the internal energy. It takes the following form. The partial derivative with respect to s of the partial derivative of u with respect to V is equal to the partial derivative with respect to V of the partial derivative of u with respect to f. Given the expression of temperature and pressure, we obtain the following Maxwell relation. Less the partial derivative of the pressure P with respect to the entropy S is equal to the partial derivative of the temperature T with respect to the volume V. We can now deduce Maxwell's relation for the free energy. The free energy F is a function of the temperature T and the volume V. The entropy S and the pressure P. These are state functions that are expressed in terms of the derivatives of the free energy S is equal to minus. The partial derivative of f with respect to t and p is equal to minus the partial derivative of f with respect to v.

Notes

Summary

2m 19s

Relation de Maxwell : enthalpie

- **Enthalpie :**

  $H(S,p)$

- **Dérivées partielles de l'enthalpie :**

$$T(S,p) \equiv \frac{\partial H(S,p)}{\partial S} \qquad \text{et} \qquad V(S,p) \equiv \frac{\partial H(S,p)}{\partial p}$$

- **Théorème de Schwarz :**

$$\frac{\partial}{\partial S}\left(\frac{\partial H(S,p)}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial H(S,p)}{\partial S}\right)$$

- **Relation de Maxwell :**

$$\boxed{\frac{\partial V(S,p)}{\partial S} = \frac{\partial T(S,p)}{\partial p}}$$

Thermodynamique

We can now explicitly apply Schwartz's theorem to free energy. It is stated as follows. The partial derivative with respect to t of the partial derivative of f with respect to V is equal to the partial derivative with respect to V of the partial derivative of f with respect to t. Given the expressions for entropy and pressure. From Schwartz's theorem we derive the following Maxwell relation. The partial derivative of the pressure P with respect to the temperature T is equal to the partial derivative of the entropy S with respect to the volume V. We can do the same exercise for the enthalpy H and deduce the corresponding Maxwell relation. The enthalpy H is a function of the entropy S and the pressure P. Temperature and volume are state functions which are expressed in terms of partial derivatives of the enthalpy. T. It is the partial derivative of the enthalpy H with respect to the entropy as and V. It is the partial derivative of the enthalpy H with respect to the pressure p. We can apply Schwartz's theorem to the enthalpy H. Is stated as follows. The partial derivative with respect to to the entropy S of the partial derivatives of the enthalpy H with respect to the pressure p is equal to the partial derivative with respect to the pressure p.

Notes

Summary

3m 46s

Relation de Maxwell : énergie libre de Gibbs

- Energie libre de Gibbs :

  $G(T,p)$

- Dérivées partielles de l'énergie libre de Gibbs :

$$S(T,p) \equiv -\frac{\partial G(T,p)}{\partial T} \qquad \text{et} \qquad V(T,p) \equiv \frac{\partial G(T,p)}{\partial p}$$

- Théorème de Schwarz :

$$\frac{\partial}{\partial T}\left(\frac{\partial G(T,p)}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial G(T,p)}{\partial T}\right)$$

- Relation de Maxwell :

$$\boxed{\frac{\partial V(T,p)}{\partial T} = -\frac{\partial S(T,p)}{\partial p}}$$

Thermodynamique

Of the partial derivative of the enthalpy H with respect to the company. This, given the expression of temperature and volume, gives us the following Maxwell relation. The partial derivative of the volume V with respect to the entropy S is equal to the partial derivative of the temperature T in relation to the pressure P. A Maxwell relation can also be deduced from the free energy of the IPS. the Free Energy of G is a function of the temperature T and the pressure P. The entropy S and the volume V are state functions that are expressed as derivatives of the free energy of Kip S is equal to minus. The partial derivative of g with respect to t and v is equal to the partial derivative of g with respect to p. We can now apply the theorem of Schwartz to the type free energy is stated as follows. The partial derivative with respect to t of the partial derivative of g with respect to p is equal to the partial derivative with respect to p of the partial derivative of g with respect to t. Given the expression of the company. And the volume V. From Schwartz's theorem we derive the following Maxwell relation. The partial derivative of the volume V with respect to the temperature T is equal to minus the partial derivative of the entropy S with respect to the pressure P.

Notes

Summary

5m 22s

Dérivées partielles d'une fonction composée

- **Fonction composée :**

$$f\left(x\left(y,z\right),y\right)$$

- **Différentielle d'une fonction composée :**

$$df\left(x\left(y,z\right),y\right)=\left(\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial y}+\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial y}\right)dy+\left(\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial z}\right)dz$$

- **Dérivées partielles :**

$$\left.\frac{\partial f}{\partial y}\right|_z\equiv\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial y}+\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial y}$$

$$\left.\frac{\partial f}{\partial z}\right|_y\equiv\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial z}$$

Thermodynamique

Finally, we will determine the partial derivatives of a compound function. We have a function f which depends on the Greek variables x and y. And the variable X is itself a state function which depends on the variables y and z. We would like to obtain expressions for the partial derivatives of f with respect to i. When we keep z constant and with respect to z when i is kept constant. We will start by calculating the differential of this compound function. This is df of x which is a function of x z and which is also a function of i Greek. This differential will be expressed in terms of infinitesimal variation according to Greek i and the infinitesimal variation according to z. Firstly. We have the partial derivatives of f with respect to X and then we have to take another partial derivative which is to the partial derivatives of x with respect to y Greek and independently. We have the partial derivative of f with respect to Greek i. All this times of the Greeks. Then the second term is the partial derivative of f with respect to x for the partial derivative of x with respect to z. However, dz. We can now derive explicit expressions for the partial derivatives.

Notes

Summary

7m 13s

Dérivées partielles d'une fonction composée

- **Fonction composée :**

$$f\left(x\left(y,z\right),y\right)$$

- **Différentielle d'une fonction composée :**

$$df\left(x\left(y,z\right),y\right) = \left(\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial y} + \frac{\partial f\left(x\left(y,z\right),y\right)}{\partial y}\right)dy + \left(\frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial z}\right)dz$$

- **Dérivées partielles :**

$$\left.\frac{\partial f}{\partial y}\right|_z \equiv \frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial y} + \frac{\partial f\left(x\left(y,z\right),y\right)}{\partial y}$$

$$\left.\frac{\partial f}{\partial z}\right|_y \equiv \frac{\partial f\left(x\left(y,z\right),y\right)}{\partial x\left(y,z\right)}\frac{\partial x\left(y,z\right)}{\partial z}$$

Thermodynamique

The partial derivative of f with respect to i when z is constant is given by the two terms in brackets here. It's from aircraft. X times on circles X circles on i circles plus f circles on Greek i circles. And then the second partial derivative, its partial derivative of f with respect to z when y is held constant. This is the partial derivative of f with respect to x, i.e. round f on round x times, round X on round. It is. The expression of these partial derivatives of a compound function are extremely useful when one is interested in, for example to a thermodynamic potential and that we want to make it depend on of variables that are not these natural state variables. Let's take an example. For example the internal energy which would depend on the entropy and the volume. Now we would like to describe in terms of temperature and volume. In this case, the entropy S is a function of the temperature of the volume. And so, if we want to obtain the partial derivative of U with respect to T. When V is constant, we will have to use one of its partial derivatives. And if we want to calculate the partial derivative of u with respect to to b, when t is constant, we will have to use other partial derivatives. I thank you very much for your attention and say goodbye.

Notes

Summary

8m 52s