

# **[119] Θερμοδυναμική Ι**

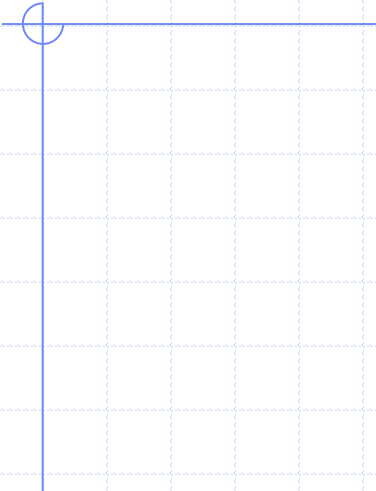
## **Τρίτο Θερμοδυναμικό Αξίωμα**

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***Εισαγωγή...***



# Εισαγωγή...

## 3<sup>rd</sup> Law of thermodynamics

The **third law of thermodynamics** is sometimes stated as follows, regarding the properties of systems in equilibrium at absolute zero temperature:

- ***“The entropy of a perfect crystal at absolute zero is exactly equal to zero”***

The Nernst–Simon statement of the third law of thermodynamics concerns thermodynamic processes at a fixed, low temperature:

- ***“The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K”***

Here a condensed system refers to liquids and solids

A classical formulation by Nernst (actually a consequence of the Third Law) is:

- ***“It is impossible for any process, no matter how idealized, to reduce the entropy of a system to its absolute-zero value in a finite number of operations”***

Physically, the Nernst–Simon statement implies that it is impossible for any procedure to bring a system to the absolute zero of temperature in a finite number of steps

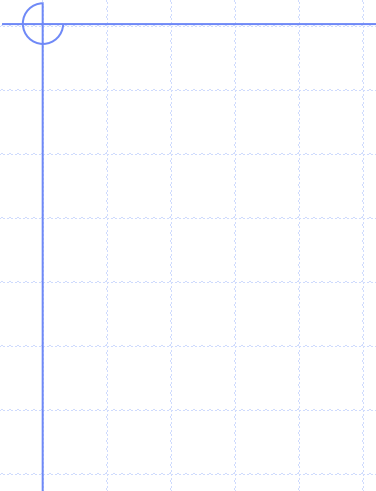


# Εισαγωγή...

## 3<sup>rd</sup> Law of thermodynamics

- ❑ At absolute zero (zero Kelvin), the system must be in a state with the minimum possible energy, and the above statement of the third law holds true provided that the perfect crystal has only one minimum energy state
- ❑ Entropy is related to the number of accessible microstates, and for a system consisting of many particles, quantum mechanics indicates that there is only one unique state (called the ground state) with minimum energy
- ❑ If the system does not have a well-defined order (if its order is glassy, for example), then in practice there will remain some finite entropy as the system is brought to very low temperatures as the system becomes locked into a configuration with non-minimal energy
- ❑ The constant value is called the residual entropy





***Ιστορία...***



# Ιστορία...

## 3<sup>rd</sup> Law of thermodynamics

- ❑ The 3<sup>rd</sup> law was developed by the chemist Warther Nernst during the years 1906–12, and is therefore often referred to as **Nernst's theorem** or **Nernst's postulate**
- ❑ The third law of thermodynamics states that the entropy of a system at absolute zero is a well-defined constant
- ❑ This is because a system at zero temperature exists in its ground state, so that its entropy is determined only by the degeneracy of the ground state
- ❑ In 1912 Nernst stated the law thus: "*It is impossible for any procedure to lead to the isotherm  $T = 0$  in a finite number of steps*"



# Ιστορία...

## 3<sup>rd</sup> Law of thermodynamics

An alternative version of the third law of thermodynamics as stated by Gilbert N. Lewis and Merle Randall in 1923:

- ❑ "If the entropy of each element in some (perfect) crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances"
- ❑ This version states *not only  $\Delta S$  will reach zero at 0 K, but  $S$  itself will also reach zero* as long as the crystal has a ground state with only one configuration
- ❑ Some crystals form defects which causes a residual entropy
- ❑ This residual entropy disappears when the kinetic barriers to transitioning to one ground state are overcome





# Ιστορία...

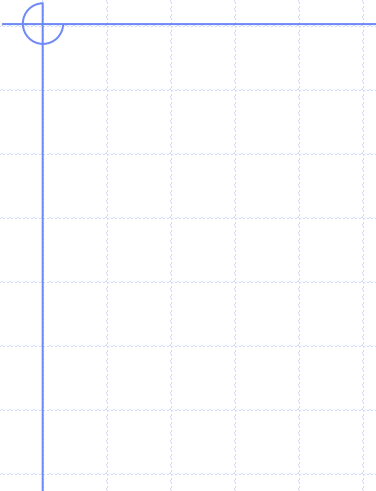
## 3<sup>rd</sup> Law of thermodynamics

- ❑ With the development of statistical mechanics, the third law of thermodynamics (like the other laws) changed from a *fundamental* law (justified by experiments) to a *derived* law (derived from even more basic laws)
- ❑ The basic law from which it is primarily derived is the statistical-mechanics definition of entropy for a large system:

$$S - S_0 = k_B \ln \Omega$$

- ❑ where  $S$  is entropy,  $k_B$  is the Boltzmann constant, and  $\Omega$  is the number of microstates consistent with the macroscopic configuration
- ❑ The counting of states is from the reference state of absolute zero, which corresponds to the entropy of  $S_0$





***Ερμηνεία...***



# Ερμηνεία...

- ❑ In simple terms, the third law states that the entropy of a perfect crystal of a pure substance approaches zero as the temperature approaches zero
- ❑ The alignment of a perfect crystal leaves no ambiguity as to the location and orientation of each part of the crystal
- ❑ As the energy of the crystal is reduced, the vibrations of the individual atoms are reduced to nothing, and the crystal becomes the same everywhere
- ❑ The third law provides **an absolute reference point** for the determination of entropy at any other temperature
- ❑ The entropy of a system, determined relative to this zero point, is then the **absolute** entropy of that system
- ❑ Mathematically, the absolute entropy of any system at zero temperature is the natural log of the number of ground states times Boltzmann's constant  $k_B = 1,38 \times 10^{-23} \text{ JK}^{-1}$



# Ερμηνεία...

- ❑ The entropy of a *perfect* crystal lattice as defined by Nernst's theorem is zero provided that its ground state is unique, because  $\ln(1) = 0$
- ❑ If the system is composed of one-billion atoms, all alike, and lie within the matrix of a perfect crystal, the number of permutations of one-billion identical things taken one-billion at a time is  $\Omega = 1$

- ❑ Hence:

$$S - S_0 = k_B \ln \Omega = k_B \ln 1 = 0$$

- ❑ The difference is zero, hence the initial entropy  $S_0$  can be any selected value so long as all other such calculations include that as the initial entropy. As a result the initial entropy value of zero is selected  $S_0 = 0$  is used for convenience

$$S - S_0 = S - 0 = 0 \Rightarrow S = 0$$



# Ερμηνεία...

- By way of example, suppose a system consists of 1 cm<sup>3</sup> of matter with a mass of 1 g and 20 g/mol. The system consists of 3x10<sup>22</sup> identical atoms at 0 K. If one atom should absorb a photon of wavelength of 1 cm that atom is then unique and the permutations of one unique atom among the 3x10<sup>22</sup> is N=3x10<sup>22</sup>. The entropy, energy, and temperature of the system rises and can be calculated. The entropy change is:

$$\Delta S = S - S_0 = k_B \ln \Omega$$

- From the second law of thermodynamics:

$$\Delta S = S - S_0 = \frac{\delta Q}{T}$$

- Hence:

$$\Delta S = S - S_0 = k_B \ln(\Omega) = \frac{\delta Q}{T}$$



# Ερμηνεία...

- Calculating entropy change:

$$S - 0 = k_B \ln N = 1.38 \cdot 10^{-23} \ln 3 \cdot 10^{22} = 70 \cdot 10^{-23}$$

- The energy change of the system as a result of absorbing the single photon whose energy is  $\varepsilon$ :

$$\delta Q = \varepsilon = \frac{hc}{\lambda} = \frac{6.62 \cdot 10^{-34} \text{ Js} \cdot 2 \cdot 10^8 \text{ ms}^{-1}}{0.01} = 2 \cdot 10^{-23} \text{ J}$$

- The temperature of the system rises by:

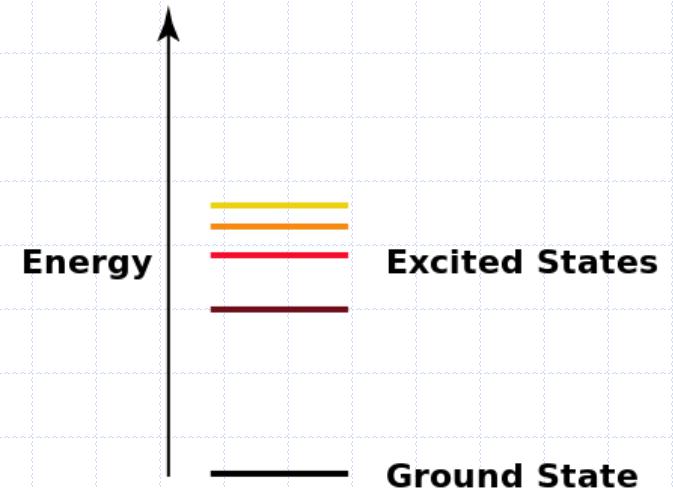
$$T = \frac{\varepsilon}{\Delta S} = \frac{2 \cdot 10^{-23} \text{ J}}{70 \cdot 10^{-23} \text{ JK}^{-1}} = \frac{1}{35} \text{ K}$$

- This can be interpreted as the average temperature of the system over the range from  $0 < S < 70 \cdot 10^{-23} \text{ J/K}$
- A single atom was assumed to absorb the photon but the temperature and entropy change characterizes the entire system



# Ερμηνεία...

- ❑ An example of a system which does not have a unique ground state is one whose net spin is a half-integer, for which time-reversal symmetry gives two degenerate ground states
- ❑ For such systems, the entropy at zero temperature is at least  $k_B \ln(2)$  (which is negligible on a macroscopic scale). Some crystalline systems exhibit geometrical frustration, where the structure of the crystal lattice prevents the emergence of a unique ground state
- ❑ Ground-state helium (unless under pressure) remains liquid
- ❑ In addition, glasses and solid solutions retain large entropy at 0 K, because they are large collections of nearly degenerate states, in which they become trapped out of equilibrium. Another example of a solid with many nearly-degenerate ground states, trapped out of equilibrium, is ice Ih, which has "proton disorder"



Ice one  
h



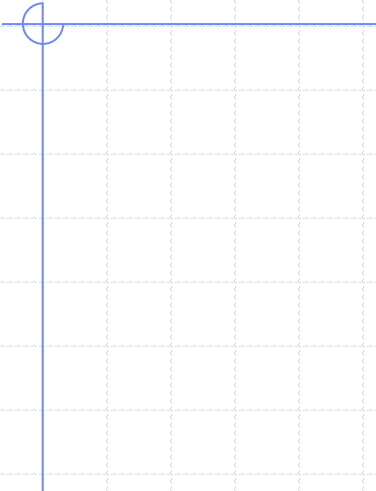


# Ερμηνεία...

- ❑ For the entropy at absolute zero to be zero, the magnetic moments of a perfectly ordered crystal must themselves be perfectly ordered; from an entropic perspective, this can be considered to be part of the definition of a “perfect crystal”
- ❑ Only ferromagnetic, antiferromagnetic, and diamagnetic materials can satisfy this condition
- ❑ However, ferromagnetic materials do not in fact have zero entropy at zero temperature, because the spins of the unpaired electrons are all aligned and this gives a ground-state spin degeneracy
- ❑ Materials that remain paramagnetic at 0 K, by contrast, may have many nearly-degenerate ground states (for example, in a spin glass), or may retain dynamic disorder (a quantum spin liquid)







***Μαθηματική διατύπωση...***

# Μαθηματική διατύπωση...

- Consider a closed system in internal equilibrium; as the system is in equilibrium, there are no irreversible processes so the entropy production is zero
- During slow heating, small temperature gradients are generated in the material, but the associated entropy production can be kept arbitrarily low if the heat is supplied slowly enough
- The increase in entropy due to the added heat  $\delta Q$  is then given by the second part of the 2<sup>nd</sup> law of thermodynamics which states that the entropy change of a system  $\Delta S$  is given by

$$\Delta S = S - S_0 = \frac{\delta Q}{T} \Rightarrow \Delta S = \frac{C(T, X)dT}{T} \Rightarrow S(T, X) = S(T_0, X) + \int_{T_0}^T \frac{C(T', X)}{T'} dT'$$
$$\delta Q = C(T, X)dT$$

- The parameter  $X$  is a symbolic notation for all parameters (such as pressure, magnetic field, liquid/solid fraction, etc.) which are kept constant during the heat supply. E.g. if the volume is constant we get the heat capacity at constant volume  $C_v$ . In the case of a phase transition from liquid to solid, or from gas to liquid the parameter  $X$  can be one of the two components



# Μαθηματική διατύπωση...

- The mathematical formulation of the third law includes three steps:

1: in the limit  $T_0 \rightarrow 0$  the integral in Eq.(4) is finite. So that we may take  $T_0=0$  and write

$$S(T, X) = S(0, X) + \int_0^T \frac{C(T', X)}{T'} dT'$$

2. the value of  $S(0, X)$  is independent of  $X$ . In mathematical form

$$S(0, X) = S(0) \quad \text{or} \quad \lim_{T \rightarrow 0} \left( \frac{\partial S(T, X)}{\partial X} \right) = 0$$

- So the equation above can be further simplified to

$$S(T, X) = S(0) + \int_0^T \frac{C(T', X)}{T'} dT'$$

- In words: at absolute zero all isothermal processes are isentropic. Equation is the mathematical formulation of the third law.



# Μαθηματική διατύπωση...

3: Classically, one is free to choose the zero of the entropy, and it is convenient to take

$$S(0) = 0 \quad \text{so} \quad S(T, X) = \int_0^T \frac{C(T', X)}{T'} dT'$$

- However, reinterpreting  $S(0) = 0$  in view of the quantized nature of the lowest-lying energy states, the physical meaning of the equation goes deeper than just a convenient selection of the zero of the entropy. It is due to the perfect order at zero kelvin as explained above



***Συνέπειες του 3<sup>ου</sup>  
Θερμοδυναμικού  
αξιώματος...***

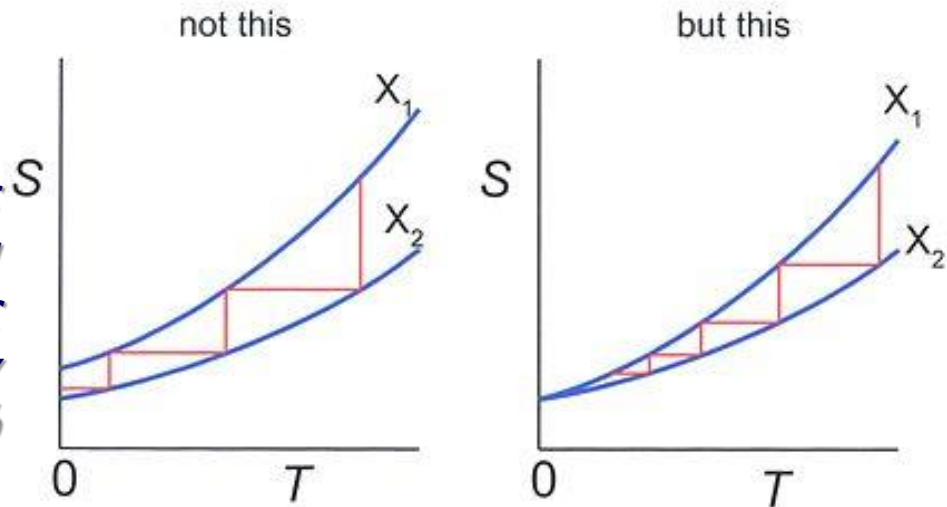


# Συνέπειες του 3<sup>ου</sup> Θερμοδυναμικού αξιώματος...

## Απόλυτο μηδέν (Absolute zero)

□ Το 3<sup>ο</sup> Θερμοδυναμικό αξίωμα είναι ισοδύναμο με την διατύπωση

*"Είναι αδύνατο με οποιαδήποτε διεργασία, ιδανική ή μη, να μειωθεί η θερμοκρασία ενός συστήματος στο απόλυτο μηδέν με πεπερασμένο αριθμό πεπερασμένων διεργασιών"*



The reason that  $T = 0$  cannot be reached according to the 3<sup>rd</sup> law is explained as :

- Suppose that the temperature of a substance can be reduced in an isentropic process by changing the parameter  $X$  from  $X_2$  to  $X_1$
- One can think of a multistage nuclear demagnetization setup where a magnetic field is switched on and off in a controlled way
- If there were an entropy difference at absolute zero,  $T=0$  could be reached in a finite number of steps
- However, at  $T = 0$  there is no entropy difference so an infinite number of steps would be needed (the process is illustrated in Figure)



# ΣΥΝΕΠΕΙΕΣ ΤΟΥ 3<sup>ου</sup> ΘΕΡΜΟΔΥΝΑΜΙΚΟΥ ΑΞΙΩΜΑΤΟΣ...

## Ειδική θερμότητα (Specific heat)

- A non-quantitative description of his third law that Nernst gave at the very beginning was simply that the specific heat can always be made zero by cooling the material down far enough. A modern, quantitative analysis follows
- Suppose that the heat capacity of a sample in the low temperature region has the form of a power law  $C(T, X) = C_0 T^\alpha$  asymptotically as  $T \rightarrow 0$ , and we wish to find which values of  $\alpha$  are compatible with the third law. We have

$$\int_{T_0}^T \frac{C(T', X)}{T'} dT' = \frac{C_0}{\alpha} (T^\alpha - T_0^\alpha)$$

- By the discussion of third law (above), this integral must be bounded as  $T_0 \rightarrow 0$ , which is only possible if  $\alpha > 0$ . So the heat capacity must go to zero at absolute zero

$$\lim_{T \rightarrow 0} C(T, X) = 0$$

if it has the form of a power law

- The same argument shows that it cannot be bounded below by a positive constant, even if we drop the power-law assumption





# ΣΥΝΕΠΕΙΕΣ ΤΟΥ 3<sup>ου</sup> ΘΕΡΜΟΔΥΝΑΜΙΚΟΥ ΑΞΙΩΜΑΤΟΣ...

## Ειδική θερμότητα (Specific heat)

- On the other hand, the molar specific heat at constant volume of a monatomic classical ideal gas, such as helium at room temperature, is given by  $C_V=(3/2)R$  with  $R$  the molar ideal gas constant. But clearly a constant heat capacity does not satisfy Eq. (12). That is, a gas with a constant heat capacity all the way to absolute zero violates the third law of thermodynamics. We can verify this more fundamentally by substituting  $C_V$  receiving:

$$S(T, X) = S(T_0, V) + \frac{3}{2} R \ln \frac{T}{T_0}$$

- In the limit  $T_0 \rightarrow 0$  this expression diverges, again contradicting the third law of thermodynamics





# ΣΥΝΕΠΕΙΕΣ ΤΟΥ 3<sup>ου</sup> Θερμοδυναμικού αξιώματος...

## Ειδική θερμότητα (Specific heat)

The conflict is resolved as follows:

- ❑ At a certain temperature the quantum nature of matter starts to dominate the behavior
- ❑ Fermi particles follow Fermi-Dirac statistics and Bose particles follow Bose-Einstein statistics
- ❑ In both cases the heat capacity at low temperatures is no longer temperature independent, even for ideal gases. **For Fermi gases**

$$C_V = \frac{\pi^2}{2} R \frac{T}{T_F}$$

with Fermi temperature  $T_F$  given by:

$$T_F = \frac{1}{8\pi^2} \frac{N_A^2 h^2}{MR} \left( \frac{3\pi^2 N_A}{V_m} \right)^{2/3}$$

Here  $N_A$  is Avogadro number,  $V_m$  the molar volume, and  $M$  the molar mass



# ΣΥΝΕΠΕΙΕΣ ΤΟΥ 3<sup>ου</sup> ΘΕΡΜΟΔΥΝΑΜΙΚΟΥ ΑΞΙΩΜΑΤΟΣ...

## Ειδική θερμότητα (Specific heat)

### □ For Bose gases

$$C_V = 1.93 R \left( \frac{T}{T_B} \right)^{3/2}$$

with  $T_B$  given by:

$$T_B = \frac{1}{11.9} \frac{N_A^2 h^2}{MR} \left( \frac{N_A}{V_m} \right)^{2/3}$$

Here  $N_A$  is Avogadro number,  $V_m$  the molar volume, and  $M$  the molar mass

- The specific heats given by the equations above, both satisfy equation  $\lim_{T \rightarrow 0} C(T, X) = 0$
- Indeed, they are power laws with  $\alpha = 1$  and  $\alpha = 3/2$  respectively



# ΣΥΝΕΠΕΙΕΣ ΤΟΥ 3<sup>ου</sup> ΘΕΡΜΟΔΥΝΑΜΙΚΟΥ ΑΞΙΩΜΑΤΟΣ...

## Τάση ατμών (Vapor pressure)

- The only liquids near absolute zero are <sup>3</sup>He and <sup>4</sup>He. Their heat of evaporation has a limiting value given by

$$L = L_0 + C_p T$$

with  $L_0$  and  $C_p$  constant. If we consider a container, partly filled with liquid and partly gas, the entropy of the liquid–gas mixture is

$$S(T, x) = S_l(T) + x \left( \frac{L_0}{T} + C_p \right)$$

where  $S_l(T)$  is the entropy of the liquid and  $x$  is the gas fraction

- Clearly the entropy change during the liquid–gas transition ( $x$  from 0 to 1) diverges in the limit of  $T \rightarrow 0$ , which, violates the mathematical expression of the 3<sup>rd</sup> law
- Nature solves this paradox as follows: at temperatures below about 50 mK the vapor pressure is so low that the gas density is lower than the best vacuum in the universe. In other words: **below 50 mK there is simply no gas above the liquid**



# ΣΥΝΕΠΕΙΕΣ ΤΟΥ 3<sup>ου</sup> ΘΕΡΜΟΔΥΝΑΜΙΚΟΥ ΑΞΙΩΜΑΤΟΣ...

## Λανθάνουσα θερμότητα τήξης (Latent heat of melting)

- ❑ The melting curves of  $^3\text{He}$  and  $^4\text{He}$  both extend down to absolute zero at finite pressure
- ❑ At the melting pressure liquid and solid are in equilibrium
- ❑ The third law demands that the entropies of the solid and liquid are equal at  $T=0$
- ❑ As a result the latent heat of melting is zero and the slope of the melting curve extrapolates to zero as a result of the Clausius-Clapeyron equation

$$S(T, x) = S_l(T) + x \left( \frac{L_0}{T} + C_P \right)$$

$$L = L_0 + C_P T$$



# Συνέπειες του 3<sup>ου</sup> Θερμοδυναμικού αξιώματος...

## Συντελεστής θερμικής διαστολής (Thermal expansion coefficient)

- ❑ Thermal expansion coefficient is defined as  $\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$
- ❑ With the Maxwell relation  $\left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S_m}{\partial P} \right)_T$
- ❑ With  $X = p$ , equation  $\lim_{T \rightarrow 0} C(T, X) = 0$
- ❑ Is shown that  $\lim_{T \rightarrow 0} \beta = 0$
- ❑ So, the thermal expansion coefficient of all materials must go to zero at zero Kelvin



# The third law of thermodynamics...

## Θεώρημα Nervst

- Η μεταβολή της εντροπίας που συνοδεύει κάθε φυσικό ή χημικό μετασχηματισμό κρυσταλλικών σωμάτων προσεγγίζει το μηδέν όταν η θερμοκρασία προσεγγίζει το απόλυτο μηδέν:

$$\Delta S \rightarrow 0 \text{ όταν } T \rightarrow 0$$

## Τρίτο Θερμοδυναμικό Αξίωμα

- Εάν για τα κρυσταλλικά στοιχεία σε θερμοκρασία  $T = 0$ , οριστεί η τιμή της εντροπίας μηδέν, τότε:

“Στο απόλυτο μηδέν ( $T = 0 \text{ K}$ ), η εντροπία όλων των κρυσταλλικών σωμάτων είναι ίση με μηδέν”

“Οι εντροπίες που αναφέρονται με βάση ότι  $S(0) = 0$ , ονομάζονται εντροπίες του *Τρίτου Θερμοδυναμικού Αξιώματος*”



***Ενέργεια Gibbs –  
Helmholtz ...***



# Ενέργεια Gibbs – Helmholtz ...

## □ Μετασχηματισμός Legendre

Μαθηματικός τελεστής της μορφής:

$$g=f-f_1x_1$$

όπου  $f=f(x_1, x_2, x_3, \dots, x_n)$  είναι μια καταστατική συνάρτηση με ολικό διαφορικό:

$$df=f_1dx_1+f_2dx_2+f_3dx_3+\dots+f_ndx_n \quad \text{και} \quad f_i=\left(\frac{\partial f}{\partial x_i}\right)_{x_j \neq x_i}$$

Η εφαρμογή του μετασχηματισμού Legendre σε μια συνάρτηση οδηγεί σε μια νέα συνάρτηση η οποία διαφέρει από την πρώτη κατά μία ανεξάρτητη μεταβλητή. Έτσι η εφαρμογή του μετασχηματισμού Legendre στην συνάρτηση  $f$  δίνει:

$$dg=df-f_1dx_1-x_1df_1$$

δηλαδή:

$$dg=-x_1df_1+f_2dx_2+f_3dx_3+\dots+f_ndx_n=\phi(f_1, x_2, x_3, \dots, x_n)$$





# Ενέργεια Gibbs – Helmholtz ...

- Εφαρμογή του μετασχηματισμού Legendre στην θεμελιώδη σχέση  $dU=TdS-PdV$

Η εσωτερική ενέργεια  $U$  είναι συνάρτηση των  $S$  και  $V$ ,  $U=U(S,V)$ . Άρα το ολικό διαφορικό της είναι:

$$dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV$$

Εφαρμόζοντας τον μετασχηματισμό Legendre παίρνουμε:

$$g = U - \left( \frac{\partial U}{\partial S} \right)_V \cdot S = U - TS$$

Η ποσότητα  $U-TS$  αντιπροσωπεύει μια νέα θερμοδυναμική καταστατική συνάρτηση που ονομάζεται **ενέργεια Helmholtz, A**:

$$A = U - T \cdot S$$

- Εφαρμογή του μετασχηματισμού Legendre στην θεμελιώδη σχέση  $dH=TdS+VdP$

Με τον ίδιο τρόπο:

$$g = H - \left( \frac{\partial H}{\partial S} \right)_P \cdot S = H - TS$$

Η ποσότητα  $H-TS$  αντιπροσωπεύει μια νέα θερμοδυναμική καταστατική συνάρτηση που ονομάζεται **ενέργεια Gibbs, G**:

$$G = H - T \cdot S$$



***Κριτήρια αυθόρμητων  
μεταβολών & εξισώσεις  
Maxwell...***



# Κριτήρια αυθόρμητων μεταβολών & εξισώσεις Maxwell...

## ▣ Αυθόρμητη μεταβολή

Σύμφωνα με την ανισότητα του Clausius για ένα σύστημα σε ισορροπία με το περιβάλλον σε θερμοκρασία  $T$ :

$$dS - \frac{dQ}{T} \geq 0$$

- ✓ Μεταβολή υπό σταθερό όγκο ( $dQ_V = dU$ ):  $dS - \frac{dU}{T} \geq 0 \Rightarrow TdS \geq dU$  ( $V = \text{σταθερός}$ )
- ✓ Μεταβολή υπό σταθερή πίεση ( $dQ_P = dH$ ):  $dS - \frac{dH}{T} \geq 0 \Rightarrow TdS \geq dH$  ( $P = \text{σταθερή}$ )

Επομένως, με βάση τους ορισμούς των ενεργειών Gibbs και Helmholtz για σταθερή  $T$  ( $dA = dU - TdS$  και  $dG = dH - TdS$ ), τα κριτήρια για αυθόρμητες μεταβολές είναι:

$$dA_{T,V} \leq 0 \quad \text{και} \quad dG_{T,P} \leq 0$$

- *Η ενέργεια Gibbs είναι πιο συνηθισμένη από την ενέργεια Helmholtz γιατί συνήθως τα πειράματα πραγματοποιούνται υπό σταθερή πίεση (και όχι σταθερό όγκο). Έτσι για να είναι αυθόρμητη μια χημική αντίδραση που λαμβάνει χώρα σε σταθερή θερμοκρασία και πίεση θα πρέπει να μειώνεται η ενέργεια Gibbs!*



# Κριτήρια αυθόρμητων μεταβολών & εξισώσεις Maxwell...

## □ Κριτήριο Euler

Για μια συνάρτηση  $f=f(x,y)$  μπορεί να γραφεί ότι  $df=gdx+hdy$  όπου τα  $g$  και  $h$  είναι επίσης συναρτήσεις των  $x$  και  $y$ . Το μαθηματικό κριτήριο έτσι ώστε το  $df$  να είναι ολικό διαφορικό (με την έννοια ότι το ολοκλήρωμά του εξαρτάται μόνο από την αρχική και τελική κατάσταση) είναι:

$$\left(\frac{\partial g}{\partial y}\right)_x = \left(\frac{\partial h}{\partial x}\right)_y$$

✓ Εφαρμόζοντας το κριτήριο Euler στις βασικές διαφορικές εκφράσεις των  $U$ ,  $H$ ,  $A$  και  $G$ :

$$dU = TdS - PdV, \quad dH = VdP + TdS$$

$$dA = -PdV - SdT, \quad dG = VdP - SdT$$

λαμβάνουμε τις εξισώσεις Maxwell:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$



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# Θερμοδυναμική Ι

ΕΥΧΑΡΙΣΤΩ ΓΙΑ ΤΗΝ ΠΡΟΣΟΧΗ ΣΑΣ!

