Ministry of Higher Education
and Scientific Research

Al-Muthanna University

College of Science

Department of Chemistry

Quantum Chemistry

- The sixth lecture -

Stage 4

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Oscillator energy varage

According to quantum mechanics, the oscillator's energy rate can be calculated through the Planck hypothesis and the Boltzman Act:

$$\bar{E} = \frac{hy}{e^{hy/KT} - 1} \ldots\ldots\ldots (1)$$

But in high temperatures the energy rate was found to be equal to KT because: -

$$e^{hy/KT} \approx 1 + e^{hy/KT}$$

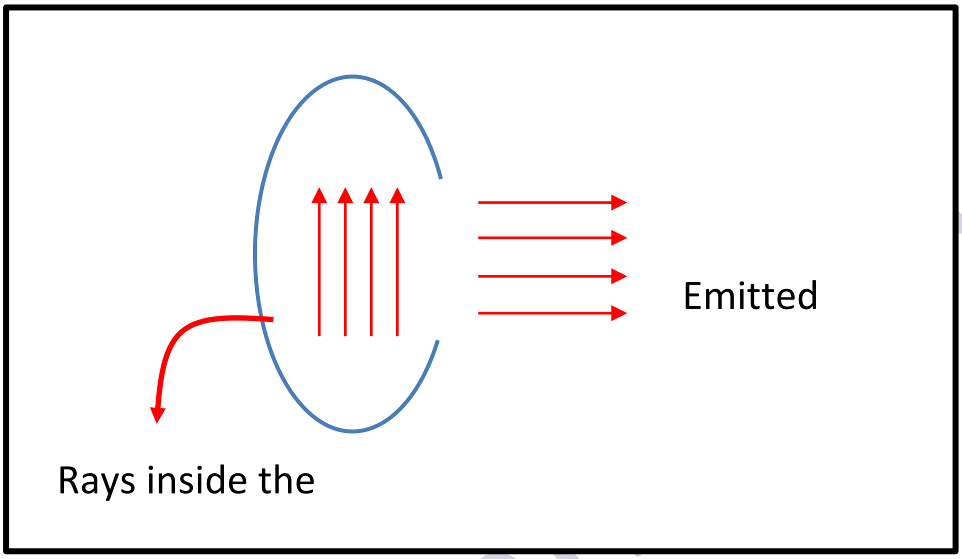
where

$$KT \gg hy$$

$$\bar{E} = \frac{hy}{\cancel{1} + e^{\frac{hy}{KT}} - \cancel{1}} \Rightarrow$$

$\boldsymbol{\bar{E} = KT}$ Oscillator energy

Energy density p^d



It is the energy in the unit of size symbolized by ϕ_y in the frequency allowance and ϕ_ϕ by the wavelength allowance, and theamount represents the energy by unit of size at the $(\rho_y + \rho_{\bar{y}})$y frequency within a range of dy frequencies.

Therefore, the energy density within the radiation gap is given in the following equation:

(derived on the basis of the oscillation energy rate and the number of stable waves within the gap so we deduce the energy by the frequency allowance)

$$\rho_y = \frac{8\pi h y^3}{c^3} \cdot \frac{1}{e^{hy/KT} - 1}$$

It can be expressed by wavelength.

$$\rho_\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda KT} - 1}$$

Instead of the wave number, it becomes:

$$\rho_{\bar{y}} = 8\pi hc\bar{y}^3 \cdot \frac{1}{e^{hc\bar{y}/KT} - 1}$$

The energy emitted from the gap is more concerned with the density within the gap than the density within the gap and is called the energy emitted.

Spectroscopic focus of radiation (M): M_y is symbolized by the frequency allowance and M_ϕ by the wavelength and M_ϕ instead of wavelength, thus obtaining the energy density emitted or released (this is done by multiplying the energy density within the gap in the amount of a quarter of the speed of light) $(\frac{c}{4})$so we conclude the following relationship:

$$M_y = \frac{c}{4} * \rho_y = \frac{2\pi h y^3}{c^2} \cdot \frac{1}{e^{hy/KT} - 1}$$

$$M_\lambda = \frac{c}{4} * \rho_\lambda = \frac{2\pi h c^2}{\lambda^5} \cdot \frac{1}{e^{hc/\lambda KT} - 1}$$

$$M_{\bar{y}} = \frac{c}{4} * \rho_{\bar{y}} = 2\pi c^2 \bar{y}^3 \cdot \frac{1}{e^{hc\bar{y}/KT} - 1}$$

Applications of black body radiation

Application of block-body radiation

Heat of capicities for sloid

1. Dowling theory and Petit theory

to find atomic thermal capacity according to this theory of solid state elements that are equal to a fixed value $6.2\ cal\ deg^{-1} \cdot g \cdot Atom^{-1}$

But with a ≈ size of 5.9. This method is useful after knowing a variable between two foundations: quantity heat and change of temperature

$$\Delta T = T_f - T_i$$

where

$$q \propto \Delta T$$

$$q = C\,\Delta T$$

C: Capacity capacity and thermal capacity is associated

with s_p specific heat in relation

$$C = S_p * m$$

So practically the amount of heat can be found in the

price

$$q = S_p \cdot m \cdot \Delta T$$

But when the pressure is proven, $q = \Delta H$

The worlds Doling and Bitt thus found this method

useful for identifying the approximate atomic weights

of some solid metal elements.

It is a new way to determine atomic weight as it depends on the atomic temperature of metals being close and that their average = 6.2 at temperatures 20-100 SLis, so the atomic heat of the metal (the amount of heat needed to raise the temperature of one mole of the element is one degree Celsius) and equal to the product of multiplying the quality temperature of the metal in the approximate atomic weight i.e.

$$6.2 = S_p * Aw\ A(Atomic\ Weight\ Approximatly)$$

Approximate atomic weight

$$\therefore\ M = \frac{Aw\ A}{eq.w}$$

Equal

E :- Equivalent Weight

eq :- equivelant Weight

$Aw = M * eq.w$ (Atomic Weight exactly)

The thermal capacity is therefore fixed for solid elements and according to the laws of conventional physics.

The material is one of the oscillators of any oscillation atoms around their poise positions, which are in the three directions equally and each atom has three degrees of freedom.

There is 3N of the degree of freedom of oscillation movement and according to the principle of equal energy distribution and thus for each oscillation movement of energy amount KT Where this movement consists of two kinetic and latent limits and each limit has half the amount of energy KT That is,:

Mobility

$$\frac{1}{2}KT + \frac{1}{2}KT = KT$$

Therefore, the value is fixed and the total energy of N_A of atoms represents the number of Avocadro, so the relationship above can be represented.

$$E = 3NKT = 3RT$$

Therefore, the thermal capacity of the mules can be found in the following relationship:

$$C_v = \left(\frac{\Delta E}{\Delta T}\right)_v = 3R$$

This relationship proves the thermal capacity does not depend on the temperature and its fixed value is equal to = 6.2 i.e. the Law of Dowling and Bitt can be used to determine the approximate atomic weight if the quality heat is inverted.

But through practical data experiment, the thermal capacity is based on temperature according to practical measurements and it reaches its highest value of 3R and this value can be reduced to zero when approaching absolute zero.

In addition, there are many elements where the value of thermal capacity is less than 3R and to explain these facts presented Einstein in 1907 is based on the quantum theory of Plank.

2. Einstein Theory

Einstein assumed all atoms were oscillated with the same oscillation of the element, but with different displacements (frequencies) at low temperatures, most atoms had little or no energy, thus contributing to a small thermal capacity.

$$E = nhy \cdots\cdots\cdots (1)$$

But the oscillation power rate by quantum mechanics

$$\bar{E} = \frac{h\gamma c}{e^{h\gamma c/KT} - 1} \cdots\cdots\cdots (2)$$

But for one ln of atoms, each atom has three degrees of oscillating thermal (x,y,z), we get 3N of oscillating temperatures and depending on the relationship:

$$E = 3N\bar{E} \cdots\cdots\cdots\cdots\cdots (3)$$

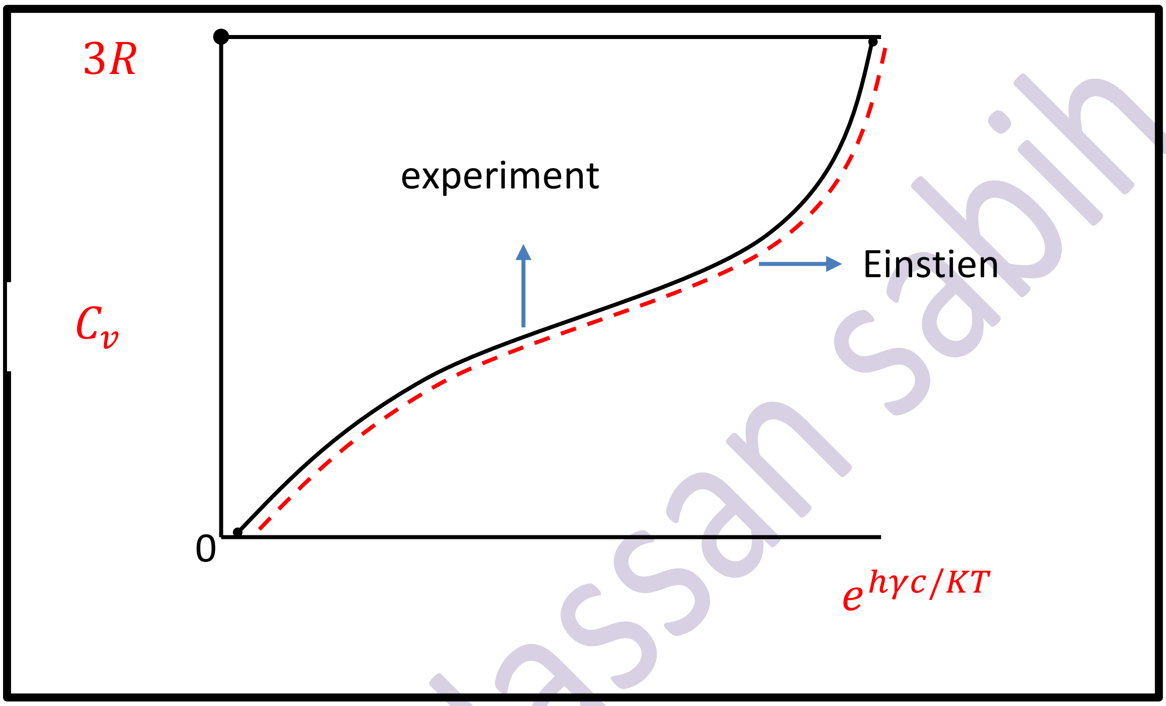
Compensation (2) in (3)

$$E = 3N * \frac{h\gamma c}{e^{h\gamma c/KT} - 1} \cdots\cdots\cdots\cdots (4)$$

$y = \frac{h\gamma c}{e^{h\gamma c/KT}}$R=NK, we impose

$$C_v = \left(\frac{\Delta E}{\Delta T}\right)_v = 3Re^y \cdot y^2(e^y - 1) \cdots\cdots (5)$$

Clear from equation 5 the reliance of thermal capacity on temperature can be explained by the followingchart:



The Einstein equation gives significant results as is evident from the shape but below the practical values.

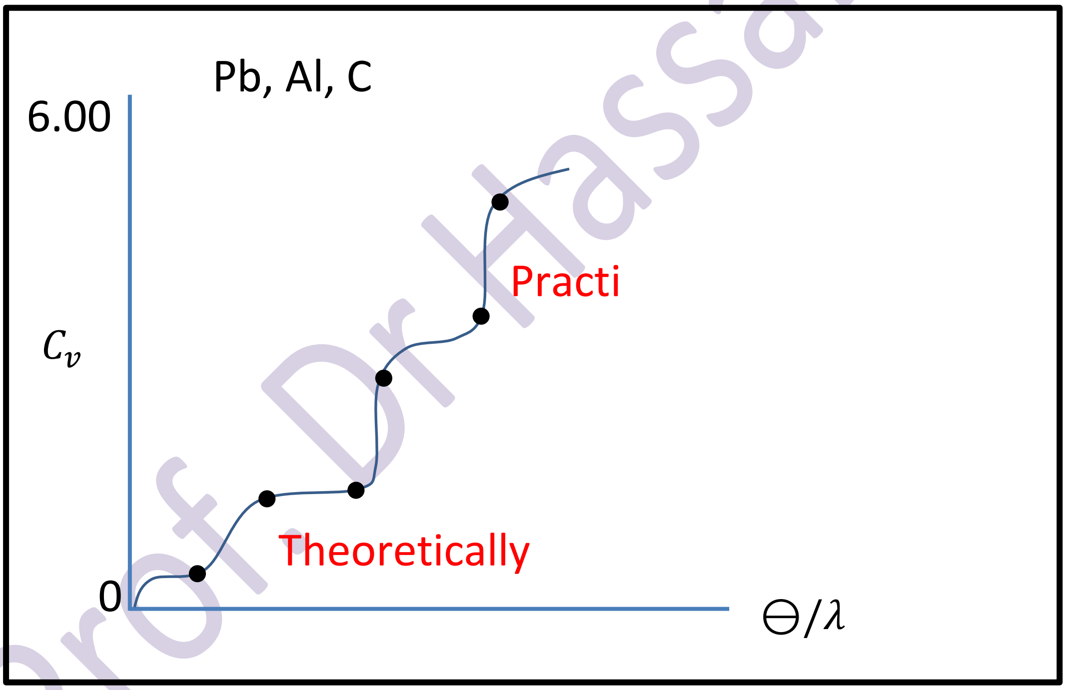
3. Debey Theory

The world assumed that the frequencies of the element's atoms were not fixed (not all atoms the element is the same frequency) but the atoms of the element vary in frequency And take Values from zero to highest value depend on the solid method i.e. the frequency of the atoms of the two elements of $(\gamma_0 - \gamma_{max})$ On this basis, Depay derived an equation showing the adoption of atomic thermal capacity by a temperature-based stabilization that is the most important conclusion of the Depay equation (the thermal capacity of an element at temperature is a function of a certain amount called thermal grade). Distinctive)

$\ominus$: $- \, charichtiri \; zation \; Temp$

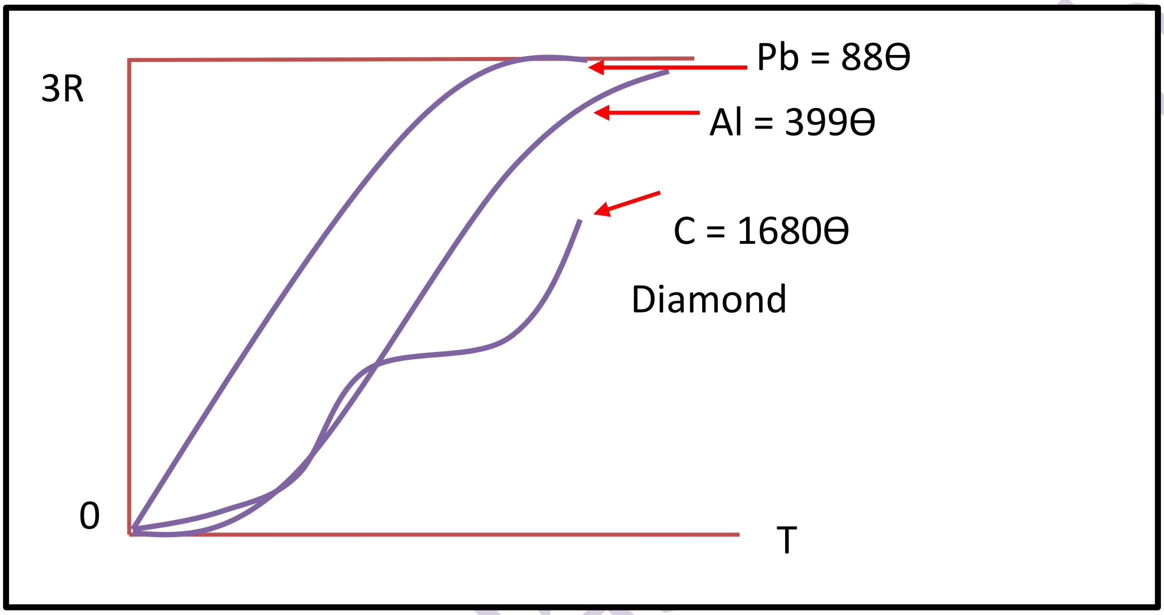
$$\ominus = \frac{h\gamma_{max}}{k}$$

This can be explained as follows:



So according to the Depay equation, it gives the same curve to the thermal capacity with the temperature and the shape above shows the thermal capacity of different solids to explain the characteristic temperature state.

As well as the following form and according to the Depay equation explains the interpretation of the atomic thermal capacity of the elements with the temperature as in the chart



We notice from the pb shape of the feature a small feature so that the value of the thermal capacity rises and then becomes slow

While when the value of ϕ is large forgotten, the thermal capacity curve rises slowly with temperatures to reach the highest value at 3R, but in the case of carbon (mas) ϕ large and so the thermal capacity does not reach the highest value of 3R and thus we recover the following

1)The distinctive heat of the carbon is greater than lead.

2)The distinctive heat of Alkali alkaline metals is greater than 3R

Thus, the Depay equation can be reduced to a simplified form of

$$C_v = 464.5\left(\frac{T}{\Theta}\right)^3 \; Cal.\deg^{-1} \; g^{-1} \; Atom^{-1}$$

$$C_v \propto T^3$$

Depay explains to us the significant change in thermal capacity with temperatures.