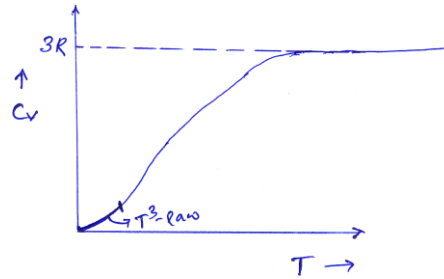


## Quantum Theory of Solids (Chapter 16.1, .2, .3)

### 16.1 Introduction:

The energy of the solid is mainly made up of vibration of the atoms along the 3-axis. The translation kinetic energy of its center of mass is neglected. So, classical approach to specific solids predicts that  $C_v$  is constant at  $6\left(\frac{1}{2}R\right) = 3R$  (equi-partition principle). This is known as Dulong–Petit’s Law. This law works very well at high temperature region. But in early twentieth century, low temperature measurements revealed an interestingly different story.



Experimental temperature dependence of  $C_v$  for solids

However additional measurements showed that the specific heat of solids varies with temperature, decreasing to zero as the temperature approaches zero. This behavior cannot be explained by the "freezing" of degrees of freedom when the temperature is decreased since the specific heat varies gradually with temperature and does not exhibit abrupt jumps by any multiple of  $R/2$  (in contrast to the specific heat of a diatomic gas). Even at room temperature the specific heat capacities of certain substances such as beryllium, boron, carbon, and silicon were found to be much smaller than  $3R$ . Quantum statistics is needed to explain these discoveries.

### 16.2 EINSTEIN'S THEORY OF THE HEAT CAPACITY OF A SOLID:

In order to explain non-classical, low temperature behavior of specific of solids, Einstein proposed a simple quantum model and assumes the following:

- 1- The crystal consists of atoms which may be regarded as identical and fixed at the lattice points.
- 2- The atoms in a crystal vibrate independently of each other about fixed lattice points.
- 3- These vibrations are all assumed to be simple harmonic, all with the same frequency.
- 4- The vibrations of any one atom can be split into three independent vibrations one along each coordinate axis.

Hence a solid containing  $N$  atoms is equivalent to  $3N$  harmonic oscillators vibrating independently of each other all with the same frequency, it is called oscillator frequency  $\nu$ . The value of this frequency depends on the strength of the restoring force,  $k$ , and the reduced mass  $\mu$ , where  $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$ . Consider any simple solid

with  $N$  atoms. These atoms are free to vibrate about their equilibrium positions. (Such vibrations are called "lattice vibrations"). The total energy of the system is written as

$$E = \sum_{i=1}^{3N} E_i, \quad E_i = \frac{p_i^2}{2\mu} + \frac{1}{2} k_i q_i^2 \quad (1)$$

Thus the total energy is considered as that of  $3N$  independent one dimensional harmonic oscillator. If the temperature  $T$  is high enough so that classical description is applicable, then the application of the equipartition theorem allows one to conclude that the total mean energy (internal energy of the crystal) is

$$U = 6N \left( \frac{1}{2} k_B T \right) = 3Nk_B T = 3RT \quad (\text{if } N = N_a)$$

Thus the specific heat at constant volume becomes

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 3R = 25 \text{ J mole}^{-1} \text{K}^{-1} \quad (\text{Douling-Petit})$$

Of course, the preceding arguments are not valid for solids at appreciably lower temperatures, which required that  $\lim_{T \rightarrow 0} C_V \approx 0$ . To do so, Einstein introduced the following assumptions:

- a- All atoms in the solid vibrate with the same angular frequency  $\omega_E$  ( or frequency  $\nu_E$  ), which implies  $k_i = m\omega_E^2$  for all terms  $i$  in equation (1).
- b- The mole of solid is equivalent to an assembly of  $3N_a$  independent one dimensional harmonic oscillators, which could be easily treated by quantum mechanics with the following results:

Using the quantum energy levels in the form

$$\varepsilon_n = (n + \frac{1}{2})\hbar\omega_E = (n + \frac{1}{2})h\nu_E,$$

the single particle partition function will be:

$$z = \sum_n e^{-\beta \varepsilon_n} = \frac{e^{-a}}{1 - e^{-2a}}, \quad a = \beta h\nu_E / 2,$$

$$Z = z^{3N} = \left( \frac{e^{-a}}{1 - e^{-2a}} \right)^{-3N} \Rightarrow \ln Z = \frac{3N\beta h\nu_E}{2} - 3N \ln(e^{\beta h\nu_E} - 1)$$

### Internal energy and heat capacity of the Einstein solid

- Now that we have the partition function, it is straightforward to determine thermodynamic quantities for the Einstein solid. First, let's derive the internal energy:

$$U = -\frac{\partial \ln Z}{\partial \beta} \quad (2)$$

$$\therefore U = -\left[ \frac{3N h\nu_E}{2} - \frac{3N h\nu_E e^{\beta h\nu_E}}{(e^{\beta h\nu_E} - 1)} \right] = \frac{3}{2} N h\nu \frac{(e^{\beta h\nu_E} + 1)}{(e^{\beta h\nu_E} - 1)} = \frac{3}{2} N h\nu_E + \frac{3N h\nu_E}{(e^{\beta h\nu_E} - 1)} \quad (3)$$

- Using the internal energy, we can calculate the heat capacity of the Einstein solid:

$$C_V = \left( \frac{dU}{dT} \right)_V \quad (4)$$

- Since  $\beta = 1/k_B T \Rightarrow \frac{d\beta}{dT} = -\frac{1}{k_B T^2}$
- Thus we can write the derivative  $\frac{dU}{dT}$  in the more convenient form:

$$C_V = \left( \frac{dU}{dT} \right)_V = \left( \frac{dU}{d\beta} \right)_V \left( \frac{d\beta}{dT} \right) = -\frac{1}{k_B T^2} \left( \frac{dU}{d\beta} \right)_V \quad (5)$$

$$C_V = 3Nk_B \beta^2 (h\nu_E)^2 \frac{e^{\beta h\nu_E}}{(e^{\beta h\nu_E} - 1)^2} = 3Nk_B (\beta)^2 (h\nu_E)^2 \frac{e^{\beta h\nu_E}}{(e^{\beta h\nu_E} - 1)^2} \quad (6)$$

- The Einstein solid heat capacity is plotted below as calculated for Diamond, compared to the experimentally measured heat capacity- and we see quite good agreement over a broad range of temperatures. In particular, at high temperatures, we see the limiting behavior of the heat capacity is:

$$C_V(T \rightarrow \infty) \approx 3Nk_B \beta^2 (h\nu_E)^2 \frac{(1 + \beta h\nu_E + \dots)}{(1 + \beta h\nu_E + \dots - 1)^2} = 3Nk_B (\beta h\nu_E)^2 \frac{1}{(\beta h\nu_E)^2} = 3Nk_B = 3R \tag{7}$$

correctly predicting the limiting value of  $C_V$  observed experimentally for many solids.

**Einstein Temperature**

Rewrite equations 3 and 6 one has:

$$U = 3R\Theta_E \left( \frac{1}{2} + \frac{1}{e^{2a} - 1} \right),$$

$$C_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{2a}}{(e^{2a} - 1)^2}$$

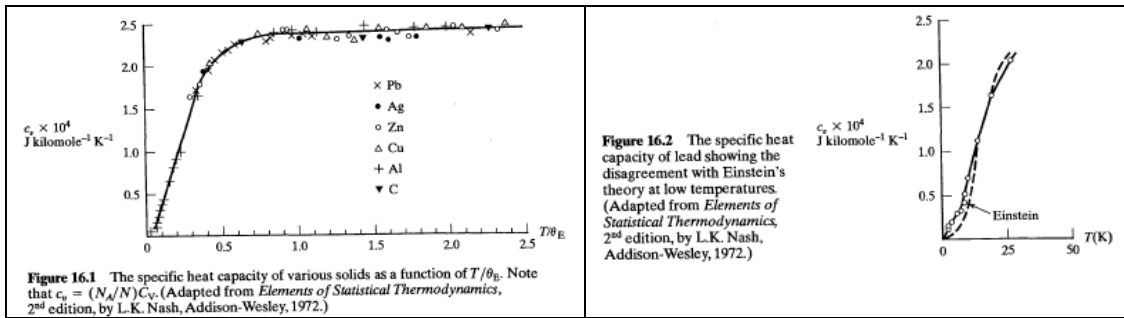
where we introduced the characteristic "*Einstein temperature*"  $\Theta_E = \frac{h\nu_E}{k_B}$ .

**Asymptotic heat capacity**

At the regions where  $T \gg \Theta_E$  and  $T \ll \Theta_E$  we have:

$$C_V = \begin{cases} 3R & T \gg \Theta_E \\ 3R \left( \frac{\Theta_E}{T} \right)^2 e^{-\Theta_E/T} & T \ll \Theta_E \end{cases} \tag{8}$$

Thus the specific heat should approach zero exponentially as  $T \rightarrow 0$ .



**PHYSICAL INTERPRETATION**

Experimentally the specific heat approaches zero more slowly than this, indeed  $C_V \propto T^3$  as  $T \rightarrow 0$ . The reason for this discrepancy is the crude assumption that all atoms vibrate with the same characteristic frequency. In reality this is not the case (even if all the atoms are identical). Nevertheless, the crude assumptions of Einstein approximation give a reasonably good description of the specific heats of solids. It also makes clear the existence of the a characteristic parameter  $\Theta_E$  which depends on the properties of the solid under consideration.

The normal modes of the crystal are its various standing waves of free vibration whose lowest frequencies are in the sonic range (wavelength = half or a third or a tenth of crystal size) and highest frequencies are in the infrared (wavelength = size of interatomic distance). Sometimes the quantized standing waves are called **phonons**. Then  $n_i$  is the number of phonons in the  $i^{\text{th}}$  wave. The phonons are related to the vibrations of the lattice in a crystal in the same fashion as photons are related to the vibrations of the electromagnetic field.

### 16.3 Debye theory:

The disagreement between Einstein’s result and the experimental data is due to the fact that Einstein’s assumptions about the atoms in a crystal do not strictly apply to real crystals. The main problem lies in the assumption that **a single frequency of vibration characterizes all  $3N$  oscillators**. Debye improved on Einstein’s theory by considering the vibrations of a body as a whole, regarding it as a **continuous elastic solid**. He associated the internal energy of the solid with stationary elastic sound waves. Each independent mode of vibration (or normal mode) is treated as a degree of freedom.

In Debye’s theory a solid is viewed as a **phonon gas**. Vibrational waves are matter waves, each with its own de Broglie wavelength and associated particle. The particle is called a phonon, with characteristics similar to those of a photon. If the interatomic distance is small as compared to the wavelength of elastic waves, the crystal can be regarded as a continuum from the point of view of the wave. Based on this idea, Debye based his theory on the following assumptions:

- a- The motion of each atom in a solid is not independent of the motions of its neighbors, as assumed by Einstein.
- b- The single frequency of Einstein should be replaced by a spectrum of vibrational frequency, with an upper frequency limit  $\nu_D$ , for the solid.  $\nu_D$  is called Debye (or cut-off) frequency.



Transverse waves in a one-dimensional lattice.

- c- Solids regard as a gas of non-interacting particles (phonons), enclosed in a volume  $V$ .

#### Density of state:

In momentum space, particles within a small volume  $\sigma_p \approx \frac{h^3}{V}$  are indistinguishable; therefore it represents an eigenstate. At any instant, all particles having the momenta between  $p$  and  $p + dp$ , will lie within a shell of volume  $4\pi p^2 dp$ . Therefore, the total number of eigenstates is given by

$$g(p)dp = a \frac{V}{h^3} 4\pi p^2 dp$$

where that  $a$  is a constant related to the “polarization” of interested system, that is

$$a = \begin{cases} 1 & \text{in case of bosons} \\ 2 & \text{in case of electrons and photons} \\ 3 & \text{in case of phonons in solids} \end{cases}$$

For photon (phonon)  $\vec{p} = \hbar \vec{k} = \frac{h}{2\pi} \vec{k}$  so

$$g(k)dk = \frac{aV}{(2\pi)^3} 4\pi k^2 dk$$

Since  $|\vec{k}| = \frac{\omega}{c}$ , then

$$g(\omega)d\omega = \frac{aV}{(2\pi)^3 c^3} 4\pi\omega^2 d\omega$$

In case  $\omega = 2\pi\nu$ , we can have the density of states for photons in the frequency range  $\nu$  to  $\nu + d\nu$  is:

$$g(\nu)d\nu = \frac{aV}{c^3} 4\pi\nu^2 d\nu$$

$$g(\nu)d\nu = 4\pi V \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \nu^2 d\nu \tag{1}$$

Define  $\left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) = \frac{3}{v_s^3}$ , where  $v_s$  is the average speed of sound in the material and the factor of 3 takes into account that there are 3 polarizations (2 transverse with speed  $v_t$  and 1 longitudinal with speed  $v_l$ ). Note that **in the Debye theory we assumed that the speed of sound is constant for all phonon frequencies**, i.e. and we use the approximation  $\frac{1}{v_t^3} \approx \frac{1}{v_l^3} = \frac{1}{v_s^3}$ . In practice this is not the case, but the Debye theory is generally used at low temperatures, where only low frequency phonons are excited, and where the approximation that they all travel at the same speed is a good one.

**Debye cutoff:**

Since each oscillator of the assembly vibrates with its own frequency, and we are considering an assembly of  $3N$  linear oscillator, there must be an upper limit to the frequency spectrum. The maximum frequency  $\nu_m$  is determined from the fact that there are only  $3N$  phonons:

$$\int_0^{\nu_D} g(\nu)d\nu = 3N, \Rightarrow 4\pi V \left( \frac{3}{v_s^3} \right) \int_0^{\nu_D} \nu^2 d\nu = 3N \tag{1.a}$$

where we obtain for the cut-off frequency

$$\nu_D^3 \approx \frac{9N}{4\pi V} \left( \frac{3}{v_s^3} \right)^{-1} = \frac{3N}{4\pi V} v_s^3 \tag{2}$$

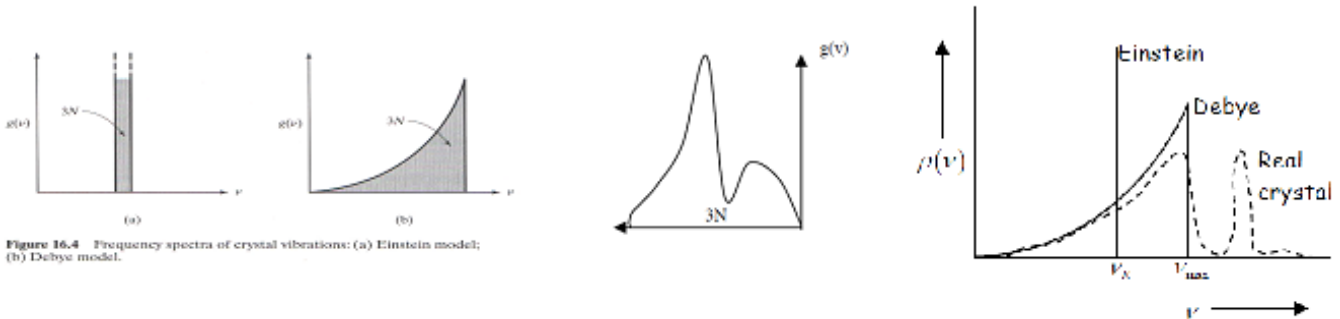


Figure 16.4 Frequency spectra of crystal vibrations: (a) Einstein model; (b) Debye model.

Last equation shows that the maximum frequency  $\nu_D \propto \left(\frac{N}{V}\right)^{1/3}$  is determined by the average interatomic spacing.

Thus the structure of the crystal sets a lower limit to the wavelength  $\lambda_D \propto \left(\frac{V}{N}\right)^{1/3}$ ; higher frequencies (shorter wavelength) do not lead to new modes of atomic vibration. Consequently,

$$g(\nu) = \begin{cases} 9NV \frac{\nu^2}{\nu_D^3} & \text{for } \nu \leq \nu_D \\ 0 & \text{for } \nu \geq \nu_D \end{cases} \quad (3)$$

### Bose-Einstein distribution law

It is given in the form:

$$dn = g(\nu)f(\nu)d\nu = \frac{g(\nu)d\nu}{e^{\beta h\nu} - 1} \quad (4)$$

then the number of phonons per unit volume in the interval  $d\nu$  is given from (3) and (4) as:

$$\frac{dn}{V} = \begin{cases} \frac{9N}{\nu_D^3} \frac{\nu^2}{e^{\beta h\nu} - 1} d\nu, & \nu \leq \nu_D \\ 0, & \nu \geq \nu_D \end{cases} \quad (5)$$

### Phonon energy

If the above equation multiplied by the energy of photon  $E = h\nu$  the result is the energy per unit volume, i.e. the energy density

$$du = h\nu \frac{dn}{V} = \frac{9Nh}{\nu_D^3} \frac{\nu^3}{e^{\beta h\nu} - 1} d\nu \quad (6)$$

### Debye temperature

By using the dimensionless parameters:

$$x = \beta h\nu = \frac{h\nu}{k_B T}, \quad (7)$$

$$x_D = \beta h\nu_D = \frac{h\nu_D}{k_B T} \equiv \frac{\Theta_D}{T}, \quad (8)$$

where

$$\Theta_D = \frac{h\nu_D}{k_B} \quad (9)$$

is the “*Debye's temperature*”.

### Back to phonon energy

Hence the internal energy per unit volume is

$$u - u_0 = \int_0^{\nu_D} du = \frac{9Nh}{\nu_D^3} \int_0^{\nu_D} \frac{\hbar \nu^3}{e^{\beta h\nu} - 1} d\nu = \frac{9Nk_B T}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx \quad (10)$$

Where  $u_0$  is the zero energy, and will not affect the final expression of the specific heat.

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**Heat capacity**

The specific heat is calculated by:

$$C_V = \left( \frac{\partial u}{\partial T} \right)_V = \frac{9Nh}{v_D^3} \frac{\partial}{\partial T} \int_0^{v_D} \frac{v^3}{e^{\beta hv} - 1} dv = \frac{9Nh}{v_D^3} \frac{hv}{k_B T^2} \int_0^{v_D} \frac{v^4 e^{\beta hv}}{(e^{\beta hv} - 1)^2} dv = \frac{9Nk_B}{x_D^3} \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (11)$$

Define Debye's function  $D(x)$  by:

$$D(x_D) = \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx = \begin{cases} 1 - \frac{3}{8}x_D + \frac{1}{20}x_D^2 + \dots & x_D^3 \ll 1 \Rightarrow T \rightarrow \infty \\ \frac{\pi^4}{5x_D^3} + O(e^{-x_D}) & x_D^3 \gg 1 \Rightarrow T \rightarrow 0 \end{cases}$$

**Asymptotic limits for energy and heat capacity**

At high temperatures,  $x \ll 1$  (Hint:  $\frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4(1+x)}{(e^x - 1)(1+x-1)} = \frac{x^4(1)}{(e^x - 1)(x)} = \frac{x^3}{(e^x - 1)}$ )

$$u - u_0 = \frac{9Nk_B T}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx = 3Nk_B T D(x_D) \approx 3Nk_B T \quad (12)$$

$$\Rightarrow C_V = 3Nk_B, \quad (\text{Douling-Petit}) \quad (13)$$

At very low temperatures,  $x \gg 1$  (Hint:  $\frac{x^4 e^x}{(e^x - 1)^2} = \frac{x^4 e^x}{(e^x)^2} = x^4 e^{-x}$ )

$$u - u_0 = \frac{9Nk_B T}{x_D^3} \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx \approx \frac{9Nk_B T}{x_D^3} \underbrace{\int_0^\infty x^4 e^{-x} dx}_{\frac{\pi^4}{15}} = \frac{3\pi^4}{5} Nk_B T \left( \frac{T}{\Theta_D} \right)^3 \quad (14)$$

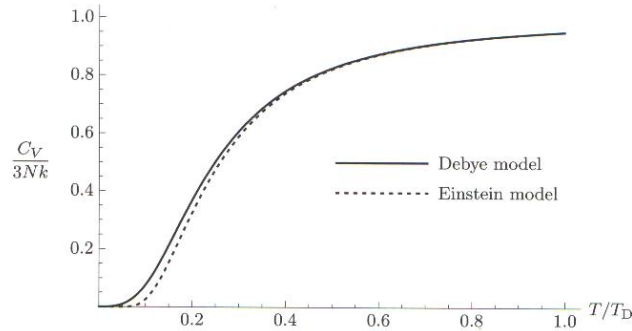
$$\Rightarrow C_V = \frac{9Nk_B}{x_D^3} \underbrace{\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} dx}_{\frac{4\pi^4}{15}} = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\Theta_D} \right)^3 \quad (15)$$

This is Debye's famous  $T^3$ -law", which is valid at low temperatures.

**H.W.** Check the above results.

Table: Debye temperatures of some material

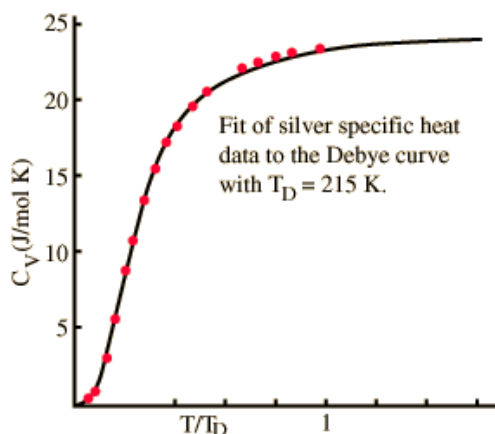
Substance	$\Theta_D$ (K)
Lead	88
Mercury	97
Silver	215
Copper	315
Iron	453
Diamond	1860



**Figure 7.29.** The Debye prediction for the heat capacity of a solid, with the prediction of the Einstein model plotted for comparison. The constant  $\epsilon$  in the Einstein model has been chosen to obtain the best agreement with the Debye model at high temperatures. Note that the Einstein curve is much flatter than the Debye curve at low temperatures.

### Limitations of the Debye Model

- i. The Debye's continuum model is valid for low frequencies (long wavelengths) only, i.e., only low frequencies are active in the solid.
- ii. The total numbers of vibrational modes are assumed to be  $3N$ . This is difficult to justify as the solid is considered to be an elastic continuum which should possess infinite frequencies.
- iii. The cut off frequency is assumed to be the same for both longitudinal and transverse waves. This is again difficult to justify because different velocities of transverse and longitudinal waves should imply different values of cut off frequency for these waves.
- iv. According to the Debye's theory,  $\Theta_D$  is independent of temperature, whereas actually it is found to vary up to an extent of 10% or even more.
- v. The theory does not take into account the actual crystalline nature of the solid. The theory cannot be applied to crystals comprising more than one type of atoms.
- vi. The theory completely ignores the interaction among the atoms and the contribution of electrons to the specific heat.



The data for silver shown at left is from Meyers. It shows that the specific heat fits the Debye model at both low and high temperatures.



**16-6** The experimental value of  $C_V$  for diamond is  $2.68 \times 10^3$  J/kmole·K temperature of 207 K. For diamond the Einstein temperature is 1450 K and the Debye temperature is 1860 K. Calculate  $c_V$  at 207 K using the Einstein and Debye models and compare the results with the experimental value.

**Answer:**

$$\text{Einstein Model: } C_V = 3Nk \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left( e^{\frac{\Theta_E}{T}} - 1 \right)^2}, \text{ so } c_V = 3N_A k \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left( e^{\frac{\Theta_E}{T}} - 1 \right)^2}$$

$$\text{or, } c_V = 3R \left( \frac{\Theta_E}{T} \right)^2 \frac{e^{\frac{\Theta_E}{T}}}{\left( e^{\frac{\Theta_E}{T}} - 1 \right)^2} = 3(8.314 \times 10^3 \text{ J/kmole} \cdot \text{K}) \left( \frac{1450 \text{ K}}{207 \text{ K}} \right)^2 \frac{e^{\frac{1450 \text{ K}}{207 \text{ K}}}}{\left( e^{\frac{1450 \text{ K}}{207 \text{ K}}} - 1 \right)^2}$$

$$c_V(\text{Einstein}) = 1.11 \times 10^3 \text{ J/kmole} \cdot \text{K}$$

This result is low.

**Debye Model:** Since  $\Theta_D \gg T$ , the low temperature heat capacity formula can be used.

$$C_V = \frac{12Nk\pi^4}{5} \left( \frac{T}{\Theta_D} \right)^3, \text{ so } c_V = \frac{12N_A k\pi^4}{5} \left( \frac{T}{\Theta_D} \right)^3 = \frac{12R\pi^4}{5} \left( \frac{T}{\Theta_D} \right)^3$$

$$\text{Then, } c_V = \frac{12(8.314 \times 10^3 \text{ J/kmole} \cdot \text{K})\pi^4}{5} \left( \frac{207 \text{ K}}{1860 \text{ K}} \right)^3$$

$$c_V(\text{Debye}) = 2.68 \times 10^3 \text{ J/kmole} \cdot \text{K}$$

This agrees with the experimental value.