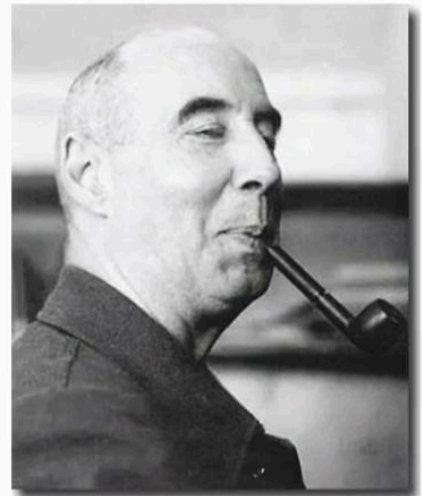


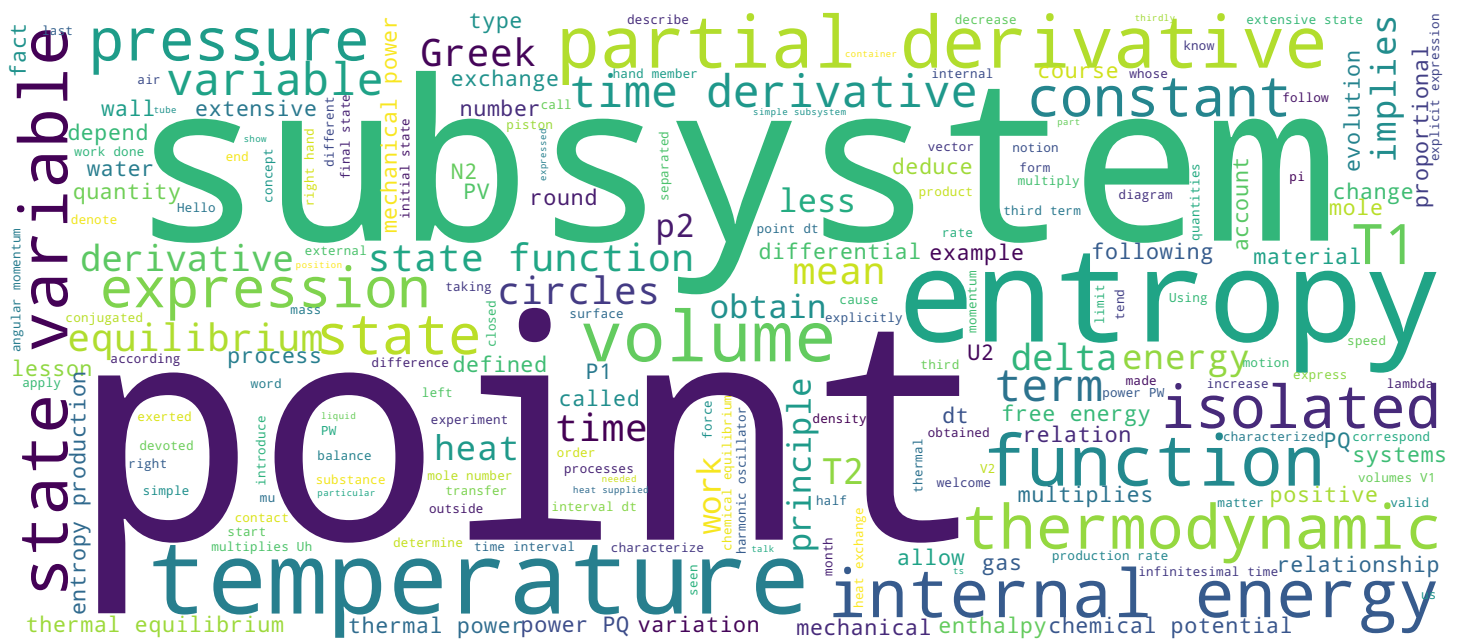
Thermodynamique

Equilibre

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Ernst Carl Gerlach Stükelberg, 1905 - 1984





- Deux sous-systèmes simples séparés par une paroi diatherme, mobile et perméable
- Equilibre
 - Thermique
 - Mécanique
 - Chimique

Thermodynamique

Hello and welcome to this word of thermodynamics. This lesson is devoted to the concept of equilibrium. To do this, we will consider. An isolated system which is made up of two sub-systems which are separated by a mobile and permeable term wall. We will deduce. The equilibrium condition. We will see that this condition of equilibrium requires. Firstly, the thermal balance. Secondly, the mechanical balance. And thirdly, the chemical balance.

Notes

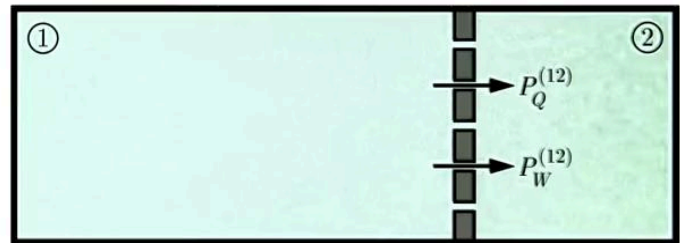
Summary



0m 05s

Paroi diatherme mobile et perméable

- Système isolé :
 $P_Q = P_W = 0$
- Sous-systèmes simples (1) et (2)
- Variables d'état extensives :
 - Entropies S_1 et S_2
 - Volumes V_1 et V_2
 - Nombre de moles N_1 et N_2



Thermodynamique

We therefore consider a system. Isolated consisting of two subsystems. Which are separated by a so-called mobile and permeable wall. The system is isolated, which means that the thermal power P_Q and the mechanical power P_W which are exerted by the outside on the system are zero. To describe the thermodynamics of this system, three types of state variables are needed extensive entropy, volume and mole number. Since there are two subsystems that are simple subsystems, two entropy variables S_1 and S_2 are needed, two variables volumes V_1 and V_2 and two variables number of moles N_1 and N_2 .

Notes

Summary



0m 41s

Dérivée temporelle de l'énergie interne

- Dérivée temporelle de l'énergie interne (sous-systèmes 1 et 2) :

$$\dot{U}_1(S_1, V_1, N_1) = T_1(S_1, V_1, N_1) \dot{S}_1 - p_1(S_1, V_1, N_1) \dot{V}_1 + \mu_1(S_1, V_1, N_1) \dot{N}_1$$

$$\dot{U}_2(S_2, V_2, N_2) = T_2(S_2, V_2, N_2) \dot{S}_2 - p_2(S_2, V_2, N_2) \dot{V}_2 + \mu_2(S_2, V_2, N_2) \dot{N}_2$$

- Energie interne (fonction d'état extensive) :

$$U(S_1, S_2, V_1, V_2, N_1, N_2) = U_1(S_1, V_1, N_1) + U_2(S_2, V_2, N_2)$$

- Dérivée temporelle de l'énergie interne (système isolé) :

$$\dot{U}(S_1, S_2, V_1, V_2, N_1, N_2) = \dot{U}_1(S_1, V_1, N_1) + \dot{U}_2(S_2, V_2, N_2) = 0$$

- Identité :

$$\dot{U}_1(S_1, V_1, N_1) = -\dot{U}_2(S_2, V_2, N_2)$$

Thermodynamique

We will now express the time derivative of the internal energy of each subsystem according to these state variables. One point. Which is a function of the state variables. From the first subsystem, i.e. S_1 and n_1 is equal to $T_1 S_1$ one point minus $p_1 V_1$ one point plus one. Two points. Which is a function of the state variables. From the second subsystem, namely. S_2 v_2 n_2 is equal to $D_2 s$ two points minus $p_2 V_2$ two points plus $U_2 n$ two points. the internal energy of the system is a state function. It is therefore a function of the set state variables of the system, namely S_1 , S_2 , V_1 and V_2 , N_1 and N_2 . It is an extensive state function, so it is the sum of internal energies of the two subsystems U of Gala U_1 plus U_2 . We can take. The time derivative of this expression of the point is equal to one point plus two points. The global system is isolated, which means that the internal energy of the system is a constant, so the point is equal to zero. Therefore, we have the following identity u one point is equal to less than two points.

Notes

Summary



1m 42s



- Entropie (variable d'état extensive) :
 $S = S_1 + S_2$
- Volume (variable d'état extensive) :
 $V = V_1 + V_2$
- Nombre de moles (variable d'état extensive) :
 $N = N_1 + N_2$
- Dérivée temporelles des variables d'état :
 $\dot{S} = \dot{S}_1 + \dot{S}_2 \quad \dot{V} = \dot{V}_1 + \dot{V}_2 \quad \dot{N} = \dot{N}_1 + \dot{N}_2$
- Système isolé :
 $\dot{N} = 0 \Rightarrow \dot{N}_1 = -\dot{N}_2$
 $\dot{V} = 0 \Rightarrow \dot{V}_1 = -\dot{V}_2$

Thermodynamique

We must now take into account explicitly of the scalability of state variables. Let's start with entropy. The entropy S of the system is the sum of the entropies S_1 and S_2 of the two subsystems. The volume V of the system is the sum of the volumes V_1 and V_2 of the two subsystems. The mole number n of the system is the sum of the mole number n_1 and N_2 . Both subsystems. We can now take the time derivative of the state variables. This point is equal to s one point plus s two points. V point is equal to V one point more. V_2 point one point is equal to n one points plus n two points. We must now take into account the fact that the system is isolated. This system is isolated. The number of moles of the system is a constant, so n is zero. This implies that n one point is equal to minus n two points. And the volume is constant, which means that V is zero. Therefore, V one point is equal to minus v two points.

Notes

Summary



3m 24s

Dérivée temporelle de l'entropie

- Dérivées temporelles de l'entropie (sous-systèmes 1 et 2) :

$$\dot{S}_1 = \frac{1}{T_1(S_1, V_1, N_1)} \left(\dot{U}_1(S_1, V_1, N_1) + p_1(S_1, V_1, N_1) \dot{V}_1 - \mu_1(S_1, V_1, N_1) \dot{N}_1 \right)$$

$$\dot{S}_2 = \frac{1}{T_2(S_2, V_2, N_2)} \left(\dot{U}_2(S_2, V_2, N_2) + p_2(S_2, V_2, N_2) \dot{V}_2 - \mu_2(S_2, V_2, N_2) \dot{N}_2 \right)$$

- Système isolé :

$$\dot{U}_2(S_2, V_2, N_2) = -\dot{U}_1(S_1, V_1, N_1) \quad \text{et} \quad \dot{V}_2 = -\dot{V}_1 \quad \text{et} \quad \dot{N}_2 = -\dot{N}_1$$

- Dérivée temporelle de l'entropie :

$$\begin{aligned} \dot{S} = & \left(\frac{1}{T_1(S_1, V_1, N_1)} - \frac{1}{T_2(S_2, V_2, N_2)} \right) \dot{U}_1(S_1, V_1, N_1) \\ & + \left(\frac{p_1(S_1, V_1, N_1)}{T_1(S_1, V_1, N_1)} - \frac{p_2(S_2, V_2, N_2)}{T_2(S_2, V_2, N_2)} \right) \dot{V}_1 \\ & - \left(\frac{\mu_1(S_1, V_1, N_1)}{T_1(S_1, V_1, N_1)} - \frac{\mu_2(S_2, V_2, N_2)}{T_2(S_2, V_2, N_2)} \right) \dot{N}_1 \end{aligned}$$

Thermodynamique

Considering. Relationships that have been established for one point and two points. We can now derive explicit expressions for the time derivatives of the entropy of the two subsystems, i.e. S one point and s two points and 5.1 on T1 which multiplies U one point plus p1 v one point less but 1.1 point. S 2.71 on two that multiplies. Uh. Two point plus p2 v two point minus U2 one two point. The system is isolated and we have just shown that if the system is isolated. It must satisfy three relationships. First of all, a point which is also in him a bridge. Then 22 points which is equal to 21 points and finally a two points which is equal to me and not a point. By summing the two expressions we have obtained. For the temporary derivatives of entropy and subsystems, we obtain. The time derivative of the entropy of the system is times, taking into account of course the three relations obtained for the isolated system. The first term is one in a month, one in two that multiplies. Uh, one for the second term CP and one on T1 minus p2 on T2 which multiplies v a point. And the third term is less U1 on T1 two on T2 which multiplies one to a point in order to extract from this expression of the time derivative of the partial derivatives of entropy with respect to U1, V1 and N-1.

Notes

Summary



4m 37s

- Identités :

$$dS = \dot{S} dt, \quad dU_1 = \dot{U}_1 dt$$

$$dV_1 = \dot{V}_1 dt \quad \text{et} \quad dN_1 = \dot{N}_1 dt$$

- Dérivées partielles de l'entropie :

$$\frac{\partial S}{\partial U_1} = \frac{1}{T_1(S_1, V_1, N_1)} - \frac{1}{T_2(S_2, V_2, N_2)}$$

$$\frac{\partial S}{\partial V_1} = \frac{p_1(S_1, V_1, N_1)}{T_1(S_1, V_1, N_1)} - \frac{p_2(S_2, V_2, N_2)}{T_2(S_2, V_2, N_2)}$$

$$\frac{\partial S}{\partial N_1} = \frac{\mu_2(S_2, V_2, N_2)}{T_2(S_2, V_2, N_2)} - \frac{\mu_1(S_1, V_1, N_1)}{T_1(S_1, V_1, N_1)}$$

- Condition d'équilibre (entropie maximale) :

$$\frac{\partial S}{\partial U_1} = 0, \quad \frac{\partial S}{\partial V_1} = 0 \quad \text{et} \quad \frac{\partial S}{\partial N_1} = 0$$

- Equilibre :

- Equilibre thermique :

$$T_1(S_1, V_1, N_1) = T_2(S_2, V_2, N_2)$$

- Equilibre mécanique :

$$p_1(S_1, V_1, N_1) = p_2(S_2, V_2, N_2)$$

- Equilibre chimique :

$$\mu_1(S_1, V_1, N_1) = \mu_2(S_2, V_2, N_2)$$

Thermodynamique

We will multiply this expression by the infinitesimal time interval dt and we obtain in the left-hand member ds which is equal to $s dt$ and in the right-hand member, we have three terms. The first is proportional to $D1$ which is equal to had a point dt . The second term is proportional to $V1$ which is equal to v a point dt and the third term is proportional. To Diana which is equal to one point DD . We thus deduce three partial derivatives of entropy. The first is the partial derivative of the entropy S with respect to one of the circles s on circles which is equal to one on $T1$ one on $T2$. The second, is the partial derivative of the entropy with respect to the volume comes from the circles s on rounds $v1$ which is equal to $P1$ on $T1$, minus $p2$ on $T2$. The third is the partial derivative of the entropy S with respect to n one of the circles S on circles n one which is equal to two on $T2$ minus but one on $T1$. The equilibrium condition of the second principle requires that the entropy be maximum at equilibrium for an isolated system. This gives rise to three conditions different on each of the derivatives, each of the derivatives must cancel out. Rounds ensure an equal zero zero one over zero and round s over round n equals zero.

Notes

Summary



- Identités :

$$dS = \dot{S} dt, \quad dU_1 = \dot{U}_1 dt$$

$$dV_1 = \dot{V}_1 dt \quad \text{et} \quad dN_1 = \dot{N}_1 dt$$

- Dérivées partielles de l'entropie :

$$\frac{\partial S}{\partial U_1} = \frac{1}{T_1(S_1, V_1, N_1)} - \frac{1}{T_2(S_2, V_2, N_2)}$$

$$\frac{\partial S}{\partial V_1} = \frac{p_1(S_1, V_1, N_1)}{T_1(S_1, V_1, N_1)} - \frac{p_2(S_2, V_2, N_2)}{T_2(S_2, V_2, N_2)}$$

$$\frac{\partial S}{\partial N_1} = \frac{\mu_2(S_2, V_2, N_2)}{T_2(S_2, V_2, N_2)} - \frac{\mu_1(S_1, V_1, N_1)}{T_1(S_1, V_1, N_1)}$$

- Condition d'équilibre (entropie maximale) :

$$\frac{\partial S}{\partial U_1} = 0, \quad \frac{\partial S}{\partial V_1} = 0 \quad \text{et} \quad \frac{\partial S}{\partial N_1} = 0$$

- Equilibre :

- Equilibre thermique :

$$T_1(S_1, V_1, N_1) = T_2(S_2, V_2, N_2)$$

- Equilibre mécanique :

$$p_1(S_1, V_1, N_1) = p_2(S_2, V_2, N_2)$$

- Equilibre chimique :

$$\mu_1(S_1, V_1, N_1) = \mu_2(S_2, V_2, N_2)$$

Thermodynamique

The first condition implies that T_1 is equal to T_2 . The first condition is therefore a condition of thermal equilibrium. The temperature must be the same in both subsystems. Given this condition of thermal equilibrium. The second condition of the circles is on circles v_1 equals zero. Implies then that P_1 equals P_2 . It then implies the condition of mechanical equilibrium, i.e. the pressure of the two subsystems must be the same. Taking into account the thermal equilibrium condition, the last condition of the circles s on circles is equal to zero implies then. That U_2 is equal to wall. This is the condition of chemical equilibrium. The chemical potential of the two subsystems must be the same. Therefore, the equilibrium condition requires the system to be in thermal equilibrium, mechanical and chemical equilibrium. What does that mean? That the set of state functions intensive, which are conjugated to the state variables extensive of the subsystems, be the same in both subsystems.

Notes

Summary



8m 11s