

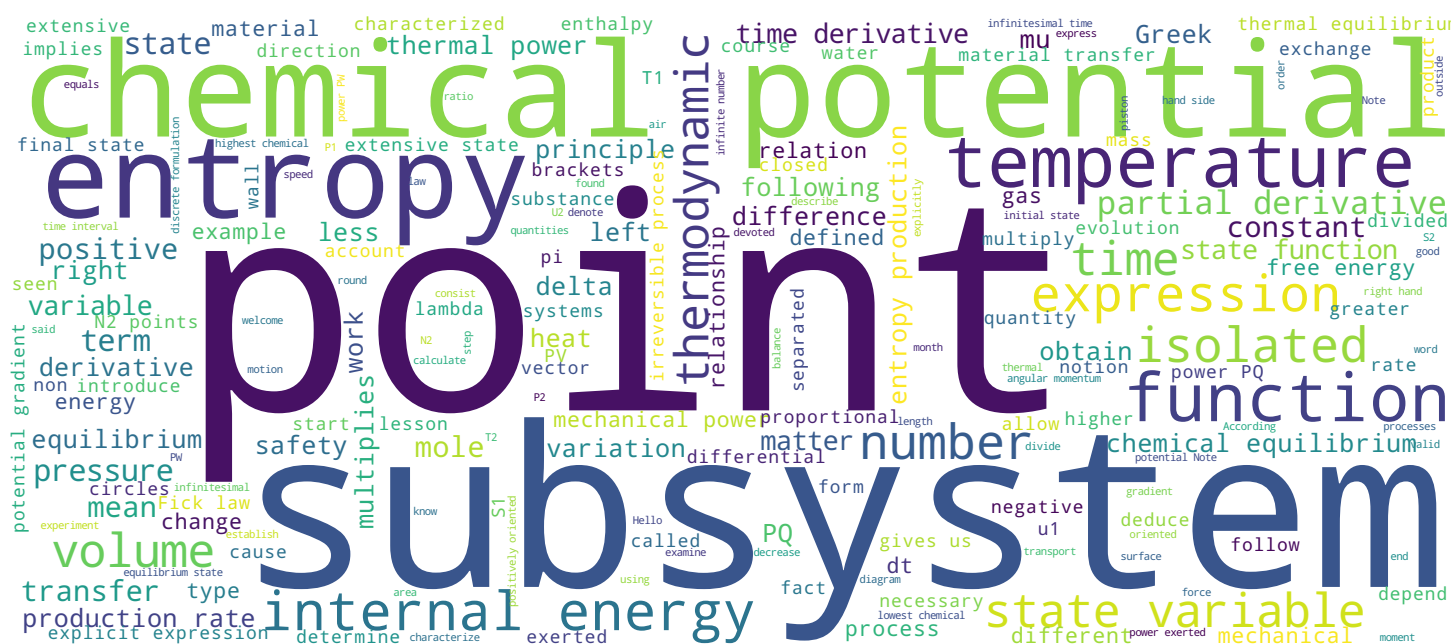
# Thermodynamique

# Equilibre chimique et transfert de matière

Dr. Sylvain Bréchet



Ernst Carl Gerlach Stükelberg, 1905 - 1984



## Video





- Deux sous-systèmes simples séparés par une paroi diatherme, immobile et perméable
- Equilibre chimique
- Transfert de matière (transport de matière)
- Loi de Fick
  - Formulation discrète (2 sous-systèmes)
  - Formulation continue ( $\infty$  sous-systèmes)

Thermodynamique

Hello and welcome to this thermodynamic moment. This lesson is devoted to chemical equilibrium and matter transfer. To do this, we consider an isolated system that consists of two sub-systems simple systems that are separated by a permeable, immobile term wall. In a first step, we will deduce the equilibrium condition chemical and in a second time, we will examine the transfer of matter. We also speak about transport of matter and we will deduce the law of Fick. First, in a discrete formulation for two subsystems, which we will then extend to a formulation continuous for an infinite number of subsystems.

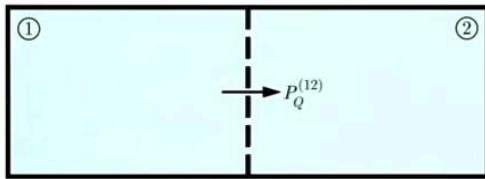
Notes

Summary



0m 05s

# Paroi diatherme immobile et perméable



- Système isolé :  $P_Q = P_W = 0$
- Paroi immobile :  $P_W^{(12)} = P_W^{(21)} = 0$
- Sous-systèmes simples (1) et (2)
- Variables d'état extensives :
  - Entropies  $S_1$  et  $S_2$
  - Nombre de moles  $N_1$  et  $N_2$
- Equilibre thermique :
 
$$T(S_1, N_1) = T(S_2, N_2)$$

- Premier principe (sous-systèmes 1 et 2) :

$$\dot{U}_1(S_1, N_1) = T(S_1, N_1) \dot{S}_1 + \mu_1(S_1, N_1) \dot{N}_1 = P_Q^{(21)}$$

$$\dot{U}_2(S_2, N_2) = T(S_2, N_2) \dot{S}_2 + \mu_2(S_2, N_2) \dot{N}_2 = P_Q^{(12)}$$

- Energie interne (fonction d'état extensive) :

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

- Premier principe (système isolé) :

$$\begin{aligned} \dot{U}(S_1, S_2, N_1, N_2) &= \dot{U}_1(S_1, N_1) + \dot{U}_2(S_2, N_2) \\ &= P_Q^{(21)} + P_Q^{(12)} = 0 \end{aligned}$$

- Identités :

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

$$P_Q^{(12)} = -P_Q^{(21)}$$

Thermodynamique

We therefore consider an isolated system consisting of two subsystems subsystem one subsystem two which are separated by a wall that is said to be immobile and permeable. The system is isolated. This means that the thermal power  $P_Q$ , the mechanical power  $P_W$  that are exerted on the system are zero. Since the wall is immobile, the mechanical power  $W$ . One is exercised by the first under system on the second subsystem is zero and in an analogous way, the mechanical power  $P_W$  two exerted by the second subsystem on the first subsystem is also zero. To characterize thermodynamics of this system, two types of state variables are needed first the entropy and then the number of moles. We have two subsystems. We need a state variable entropy for each subsystem. These state variables are  $S_1$  and  $S_2$ . We also need a state variable. Number of moles for each subsystem. So the number of moles of the first subsystem with seven  $n_1$  is the number of moles of the second subsystem seven  $N_2$ . It is assumed that the system has already reached a state of thermal equilibrium, but not yet a state of chemical equilibrium. The thermal equilibrium is characterized by the equality of the temperatures.

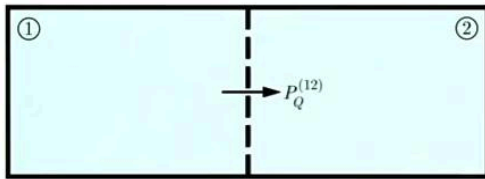
Notes

Summary



0m 51s

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Thermodynamique

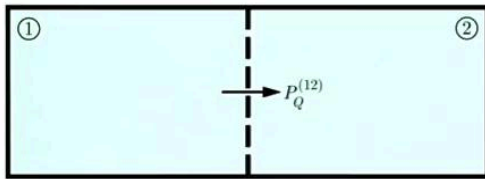
Temperature is a state function. It is therefore a function of the state variables of each subsystem. So the thermal equilibrium is formally written as follows. The temperature  $T$  of the first subsystem, which is a function of  $S_1$  and  $N_1$ , is equal to the temperature  $T$  of the second subsystem which is a function of  $S_2$  and  $N_2$ . Internal energy, temperature and chemical potential are state functions. They are therefore functions of the state variables of each subsystem. It was five points plus one and one point. And the cause of the temporal variation of the internal energy of the first subsystem, is the thermal power exerted by the second subsystem on the first subsystem, i.e.  $P_Q^{(21)}$ . In a similar way  $U_2$  and  $N_2$ . Is it two points plus two  $N_2$  points? The cause of the variation of the internal energy of the second subsystem. It is the thermal power exerted by the first subsystem on the second subsystem. This is  $P_Q^{(12)}$ . the internal energy, it is a state function, so the internal energy of the whole system  $U$  is a function of the set of state variables of the system. It is therefore a function of  $S_1$ ,  $S_2$ ,  $N_1$  and  $N_2$ . It is an extensive state function.

Notes

Summary



# Paroi diatherme immobile et perméable



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

- Premier principe (système isolé) :

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- Identités :

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

$$P_Q^{(12)} = -P_Q^{(21)}$$

Thermodynamique

It is therefore the sum of the internal energy of the first subsystem one of the internal energy of the second subsystem  $U_2$ . Can now take the derivative time of this expression of point seven one point plus two point. According to the first principle. Uh one point is  $P_Q$  of one and two points is  $P_Q$  of two. Moreover, we know that the system is isolated. If the system is isolated, the internal energy of the system is constant, so the point is zero. This gives us two identities. First of all, having a point is equal to -2 points and secondly  $P_{Q12}$  is equal to minus  $P_{Q21}$ .

Notes

Summary



4m 07s





- Dérivées temporelles de l'entropie :

$$\dot{S}_1 = \frac{1}{T(S_1, N_1)} \left( \dot{U}_1(S_1, N_1) - \mu_1(S_1, N_1) \dot{N}_1 \right)$$

$$\dot{S}_2 = \frac{1}{T(S_2, N_2)} \left( \dot{U}_2(S_2, N_2) - \mu_2(S_2, N_2) \dot{N}_2 \right)$$

- Système isolé :

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

- Dérivée temporelle de l'entropie :

$$\dot{S} = \frac{1}{T(S_1, V_1)} \left( \mu_2(S_2, V_2) - \mu_1(S_1, V_1) \right) \dot{N}_1$$

- Identités :  $dS = \dot{S} dt$  et  $dN_1 = \dot{N}_1 dt$

- Dérivée partielle de l'entropie :

$$\frac{\partial S}{\partial N_1} = \frac{1}{T(S_1, N_1)} \left( \mu_2(S_2, N_2) - \mu_1(S_1, N_1) \right)$$

Thermodynamique

One must now explicitly take into account the fact that the entropy and the number of moles are extensive state variables. So the entropy  $S$  of the system is equal to the sum of entropy  $S$  one and  $s$  two of the two subsystems, and the number of moles  $n$  of the system is equal to the sum of the number of moles  $N_1$  and  $N_2$  of the two subsystems. To take the time derivative of these two expressions, we obtain that is this point equal to  $s$  one point plus  $s$  two points and  $n$  one is equal to one point plus  $n$  two points. The system is an isolated system. By the second principle of thermodynamics. This point is then equal to  $P_i$  of  $S$  which is greater than or equal to zero. And then the number of deaths of the system is a constant since the system is isolated, so 1.0, which implies that one point is equal to -1 two points. So if the number of moles. Dassault Systèmes is growing. This will imply that the number of moles of the other subsystem will decrease using the expressions we have established for one point and two points. We can now determine the explicit expressions of  $S$  one point and  $s$  two points and 5.71 safety which multiplies  $U$  one point less, better 1 $N_1$  point and  $s$  2.7.

Notes

Summary



4m 54s

- Dérivée partielle de l'entropie :

$$\frac{\partial S}{\partial N_1} = \frac{1}{T(S_1, N_1)} (\mu_2(S_2, N_2) - \mu_1(S_1, N_1))$$

- Deuxième principe (condition d'équilibre) :

$$\frac{\partial S}{\partial N_1} = 0 \quad (\text{maximum d'entropie})$$

- Equilibre chimique :

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

*Le premier et le deuxième principes requièrent que les potentiels chimiques des sous-systèmes aient la même valeur à l'équilibre chimique.*

Thermodynamique



A safety that multiplies u two points mu 2N2 points. As we have seen, the system is isolated. This gives us two relationships. First of all. Two points is equal to less than one point and secondly, a two point is equal to less than one point. We can now calculate the expression of the time derivative of the entropy. Is this the point? It is the sum of s one point plus s two points. We sum the two expressions of the time derivatives of entropy. These expressions. And we get the following results. Is it good? It is a safety that multiplies for two months a liver and a weight. We would now like to express this relation in terms of the differential of entropy and the number of moles associated with the first subsystem. We multiply this relation by DT. In the left-hand member, we obtain ds and in the right hand side we get dn or dt. This is the infinitesimal time interval. This allows us to to calculate explicitly the partial derivative of the entropy, i.e. circles s on circles n one that is equal to one safety that multiplies U2 minus u1 the equilibrium condition of the second principle. Requires that the entropy is maximal at equilibrium for an isolated system.

Notes

Summary



6m 26s



- Dérivée partielle de l'entropie :

$$\frac{\partial S}{\partial N_1} = \frac{1}{T(S_1, N_1)} (\mu_2(S_2, N_2) - \mu_1(S_1, N_1))$$

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Thermodynamique

Therefore, for an isolated system, of the prowess on rounds is equal to zero at equilibrium. Given the expression of a derivative of the entropy that is found here. This condition implies that. The difference between the two terms are in brackets in this expression. And lame. This gives us the chemical equilibrium condition which is the following the chemical potential of the first subsystem must be equal to at the chemical potential 1002 of the second subsystem. Therefore, the first and second principles require that the potentials of the subsystems and the same value at the chemical equilibrium before the system reaches a state of chemical equilibrium.

Notes

Summary



8m 10s



- Dérivée temporelle de l'entropie ( $\mu_1 \neq \mu_2$ ) :

$$\dot{S} = \frac{1}{T(S_1, V_1)} \left( \mu_2(S_2, V_2) - \mu_1(S_1, V_1) \right) \dot{N}_1$$

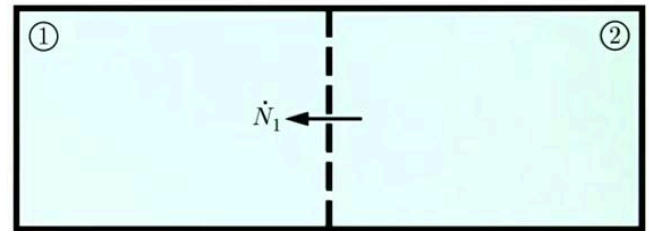
- Système isolé (processus irréversible) :

$$\dot{S} = \Pi_S > 0$$

- Taux de production d'entropie :

$$\Pi_S = \frac{1}{T(S_1, V_1)} \left( \mu_2(S_2, V_2) - \mu_1(S_1, V_1) \right) \dot{N}_1 > 0$$

- $\mu_2 > \mu_1 \Rightarrow \dot{N}_1 > 0$
- $\mu_1 > \mu_2 \Rightarrow \dot{N}_2 = -\dot{N}_1 > 0$



- Transfert de matière :

- Matière :  $\mu_+ \Rightarrow \mu_-$
- Processus irréversible :  $\Pi_S > 0$
- Nul à l'équilibre chimique :  $\mu_1 = \mu_2$

Thermodynamique

There is a transfer of matter between these two subsystems. The chemical equilibrium is characterized by the same value of the chemical potential. So during the material transfer, the chemical potential of the first subsystem is different of the chemical potential of the second subsystem. To examine this transfer of material. We base ourselves on the temporal derivative of entropy. Is it a point that equals a safety that multiplies mu by mu one times a point mu two is different from one, so the difference of the terms in brackets is non-zero. There is a transfer of matter, so the number of moles of the first subsystem will vary, which means that n a point is non-zero. So do we not suck? We have an isolated system for an isolated system. This point is equal to Pie of S as S is non-zero and it is equal to Fido. And this point must be positive, which means that this transfer of matter is an irreversible process. We have an explicit expression for the rate of entropy production and then of decrease which is equal to a safety which multiplies 2001 times n a point and this entropy production rate is positive. We must now consider two cases.

Notes

Summary



9m 01s

- Dérivée temporelle de l'entropie ( $\mu_1 \neq \mu_2$ ) :

$$\dot{S} = \frac{1}{T(S_1, V_1)} \left( \mu_2(S_2, V_2) - \mu_1(S_1, V_1) \right) \dot{N}_1$$

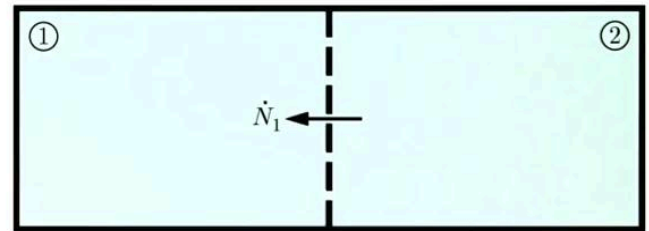
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- $\mu_2 > \mu_1 \Rightarrow \dot{N}_1 > 0$
- $\mu_1 > \mu_2 \Rightarrow \dot{N}_2 = -\dot{N}_1 > 0$



- Transfert de matière :

- Matière :  $\mu_+ \Rightarrow \mu_-$
- Processus irréversible :  $\Pi_S > 0$
- Nul à l'équilibre chimique :  $\mu_1 = \mu_2$

Thermodynamique

In the first case, the chemical potential of the second sub system U two is higher than the chemical potential MU one of the first subsystem. This means that the difference of the terms which is found here in brackets in the expression of the entropy production rate is positive. Therefore, for pi ds to be positive, it is necessary that it is also positive. This means that if the chemical potential of the second subsystem is greater than the chemical potential of the first subsystem, there will be a transfer of material. From the second subsystem to the first subsystem. Second scenario, the chemical potential of the first subsystem is higher at the chemical potential 1002 of the second subsystem. In this case, the difference of the terms in brackets will be negative. Therefore, in order for the rate of entropy production is defined positive. N-1 points must be negative. Now one point is equal to minus N2 points. So N2 points must be positive. Therefore, if the chemical potential of the first subsystem is greater than the chemical potential of the second subsystem, there is a transfer of material from the first subsystem to the second subsystem. In general.

Notes

Summary



- Dérivée temporelle de l'entropie ( $\mu_1 \neq \mu_2$ ) :

$$\dot{S} = \frac{1}{T(S_1, V_1)} \left( \mu_2(S_2, V_2) - \mu_1(S_1, V_1) \right) \dot{N}_1$$

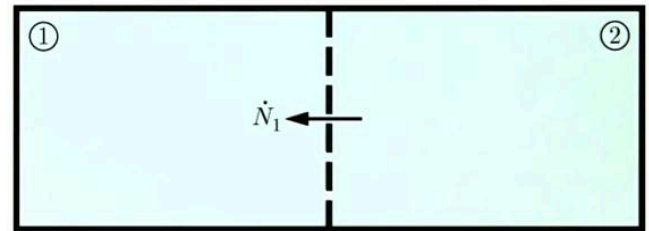
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- Matière :  $\mu_+ \Rightarrow \mu_-$
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Thermodynamique

Material transfer takes place of the subsystem with the highest chemical potential. Note the mucus to the subsystem with the lowest chemical potential. Note the mu minus and this transfer of matter is an irreversible process, i.e. pi of s is positive. There is a transfer of matter before reaching the equilibrium state and a chemical equilibrium state MU one is equal to 1002. The two chemical potentials, the two subsystems are equal and at this moment, the transfer of matter stops.

Notes

Summary





- Taux de production d'entropie :

$$\Pi_S = \left( \frac{\mu_2(S_2, N_2) - \mu_1(S_1, N_1)}{T(S_1, N_1)} \right) \dot{N}_1 > 0$$

- Loi de Fick « discrète » :

$$\dot{N}_1 = F \frac{A}{\ell} \left( \mu_2(S_2, N_2) - \mu_1(S_1, N_1) \right)$$

$F$  : Diffusion de la matière

$A$  : Aire de l'interface entre (1) et (2)

$\ell$  : Longueur caractéristique

Thermodynamique

We can now deduce Fick's law in its discrete formulation. We can rewrite the entropy production rate as follows. Pompidou-Metz C.  $U_2$  minus  $\mu_1$  in three times  $n$ . A point and then of  $S$  is positive. To guarantee the positivity of Peano. It is necessary that  $N$  a point is proportional to  $U_2$  minus  $\mu_1$ , which means that the production rate of entropy will be proportional to  $\mu_1$  of one squared. It is necessary that  $n$  one points is proportional to better of less  $\mu$  and that the constant of proportionality is in fact positive. This too is the discrete Fick law and not point is equal to the product the diffusion coefficient of the material  $f$  times the area of the interface between the two subsystems to divided by the characteristic length  $L$  all times  $U_2$  minus  $u_1$ .

Notes

Summary



12m 29s

# Loi de Fick "continue"

- Loi de Fick « discrète » :

$$\dot{N} = F \frac{A}{\ell} (\mu_+ - \mu_-)$$

- Gradient de potentiel chimique :

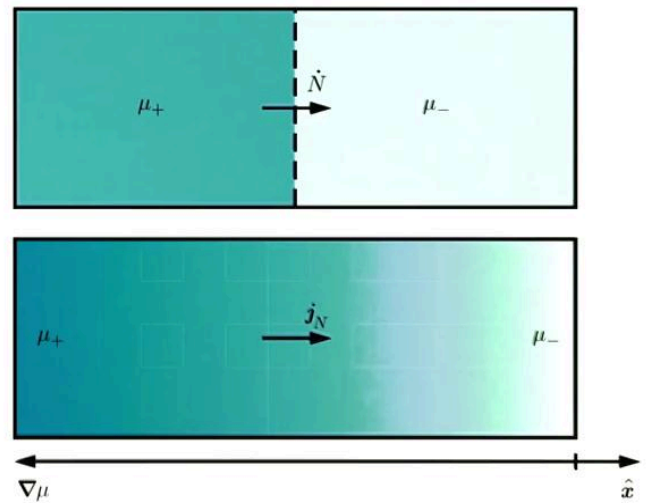
$$\nabla \mu = - \frac{\mu_+ - \mu_-}{\ell} \hat{x}$$

- Densité de courant de matière :

$$\mathbf{j}_N = \frac{\dot{N}}{A} \hat{x}$$

- Loi de Fick « continue » :

$$\mathbf{j}_N = -F \nabla \mu$$



Thermodynamique

In physics, we are often confronted with a system where the chemical potential of the substance varies gradually linearly between the two ends. Considering that the lowest chemical potential is on the right at least, and that the highest chemical potential is on the left. But more, if it varies linearly, we will have to consider an infinite number of subsystems whose length is infinitesimal. And then, the variation of the chemical potential from the right to the left is described mathematically by the chemical potential gradient. The chemical potential gradient. It is a variation of chemical potential per unit distance. In the increasing direction of the chemical potential, i.e. it is oriented from the right to the left. The  $\hat{x}$  vector is a physical dimensionless normed vector. Which is oriented to the right. Thus the gradient between chemical potential which is noted  $\mu$  is equal to minus the chemical potential difference, i.e. more or less badly divided by the length of the system, i.e.  $\ell$  the all in the direction  $\hat{x}$  and the minus sign comes from the fact that the gradient is positively oriented to the left and that  $\hat{x}$  is positively oriented to the right.

Notes

Summary



13m 40s



# Loi de Fick “continue”

- Loi de Fick « discrète » :

$$\dot{N} = F \frac{A}{\ell} (\mu_+ - \mu_-)$$

- Gradient de potentiel chimique :

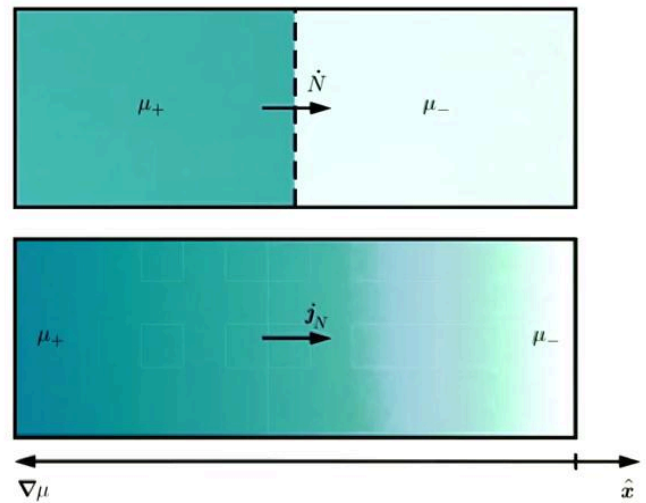
$$\nabla \mu = - \frac{\mu_+ - \mu_-}{\ell} \hat{x}$$

- Densité de courant de matière :

$$\mathbf{j}_N = \frac{\dot{N}}{A} \hat{x}$$

- Loi de Fick « continue » :

$$\mathbf{j}_N = -F \nabla \mu$$



Thermodynamique

It is also necessary to introduce the notion of density, of current, of matter that we note  $j_N$ . It is defined as the ratio of the time derivative the number of mole  $n$  points divided by the area, which is orthogonal to the material transfer, all in the direction  $\hat{x}$  is the direction of the material transfer. Therefore, we are now able to establish the expression of the continuous Fick's law. For this, we start with the discrete Fick's law. We divide it by one and multiply it by  $\hat{x}$ . In the left limb, we will obtain the current density, matter which is a vector, and in the right-hand side, we obtain another vector which is less the diffusion constant of Fick large  $F$ , the chemical potential gradient. But.

Notes

Summary



15m 16s