

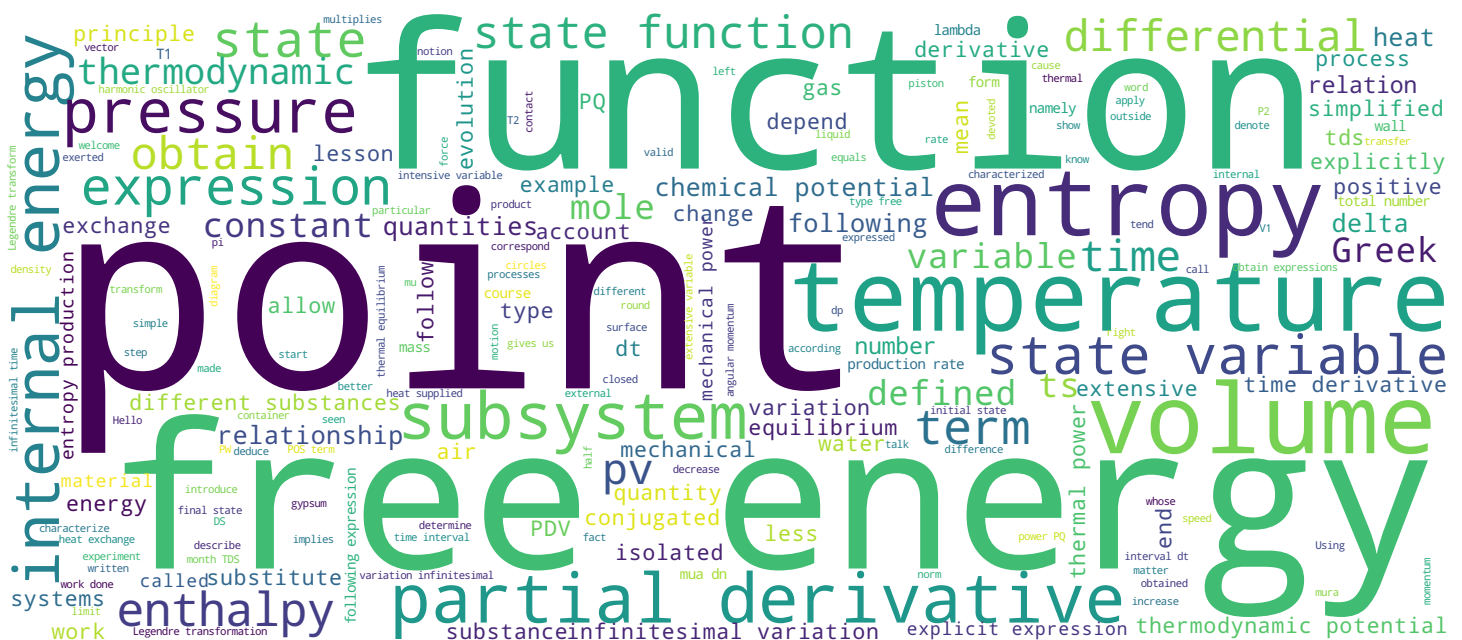
Thermodynamique

Potentiels thermodynamiques

Dr. Sylvain Bréchet



Hermann Ludwig Ferdinand von Helmholtz, 1821 - 1894





- Définition
- Energie libre
- Enthalpie
- Energie libre de Gibbs

Thermodynamique

Hello and welcome to this thermodynamic moment. This lesson is devoted to thermodynamic potential. First, we will define what is a thermodynamic potential. We will then consider the three most important thermodynamic potentials. These thermodynamic potentials are free energy, enthalpy and type free energy.

Notes

Summary



0m 05s



- Potentiel thermodynamique :

On appelle potentiel thermodynamique toute fonction extensive obtenue par transformation de Legendre de l'énergie interne.

- Exemples :

- Energie interne : $U(S, V, \{N_A\})$
- Energie libre : $F(T, V, \{N_A\})$
- Enthalpie : $H(S, p, \{N_A\})$
- Energie libre de Gibbs : $G(T, p, \{N_A\})$

Thermodynamique

We call thermodynamic potential any extensive function which is obtained by Legendre transformation of the internal energy. By performing two Legendre transformations on the internal energy, first in relation to one of these extensive variables, and then in relation to the conjugate intensive variable, we obtain again the internal energy. So the first example of a thermodynamic potential, is the internal energy u which is a function of the entropy S , the volume V and the total number of moles of the different substances in the system. The second example is free energy F which is a function of the temperature T , the volume V and the set of the numbers of moles of the different substances of the system. The third example is the enthalpy h which is a function of the entropy S , the pressure P and the total number of moles of the different substances in the system. Last example, it is the free energy of gypsum G which is function of the temperature T , the pressure P and the set of the number of moles of the different substances in the system.

Notes

Summary



0m 29s

- Variables d'état : $T, V, \{N_A\}$
- Energie libre F (transformée de Legendre de U par rapport à S) :

$$F \equiv U - TS$$

$$F(T, V, \{N_A\}) = U(S(T, V, \{N_A\}), V, \{N_A\}) - TS(T, V, \{N_A\})$$

- Relation d'Euler :

$$U = TS - pV + \sum_{A=1}^r \mu_A N_A$$

- Energie libre :

$$F = -pV + \sum_{A=1}^r \mu_A N_A$$

Thermodynamique

the Free Energy is a function of the following state variables. The temperature T . The volume V is the total number of moles of the different substances in the system. the Free Energy F is defined as the transform of the internal energy of U with respect to the entropy S . By definition, f is equal to u minus ts of free energy f and entropy S are state functions. They are therefore functions of the state variables of the system, namely T, V and the set DN . We will now explicitly take into account the relationship of air which is the following one equals DS minus PV , plus the sum of the moray R . And we will substitute this relationship of the air in the expression of the free energy. F The term in DS is simplified with the term in TS and finally we obtain the following expression. For free energy. F is equal to minus pv plus the sum of a r from better to n .

Notes

Summary



1m 48s

Différentielle de l'énergie libre

- Variation infinitésimale de l'énergie libre :

$$dF = dU - T dS - S dT$$

- Relation de Gibbs :

$$dU = T dS - p dV + \sum_{A=1}^r \mu_A dN_A$$

- Différentielle de l'énergie libre :

$$dF = - S dT - p dV + \sum_{A=1}^r \mu_A dN_A$$

- Grandeurs conjuguées :

- Entropie :

$$S(T, V, \{N_A\}) = - \frac{\partial F(T, V, \{N_A\})}{\partial T}$$

- Pression :

$$p(T, V, \{N_A\}) = - \frac{\partial F(T, V, \{N_A\})}{\partial V}$$

- Potentiel chimique substance A :

$$\mu_A(T, V, \{N_A\}) = \frac{\partial F(T, V, \{N_A\})}{\partial N_A}$$

Thermodynamique

We would now like to obtain an explicit expression for the differential of the free energy. the free energy f is equal to u ts. In a first step, we will take the infinitesimal variation of this free energy which is the following $df = du - Tds - SdT$. And this is where we will explicitly take into account the D-type relationship. U is equal to TDS minus PDV plus the sum of A R of Miura DN . And this relationship is not working, we will substitute it in the expression of the variation of the free energy. And in the end, we obtain the expression of the differential of the free energy. DF is equal to minus SdT . Minus POS , plus the sum of A to R from Elena's memory. Using this expression of the differential of the free energy, we can obtain expressions explicit for the quantities that are conjugated to the state variables of the system. These quantities are state functions. They are therefore functions of T , V and the set of norms. The first quantity is the entropy s s is equal to minus the partial derivative of f with respect to d . The second quantity is the pressure p . P is equal to minus the partial derivative of f with respect to v . The third quantity is the chemical potential which is equal to the partial derivative of f with respect to n .

Notes

Summary



3m 02s

Différentielle de l'enthalpie

- Variation infinitésimale de l'enthalpie :

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

- Relation de Gibbs :

$$dU = T dS - p dV + \sum_{A=1}^r \mu_A dN_A$$

- Différentielle de l'enthalpie :

$$dH = T dS + V dp + \sum_{A=1}^r \mu_A dN_A$$

- Grandeurs conjuguées :

- Température :

$$T(S, p, \{N_A\}) = \frac{\partial H(S, p, \{N_A\})}{\partial S}$$

- Volume :

$$V(S, p, \{N_A\}) = \frac{\partial H(S, p, \{N_A\})}{\partial p}$$

- Potentiel chimique substance A :

$$\mu_A(S, p, \{N_A\}) = \frac{\partial H(S, p, \{N_A\})}{\partial N_A}$$

Thermodynamique

The enthalpy is a function of the state variables. Between pressure p and the set of mole numbers of the different chemicals in the system. The enthalpy H is defined as the Legendre transform of the internal energy U with respect to the volume V . Therefore, h is defined as u plus $p v$. The enthalpy H and the volume V are state functions. They are therefore functions of the state variables of the system. That is, s , p and the set of norms. We will now explicitly consider the relationship of the area UE is equal to TS PV plus the sum of a r of μ_A and not. And this relation, we will substitute it in the expression of the enthalpy H . And in the end, we get the following expression. H is equal to ts plus the sum of r of μ_A and not. We now want to obtain an explicit expression for the differential of the enthalpy, thus an infinitesimal variation of the enthalpy. The enthalpy h is equal to u plus $p v$ and thus the variation infinitesimal enthalpy dh is equal to u plus $p dv$ plus $v dp$. We have to take into account the exact relationship which is the following. Is equal to $T dS$ minus $P dV$ plus the sum of a r of $\mu_A dn$.

Notes

Summary



4m 50s

Energie libre de Gibbs

- Variables d'état : $T, p, \{N_A\}$

- Energie libre de Gibbs G (transformée de Legendre de U par rapport à S et à V) :

$$G \equiv U - TS + pV = F + pV = H - TS$$

$$G(T, p, \{N_A\}) = U\left(S(T, p, \{N_A\}), V(T, p, \{N_A\}), \{N_A\}\right) - TS(T, p, \{N_A\}) + pV(T, p, \{N_A\})$$

- Relation d'Euler :

$$U = TS - pV + \sum_{A=1}^r \mu_A N_A$$

- Energie libre de Gibbs :

$$G = \sum_{A=1}^r \mu_A N_A$$

Thermodynamique

This couple relationship is substituted in the expression of the infinitesimal variation of the enthalpy and finally, we obtain an expression for the differential of the enthalpy which is the following. dH is equal to Tds plus Vdp plus the sum of one to r of $\mu_A dn_A$ using this enthalpy differential. We can now deduce expressions for the quantities which are conjugated to the state variables of the system. These quantities are the temperature T , the volume V and the chemical potential of substance A . These quantities are functions of state, so they are functions of variables of state of the system, namely s, p and the set DN at temperature T is equal to the partial derivative of H with respect to s . The volume V is equal to the partial derivative of h with respect to p . The chemical potential of the substance one is equal to the partial derivative of h with respect to n . Gap Free Energy is a function of the state variables temperature T , pressure p and the set of the numbers of moles of the different substances of the system. the Group Free Energy CG is defined as the transform of Legendre of U with respect to the entropy S and the volume V . I have by definition this EU ts plus pv.

Notes

Summary



6m 33s

Différentielle de l'énergie libre de Gibbs

- Variation infinitésimale de l'énergie libre de Gibbs :

$$dG = dU - T dS - S dT + p dV + V dp$$

- Relation de Gibbs :

$$dU = T dS - p dV + \sum_{A=1}^r \mu_A dN_A$$

- Différentielle de l'énergie libre de Gibbs :

$$dG = - S dT + V dp + \sum_{A=1}^r \mu_A dN_A$$

- Grandeurs conjuguées :

- Entropie :

$$S(T, p, \{N_A\}) = - \frac{\partial G(T, p, \{N_A\})}{\partial T}$$

- Volume :

$$V(T, p, \{N_A\}) = \frac{\partial G(T, p, \{N_A\})}{\partial p}$$

- Potentiel chimique substance A :

$$\mu_A(T, p, \{N_A\}) = \frac{\partial G(T, p, \{N_A\})}{\partial N_A}$$

Thermodynamique

Given the definition of the free energy f and the enthalpy H . G is equal to f plus bv or h minus ts . C.G. Free Energy. The entropy S and the volume V are state functions. They are therefore functions state variables of the system, namely TP and the set of standards. The relationship of the R is now explicitly considered as follows u equals ts minus pv plus the sum of the R of Miura and na . We substitute this relation in the expression of the free energy. The term nts is simplified with the term ts . The nested term is simplified with the term in PV and finally the free energy of type is written g which is equal to the sum of the r of μ_A and not . We now want to obtain an expression explicit for the differential of the type free energy. So we'll do the variation infinitesimal of this free energy of gypsum. I had me ts more PV . So this infinitesimal variation gives us the following expression DG is equal to $start$ month. TDS minus dt plus. PDV plus $v dp$. It is at this point that we take into account explicitly from the relationship $beep u$ which is equal to tds PDV more than the sum of Burda's R , and we substitute it in the expression of the infinitesimal variation of the free energy of cups.

Notes

Summary



8m 07s

Différentielle de l'énergie libre de Gibbs

- Variation infinitésimale de l'énergie libre de Gibbs :

$$dG = dU - T dS - S dT + p dV + V dp$$

- Relation de Gibbs :

$$dU = T dS - p dV + \sum_{A=1}^r \mu_A dN_A$$

- Différentielle de l'énergie libre de Gibbs :

$$dG = - S dT + V dp + \sum_{A=1}^r \mu_A dN_A$$

- Grandeurs conjuguées :

- Entropie :

$$S(T, p, \{N_A\}) = - \frac{\partial G(T, p, \{N_A\})}{\partial T}$$

- Volume :

$$V(T, p, \{N_A\}) = \frac{\partial G(T, p, \{N_A\})}{\partial p}$$

- Potentiel chimique substance A :

$$\mu_A(T, p, \{N_A\}) = \frac{\partial G(T, p, \{N_A\})}{\partial N_A}$$

Thermodynamique

The term in tds is simplified with the term $month tds$. The minus POS term is simplified with the POS term and finally we obtain the differential of the free energy of the IPS. Which is the following. DG is equal to $me. SD, t+, v, d+$. The sum of a also a ? R ? De mua ? DN in. Using this expression of the differential of the DOCTYPE energy, we can obtain expressions for the quantities that are conjugated to state variables of the secondary system to state functions. This is the entropy S . The volume V and the chemical potential of the substance one are state functions, so they depend on state variables of the system, i.e. TCP and the set of nodes. And their expressions are as follows. S is equal to minus. The partial derivative of g with respect to $t v$ is equal to the partial derivative of g with respect to p , and finally $mura$ is equal to the partial derivative of g with respect to $Enna$.

Notes

Summary

