



# Transitions de phase du 1<sup>er</sup> ordre



- Présentation des transitions courantes
- Classification des transitions
- Transitions du premier ordre

Thermodynamique

Hello to all. Continuing now with the second module of our Lessons on phase transitions. This module has three main parts. The presentation of current proposals. The classification of transitions and finally. The transition study of the first.

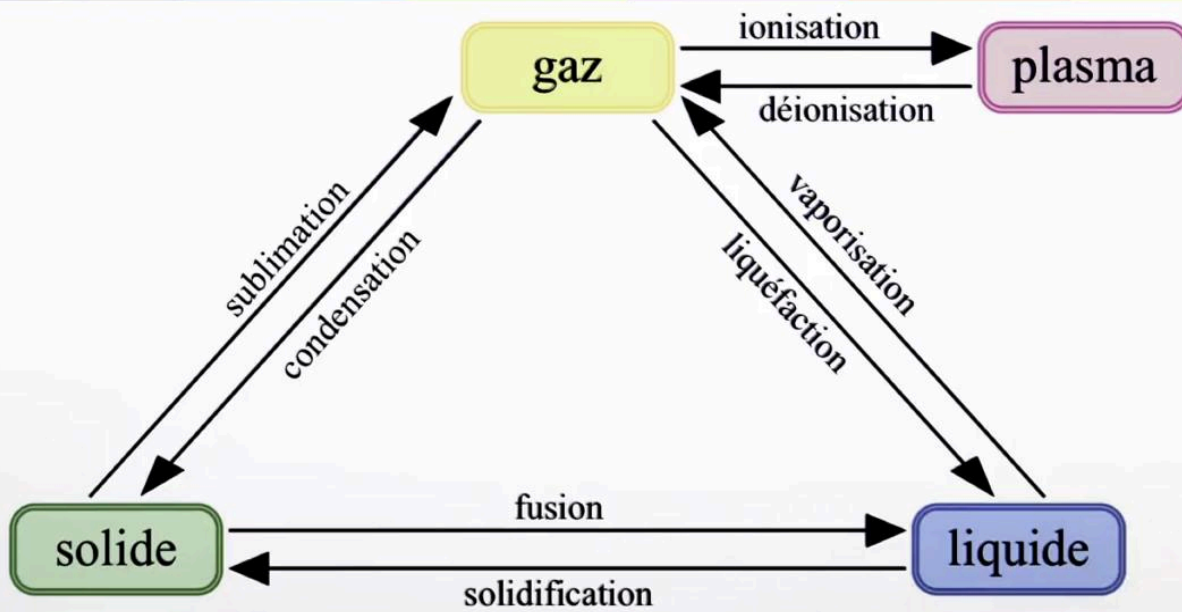
Notes

Summary



0m 04s

# Phases et transitions courantes



Thermodynamique

In our daily life, we observe three main phases. The liquid phase. The solid phase and the gas phase. There is a fourth phase. Very present in the upper atmosphere and in the laboratory which is constituted by the plasma between these different phases in a place of transition, the fusion. And the solidification between solids and liquids. Sublimation and condensation between solids and gases. Liquefaction and vaporization between gases and liquids. Between gases and plasmas, we observe ionization and ionization.

Notes

Summary



0m 33s

# Autres transitions



- Transition magnétique:

Paramagnétique  $\longrightarrow$  ferromagnétique

- Transition dans les cristaux liquides

liquide Isotrope  $\longrightarrow$  nématique

Thermodynamique

Beside these common phase changes. There are others, such as the example of the transition paramagnetic ferromagnetic in metals and neumatic liquid isotropic liquid transition in liquid crystals.

Notes

Summary



1m 33s

# Classification des transitions de phase : 2<sup>nd</sup> ordre



- 2<sup>nd</sup> ordre

Pas de chaleur latente de transition		
$g$	$\left(\frac{\partial g}{\partial T}\right)_{P_T} = -s$	$\left(\frac{\partial^2 g}{\partial T^2}\right)_{P_T} = -\left(\frac{\partial s}{\partial T}\right)_{P_T} = -\frac{C_p}{T}$

Thermodynamique

There are two main classes of transition. First-order transitions, also known as common transitions. And the second round transitions. Transitions from one to the other need a latent heat of phase change. Either the system is absorbing heat or it has been animated elsewhere. While the free enthalpy function is continuous at the transition. This first derivative. In relation to the pressure here and in relation to the temperature there. Discontinuous sound. The second order transitions do not no latent heat of transition is involved. The free enthalpy function and its derivative first remain continuous and we observe a discontinuity. For the second derivative of the free enthalpy with respect to temperature.

Notes

Summary

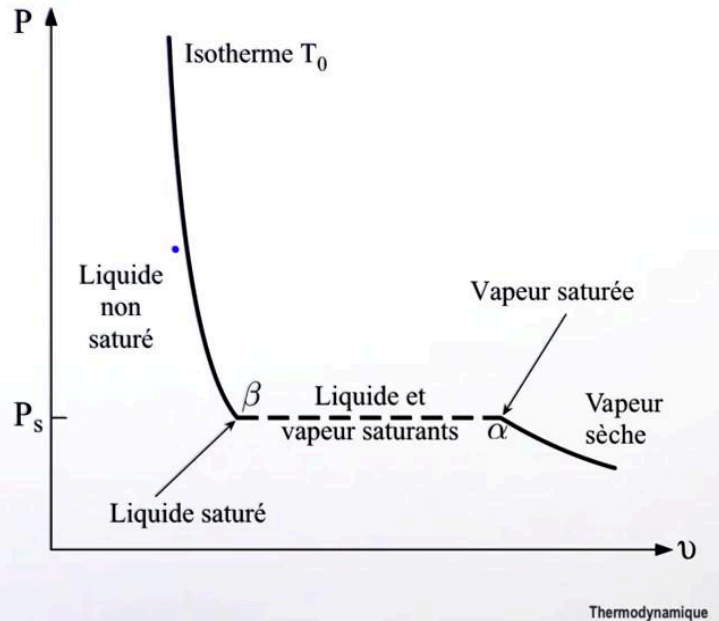


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# Liquefaction par compression isotherme d'un gaz



- Compression isotherme de la vapeur sèche à la vapeur saturée  $\alpha$  à  $P=P_s$
- Palier de liquéfaction, coexistence liquide-vapeur saturants ( $\alpha$ - $\beta$ )
- Liquéfaction totale ( $\beta$ )
- $P > P_s$  Compression du liquide saturé au liquide non-saturé



Latent heat is the heat required to achieve reversible, at constant temperature and pressure, the transition of a body of mass. Unit from alpha to beta phase. This definition allows us to give the expression of the latent heat of phase change. The transformation being reversible. We can write.  $\Delta u = T ds$ . The temperature being constant during the transition, the integration of this equation allows us to obtain that the heat is equal to  $t \cdot \Delta s$ . This is the expression of the latent heat of phase change  $l_{\alpha\beta}$ . Since this transformation takes place at constant pressure, the heat is equal to the enthalpy variation and we note  $Q = \Delta H_{\alpha\beta}$ . Observing the completion it to the end of a gas. We take dry steam. Not the achievement to a pressure, noted  $P_s$ . Traces of liquid appear. The steam is said to be saturated at this point and the pressure is called vapor pressure. Saturating. A liquefaction level is observed at saturation pressure. Liquid water and saturated steam are in equilibrium. At the end of the landing. The liquefaction is total. From. From the  $P_s$  if we continue to compress. We pass from saturated liquid. To unsaturated liquid. Then a similar mechanism allows to pass from liquid to solid.

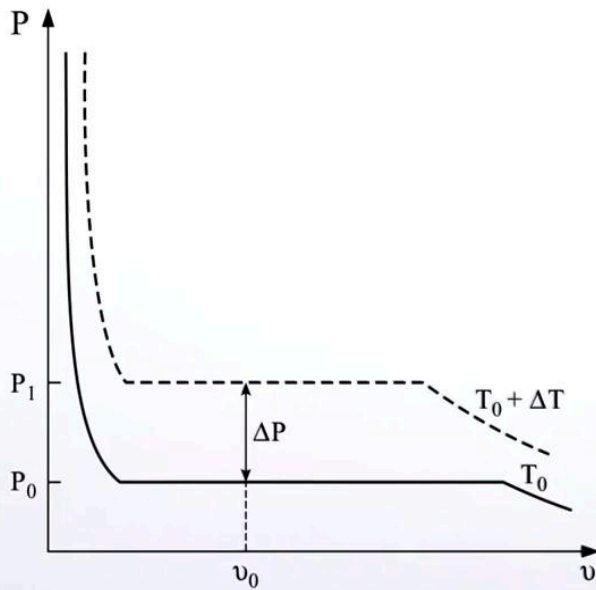
Notes

Summary



3m 10s

# Relation de Clausius - Clapeyron



- Soit  $P_0$  la pression de saturation à  $T_0$
- Soit  $P_1 = P_0 + \Delta P$  celle à  $T_0 + \Delta T$
- La relation de Clausius–Clapeyron permet de calculer la pente  $\left(\frac{\Delta P}{\Delta T}\right)_{v_0}$  des courbes d'équilibre

Thermodynamique

Let  $p_0$  be the saturation pressure. When operating at  $T_0$ , the Clausius–Clapeyron relation allows to calculate the pressure  $P_1$ . When operating at the temperature  $T_0 + \Delta T$  close to  $T_0$ . In other words, this relation allows us to obtain the slope  $\Delta P$  over  $\Delta T$  at  $v_0$  of the equilibrium curve. In the pressure-temperature diagram, we will in the following. Establish this relationship.

Notes

Summary



5m 46s



# Relation de Clausius - Clapeyron



- $\delta q = T \left( \frac{\partial s}{\partial v} \right)_T dv + T \left( \frac{\partial s}{\partial T} \right)_v dT$

- $\delta q = T \left( \frac{\partial s}{\partial v} \right)_T dv$ , à T constante

Avec la relation de Maxwell :  $\left( \frac{\partial P}{\partial T} \right)_v = \left( \frac{\partial s}{\partial v} \right)_T$

- $\left( \frac{\Delta P}{\Delta T} \right)_v = \frac{L_{\alpha\beta}}{T(v_\beta - v_\alpha)}$

- Soit encore  $\left( \frac{\Delta P}{\Delta T} \right)_v = \frac{s_\beta - s_\alpha}{v_\beta - v_\alpha}$

(Relation de Clausius-Clapeyron)

$$q = T \left( \frac{\Delta P}{\Delta T} \right)_v \Delta v = L_{\alpha\beta}$$

Thermodynamique

The transformations being reversible, we start from the expression  $\delta q = T ds$ . Expressed in variable  $dv$  at constant temperature. The second term on the right-hand side cancels if we replace  $ds$  on  $dv$  at  $T$  by  $dp$  on  $dv$  by integration, we get  $q$  equal to  $T \Delta p$  on constant  $dv$  multiplied by the variation of the mass volume. We can deduce from this relation that the slope of the curve in the pressure temperature equilibrium diagram is  $\Delta p$  at  $T$  equal to  $\alpha \Delta T$  times  $V_\beta - V_\alpha$ . The relation of Clapeyron and so is established. We can put it in the form  $\Delta p$  at  $T$  equal to  $\Delta S$  on  $\Delta V$ .

Notes

Summary



6m 25s



# Courbes de coexistence de phase (Diagramme (P,T))



- Courbe de l'équilibre vapeur-liquide

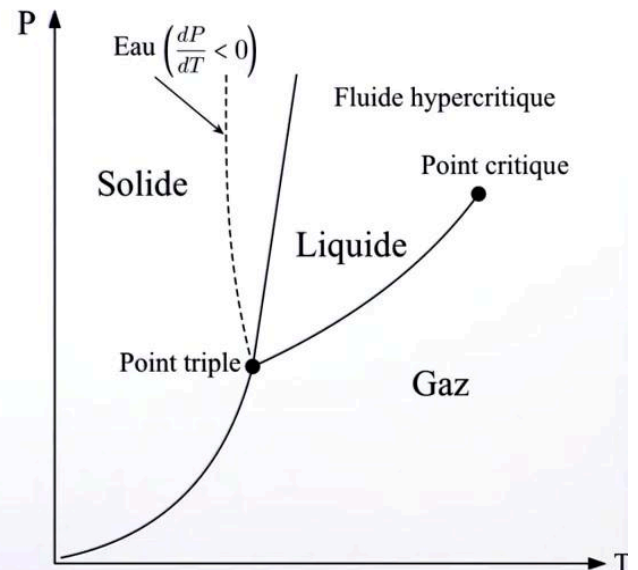
$$\left. \begin{array}{l} s_l - s_g < 0 \\ v_l - v_g < 0 \end{array} \right\} \rightarrow \frac{dP}{dT} > 0$$

- Courbe de l'équilibre liquide-solide

$$\left. \begin{array}{l} s_s - s_l < 0 \\ v_s - v_l < 0 \end{array} \right\} \rightarrow \frac{dP}{dT} > 0$$

- Courbe de l'équilibre solide-vapeur

$$\left. \begin{array}{l} s_g - s_s > 0 \\ v_g - v_s > 0 \end{array} \right\} \rightarrow \frac{dP}{dT} > 0$$



Thermodynamique

The Clausius relationship. Clapeyron allows to draw the curves of equilibrium in the pressure-temperature diagram. We start with the liquid-vapor equilibrium curve. The entropy variation  $s$  liquid  $s$  vapor is less than zero, the variation of the mass volume  $V$  liquid at least  $v$  vapor and lower than zero. The Clausius relationship, remember, allows to establish that the slope  $DP$  on  $DT$  of the equilibrium curve is positive. We represent here. In our  $PT$  diagram, the liquid-vapor equilibrium curve is limited in its upper part by a critical point beyond this point. You can't, just by a transition ISO term, change from steam to liquid above this point. Fluid water is called hypercritical. In a similar way, we establish that the slope of the solid liquid equilibrium curve here. Is positive, except for the exceptional case of water. Or. The mass volume of the solid is greater than the mass volume of the liquid. The cup for water and signs, no. Finally. For the solid-vapor equilibrium. We have an entropy variation positive when going from solid to steam. We have a mass volume of the vapor that is greater than that of the solid. We, by deducing that the slope of the curve is greater than zero, the slope of the sublimation curve. Can be found here. The three curves meet at a point which is called triple point.

Notes

Summary



7m 39s

# Transitions de phase entre variétés allotropiques



- Allotropie: Existence d'un corps simple, dans le même état, sous plusieurs formes
- Exemple de variétés allotropiques:
  - carbone amorphe, graphite, diamant....
  - étain blanc  $\text{Sn}(\beta)$ , étain gris  $\text{Sn}(\alpha)$
- Transition allotropique
  - $\text{Sn}(\beta) \xrightarrow{<12^\circ\text{C}} \text{Sn}(\alpha)$

Thermodynamique

We open a parenthesis here to say that. For a simple body in the same solid state, there can be phase changes. These phase changes are called allotropic. As examples of allotropic varieties. We will quote the carbon with the varieties carbon, amorphous, diamond, graphite. We will quote the white terms gray times, an example of allotropic transition. We have the transition from white tin to gray tin. For temperatures below twelve degrees. The white tin becomes unstable and turns into the gray ones.

Notes

Summary



10m 10s

# Règle de phase de Gibbs: Détermination de la variance $v$



- Soit un système  $S$  comprenant:
  - $C$  constituants (pas de réaction chimique)
  - $\phi$  phases
- Description à  $(C\phi + 2)$  variables
  - $C$  concentrations dans chaque phase ( $C\phi$ )
  - la température et la pression (2)
- $\phi + C(\phi - 1)$  équations pour  $S$ :
  - Conservation de la matière:
 
$$\sum_{i=1}^c X_{i,j} = 1, j = 1 \text{ soit } \phi \text{ équations}$$
  - Egalités des potentiels chimiques par espèce:
 
$$\mu_{i,k} = \mu_{i,j}, i = 1..C$$
 soit  $C(\phi - 1)$  équations
- Conclusion:  $V = C + 2 - \phi$

Thermodynamique

The variance of a thermodynamic system is the number of factors that can be changed independently from each other without breaking the balance. Let be a system  $S$  including its constituents. We will assume here that there is no chemical reaction between the constituents that we can throw constituents and phase. The number of variables here is  $C$  if plus two. We count these concentrations in each phase, which implies these variables and the two variables temperature and pressure. Selfie also corresponds to the concentrations in each side. And two corresponds to the variables temperature and pressure. The system also offers more its times an equation. The first equation are given by the conservation of matter left once in equation. Are given by the equality of the chemical potentials by species. Variance. Which is given by the difference between the number of equations and the number of variables is equal to  $c$  plus two minus fit.

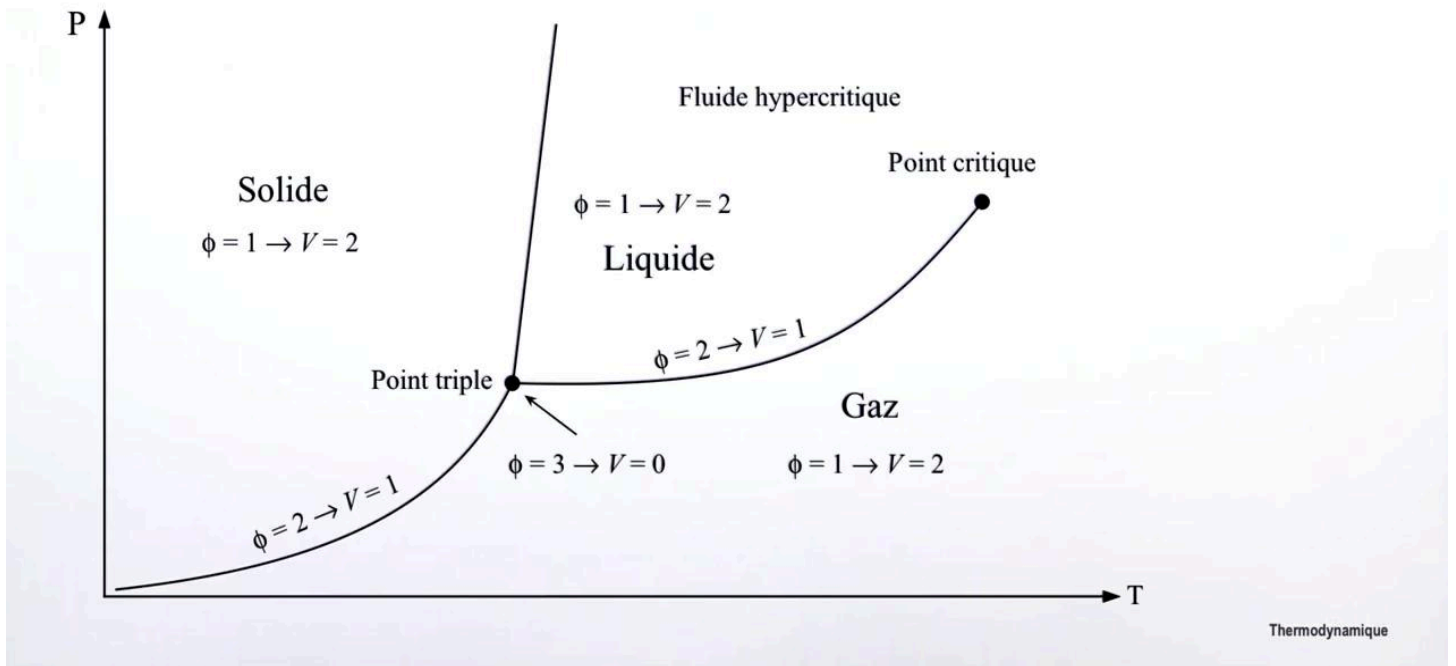
Notes

Summary



11m 06s

# Variance d'un corps pur (c=1)



Let us apply this variance rule to a pure body. In the equilibrium domain of solids, we will write that  $\phi$  is equal to one. There is only one phase, it is equal to one since we have even more. We obtain  $v$  the variance which is equal to two. We can therefore here independently, vary two factors the temperature and pressure, and remain in the equilibrium domain of solids. Let's put ourselves on the equilibrium curve of two phases. Liquid gas for example. On this curve, we have  $\phi$  equal to two since we have gas and liquid water  $c$  is equal to one. As previously stated, the variance rule gives us  $V$  equal to one. This unit variance indicates that only one parameter can be changed. If we change a second independent of the first, we will switch to either the vapor or the liquid phase. To stay on the equilibrium curve. Only one parameter can be changed at a time. In an analogous way, we calculate  $V$  equal to zero at the triple point. This means that there is only one PT couple that allows to realize this point.

Notes

Summary



# Transitions de phase du premier ordre



- Classification des transitions de phase
- Etude des transitions courantes

Thermodynamique

We have reached the end of this module. Or we filed. The different transitions in two large groups, first and second, and we studied common transitions. Next time, we will come back in more detail on the liquid-vapor transition. By observing the wine model of the wines. Thank you for your attention.

Notes

Summary



14m 19s