Measurements of Heat Capacity from Lattice Vibrations of Gasses Using Debye Model

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Date: 16/11/2016
Holly Quran

بسم الله الرحمن الرحيم

قال تعالى: (فَمَنْ يُرِدَ اللَّهُ أَنْ يَهدِيَهُ يَشْرَحْ صَدْرَهُ لِلْإِسْلَامِ وَمَنْ يُرِدْ أَنْ يُضِلَّهُ يَجْعَلْ صَدْرَهُ ضَيِّقًا حَرَجًا كَأَنَّمَا يَصَّعَّدُ فِي السَّمَاءِ كَذَلِكَ يَجْعَلُ اللَّهُ الرِّجْسَ عَلَى الَّذِينَ لَا يُؤْمِنُونَ)

صدق الله العظيم

سورة الأنعام (الآية 125)
Dedication

This work is dedicated with great thanks to my parents, my wife, my sons and douters, to my brothers and sisters.

To my relatives.

To everyone taught me a letter and

My friends and colleagues
Acknowledgements

First I am gratefully indebted to my God almighty who help me to complete my work. Thanks university of Gezira and also for all professors of the Department of Electronic Engineering Faculty of Engineering and Technology. I would like to thank my thesis supervisor Dr. Hasab alrsoul Gemalhi Ismail the door to Dr office was always open about my research or writing. He whenever I ran into a trouble spot or had question consistently allowed this paper to be my own work, but steered me in the right the direction whenever he thought I needed it.

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Finally, I must express my very profound gratitude to my parents, my family members, my friends, and all the teachers they taught us all these years, for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis.

This accomplishment would not have been possible without them.

Thank you.
Measurements of Heat Capacity from Lattice Vibrations of Gasses Using Debye Model

ELMUZAMIL ABDALLA AHMED BELIL
Department of Electronics Engineering
M. Sc. Physics

Abstract
The practical experience showed that the amount of heat needed to raise the temperature of the material depends on the nature of the material, thus it was needed to define a new physical amount which takes into account the nature of the material, is known as the heat capacity which is defined as the quantity of heat that is required to raise the temperature of abodes by one degree Celsius. The theory of specific heat in gases shows that specific heat capacity for a material normally increases with temperature, due to the change in substance structure, more precisely, it depends on how many degree of freedom are available in the substance particles, where a degree of freedom is a form of energy stored in the particles. In the past Debye theory was used explicitly for solids. The objective of this research is to study the total energy of the phonon at temperature T, heat capacity of the gases and Debye heat capacity model. The experiments select three samples of three gases (oxygen – nitrogen – and carbon dioxide). The samples are placed in a gas cylinder connected to a bottle Registrar Pro belted with a computer to monitor the pressure on a (T) key. The system has been cleansed of any other gases by allowing the gas to sweep the flask for five minutes. Most notably the gas heat capacity depends on the surrounding circumstances. There a distinction between the heat capacity of the gas when the pressure is constant (C_P) and the heat capacity of the gas when volume in constant (C_V). When the volume constant change occurs via the supply of the gas from outside warmly working to the high temperature of the gas and this means increasing the gas molecules kinetic energy. As in the case of gas supply heat from the outside while maintaining the stability of the pressure, we find that the performance of gas filled as increasing the volume of gas. The results show that the heat capacity of samples at different temperatures varies with temperature at 1C^0 and at 100 C^0. At temperatures 25, 50, 75 C^0, the heat capacities (C_P) of O_2, N_2, and CO_2 were (5.49, 6.22, 5.04, 10.99, 12.44, 10.08, 16.44, 18.60, 15.08 Kcal.k^{-1}. Kg^{-1}) for O_2, N_2, and CO_2 respectively. These results were found to fit Debye relation for the heat capacity of solids. Therefor this work shows that Debye the relation is suitable for measurement of heat capacities of gases. This work recommends future studies for other gases, and using other suitable methods to find heat capacity for gases such as measuring radiation and convection.
قياسات السعة الحرارية للغازات باستخدام نموذج ديباي من اهتزازات الشبيكة
المؤلف: عبد الله احمد بليل
قسم هندسة الالكترونيات
ماجستير العلوم في الفيزياء

ملخص الدراسة

وجد بالتجربة العملية أن كمية الحرارة اللازمة لرفع درجة حرارة المادة تختلف حسب طبيعة المادة، ولذا فاننا نحتاج الي تعريف كمية فزيائية جديدة تأخذ في الحسبان طبيعة المادة وهذه الكمية هي السعة الحرارية وتعبر بأنها كمية الحرارة اللازمة لرفع درجة حرارة الجسم درجة مئوية واحدة. تقوم نظرية السعة الحرارية المحددة في الغازات علي أن تزيد السعة الحرارية المحددة للمادة بزيادة درجة الحرارة. وذلك يعني أن السعة الحرارية المحددة نفسها تؤدي وظيفة تركيب المادة وبطريقة أكثر دقة تعتمد السعة الحرارية علي مدى وجود درجات حرية في جزيئات المادة لكي تسمح بتقليل الحارة في الجسم وتخزينها. في الماضي استخدمت نظرية ديباي للمواد الصلبة فقط. هدف هذا البحث إلى دراسة الطاقة الكلية للغزات عند درجة حرارة T، دراسة السعة الحرارية للغازات ودراسة نموذج ديباي للسعة الحرارية. تم اختيار ثلاثة غازات (الاكسجين – النيتروجين – ثاني أكسيد الكربون) ووضع في جهاز حساس لمراقبة الضغط (T) وتم تنظيف النظام من أي غازات اخري والسماح للغاز للاكتساح القاروة لمدة خمس دقائق. نفرق بين السعة الحرارية للغاز عند ثبوت الضغط (C_P) وبين السعة الحرارية للغاز عند ثبوت الحجم (C_V). عبد ثبوت الحجم يحدث تغيير الحالة عن طريق امداد الغاز بحرارة من الخارج فعند ثبوت الحجم من الخارج تلامع على ارتفاع درجة حرارة الغاز. وهذا معناه زيادة طاقة حركة جزيئات الغاز. أما في حالة امداد الغاز بحرارة من الخارج مع المحافظة على ثبوت الضغط ففجأ الغاز يقوم بإعداد شغل حيث يزداد حجم الغاز. النتائج توضح السعة الحرارية عند درجات الحرارة من 1 إلى 100 درجة مئوية عند درجات الحرارة 25 , 50 , 75 درجة مئوية السعة الحرارية لألكسيجين, النيتروجين وثاني أكسيد الكربون (5.49 , 6.22 , 6.04 , 10.99 , 12.44 , 10.08) كيلو كالوري لكل كجم درجة مطلقة للأكسجين, النيتروجين وثاني أكسيد الكربون على الترتيب. هذه النتائج وجدت ملائمة لعلاقة ديباي للسعة الحرارية للمواد الصلبة. لذلك هذا العمل توصل بناء علاقة ديباي مناسبة لقياس السعة الحرارية للغازات. يوصى هذا العمل بإجراء دراسات مستقبلي للغازات الأخرى واستخدام طرق أخرى مناسبة لقياس السعة الحرارية للغازات مثل الابشع والحمل.
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CHAPTER ONE

Introduction

1.1 Overview

There is one type of contribution comes from gas properties phonons (lattice vibrations). This research is dedicated to the study of the thermal capacity of the gases due to the lattice vibrations. Heat capacity is the amount of heat energy needed to raise the temperature of one degree Celsius. Take into account the gas sample containing N of molecules (Lemer, 1991).

Gas molecules in the case of a quick and random constant motion because of possession of kinetic energy (contrary to what the gases). It consists molecule energy than three degrees of private traffic card freedom (movement in the x direction, and move in the direction Y, and move in the direction of the axis p), and add to it. "Rotational energy" with a number of degrees of freedom between zero and 3 which specializes Batch rotation of a molecule on himself (and be zero if monatomic molecule), and add them as well, "energy vibration" of the number of degrees of freedom of vibration of a molecule components (David Griffiths 2008).

Number of degrees of freedom of the gas molecules based on the gas particles Is atoms individually or dual gas atoms or gas molecule composed of three atoms. I have some other methods been listed for consideration in the vibration problems in the Debye model and Einstein model. (Laurendeau, 2005)

1.2 Research problem

The result of classical theory is in reasonably good agreement with experiment at sufficiently high temperatures, but at low temperatures the observed heat capacities fall to very low values, the contribution of the phonons to the heat capacity of crystal and the average thermal energy per a degree of freedom, Number of degrees of freedom of the gas molecules based on the gas particles. Is atoms individually or dual gas atoms or gas molecule composed of three atoms. some other methods been listed for consideration in the vibration problems in the Debye model and Einstein model. (Laurendeau 2005).
1.3 Research Objectives

The objects of this research are:

1) Study the Total energy of the phonon at temperature $T$.
2) Study the heat capacity of gases.
3) Study the Debye heat capacity model.

1.4 Research Methodology

Was selected a sample of three gases (oxygen - nitrogen - carbon dioxide) and placed in a gas cylinder connected to a bottle Registrar Pro belted with a computer to monitor the key is pressed ($T$). The system is purging than any other gases and then allowing the gas to sweep the flask for five minutes.

1.5 Presentation of thesis

This research include four chapters, chapter one is the introduction, chapter two is the theoretical background and previous Studies, chapter three is material and method, chapter four is results and discussion.
CHAPTER TWO
THEORETICAL BACKGROUND AND PREVIOUS STUDIES

2.1 Introduction

For solids and liquids heat capacity does not vary at a constant pressure from those measured at constant volume. As for the gases distinguish between heat capacity at constant pressure, heat capacity at constant volume, where the gas expands too much heat.

Heat capacity is the rate of change internal energy of the material change temperature.

Or the rate of change Ant alba material change temperature. (Which is a more general power of internal energy). And reflect the temperature of the gas from the average gas atoms and molecules kinetic energy.

Contrary to what happens in the free gas liquids does not occupy a fixed size but Tmlae any vacuum allow them to. Gas kinetic energy is the second most important thing in the states of matter (after plasma). Due to the increased kinetic energy of gases, the molecules and atoms Gas tends to occupy each the size of its available, But also through the force of the hail of porous material, And increases by increasing kinetic energy. And vary the gas particles movement for movement of fluid particles that come into contact. It is the physical properties of gases that depend on the degrees of freedom molecules, we find the thermal capacity.

And know the degrees of freedom of the gas important ones where we can see the potential energy in the gas molecules. And different degrees of freedom gases depending on the composition and components. Gas molecules composed of two atoms such as oxygen, when we study the random motion of gas, we find that the molecule of oxygen that can move in the direction of the X-axis and can move in the direction Y and can move valuable kind direction (as the coordinates of the position x, y, z) (Poland, 2008).

We describe the oxygen molecules movement in the gas then that her "three degrees of freedom", soon the (transitional movement "of the particles. If the molecule of oxygen is
about the same then it also be a degree of freedom of the molecule of oxygen, in exercise of the rotation by absorbing energy from the outside (Meyer, 2005).

And carefully study the rotational movement of the oxygen molecule, we find that his "two degrees of freedom" around the rotational axes vertical on the bond between two atoms of oxygen constituent part. We can thus say that a molecule of oxygen gas in his "five degrees of freedom", including the "three transition" and "two rotational" (part oxygen circulation, a dual-atoms, he cannot turn around the third axis which is the link between the atoms) (Dole, (1965).

In contrast to the classical theory which takes vibration molecule in mind also at room temperature, it became clear that the vibratory motion of the particles can be neglected for its small participation in the heat capacity of the material, and because the degrees of freedom for the Vibrating be "inert" because the room temperature not enough to give the movement vibrating "energy KT" needed to shake.

It can be neglected degrees of freedom on the vibrating due to the small what you add to the total energy of the system and thus to add to the heat capacity. But it cannot be neglected at very high temperatures (Amao , 2003).

2.2 Lattice Vibrations

The Hamiltonian of a thermally vibrating lattice is the same as the Hamiltonian of a free gas of free particles with energy h\( \omega(q) \). The same formula is obtained when the Hamiltonian of the radiation field is expressed in terms of the creation and annihilation operators of photons, the quanta of the electro- magnetic field (Donovan & Angress , 2001).

Hamilton equation in dealing with a serious case of a mass m vibrates in harmonic effort

\[
V(x) = \frac{1}{2} kx^2
\]

(Motion of the electron around the nucleus of the atom in its field electrophoresis, are typical of those harmonic motion.)Where: \( k = ma^2 \) (2,2,2) And \( \omega \) (Omega) is a self-rocking harmonic frequency.
The equation is the total particle energy in this case are:

\[ H = \frac{p^2}{2m} + \frac{m \omega^2 x^2}{2} \]  \hspace{1cm} (2,2,3)

Hamilton equation describes the total energy of the system of energy, ie, as the sum of the kinetic energy (the first part) and potential energy (the second part).

And now we replace guide the place and momentum movement with quantum transactions, where:

Coefficient place: \( \hat{x} \rightarrow \vec{x} = \hat{x} \), Momentum coefficie \( \hat{p} \rightarrow \vec{p} \) = \(-i\hbar \nabla\) is called [Nabla-Operator].(NB "arrow above variable means that we are dealing with the vectors and therefore there must be a vector calculus.).

In the last figure we have formulated coefficient place, and thus Hamilton equation formula changed to Hamilton coefficient formula which expresses the change in the position of the particle (Dole. Malcolm,1965)

\[ \hat{H} = \frac{\vec{p}^2}{2m} + \frac{m \omega^2 x^2}{2} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{m \omega^2 x^2}{2} \]  \hspace{1cm} (2,2,4)

\[ W_{\nabla^2} = \Delta \text{called [Laplace-Operator].} \]

The abbreviated Nabla - operator \( \nabla \) in the case of movement on the X-axis and the differential alone derivative \( \frac{\partial}{\partial x} \).

We will deal with that issue resolved in the case of the particle movement in only one direction let the x-axis.

Hamilton described by coefficient above we get the equation of eigenvalues for the harmonic oscillator - (the Schrodinger equation stable, ie, that do not change with time).

\[ \hat{H} \psi_n = E_n \psi_n \]  \hspace{1cm} (2,2,5)

In the formula that allows changing the particle place only:

\[ -\frac{\hbar^2}{2m} \Delta \psi_n (x) + \frac{1}{2} m \omega^2 x^2 \psi_n (x) = E_n \psi_n (x). \]  \hspace{1cm} (2,2,6)
In quantum mechanics are dealing with is not a material particle and as (a wave qualities) but it is the symbol $\psi_n$ which has the characteristics of the particle. It produces a solution of differential Schrödinger equation differential functions of self- functions $\psi_n(x)$ of the harmonic oscillator. Called Hermite functions:

$$\psi_n(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n \left(\sqrt{\frac{m\omega}{\hbar}} x\right) e^{-\frac{1}{2} \frac{m\omega}{\hbar} x^2} \tag{2.2,7}$$

Where $n(x)$ many border Hermite.

Part describes the $e^{-\frac{1}{2} \frac{m\omega}{\hbar} x^2}$ exponential decrease of the probability of the existence of the particle outside the oscillator effort. (In physics are like oscillator effort affecting the existence of the particle in the particle, "Well my effort", and thus the probability of the existence of the particle out of the well is very small, and this is reflected in the wave functions of the particle in the topical form).

Status benthic the lowest energy state of a particle is associated with a in the form of a Gaussian curve, and noted that they represented half the wavelength.

The upper figure shows the first eight cases of solutions Schrodinger equation $\psi_n(x)$ it is called self-functions. In addition to the wave functions of the particle in the energy states form $n=0, 1, 2$, the lower shaped describes the square value of the wave function, which gives the probability of the existence of the particle in the harmonic voltage supposed (and harmonic effort here described sinusoidal blue) (Peng and Robinson, 1976).

The meaning of self-functions as separate functions and are not continuous, every function realized the existence of a number of full length of the particle wave except benthic situation that is serious where owned least possible energy to him, a solution when they are $n=0$.

Next level of energy is featured solving the Schrodinger equation when they are $n=1$ and we note that the wave function, it consists of a single wavelength of the particle.

When the particle acquires energy overworked when it is in the case $n=1$ jumps to the situation $n=2$ which is characterized here as consisting of a wave and half-wave.
This interpretation explains the meaning of quantum energy, in the body can possess certain discrete energies called energies subjective. It cannot possess particle interface energy between the two levels of energy solutions in accordance with the Schrödinger equation. This is really what we find in the reality of atoms and molecules properties (Donovan and Angress, 2007).

Quantum theory requires that the energy levels that can be owned by a grave in an effort to affect him to be Schrödinger equation solutions have had a placement for one. While the differential equation gives different solutions to the particle energy, it requires portability solution condition for unification to be:

\[ \int_{-\infty}^{\infty} |\psi_n(x)|^2 \, dx = 1 \quad (2,2,9) \]

That is, the particle exists wherever between infinity to infinity.

Conduct uniformity on particle equation gives solutions with discrete energy levels of the particle:

\[ E_n = \omega h \left( n + \frac{1}{2} \right) \quad (2,2,10) \]

Where \( n \) it is equal to the integer or equal to zero.

This equation represents the different energy levels that can possess particle in the harmonic effort, if we consider the \( n = 1 \) becomes:

\[ E_0 = \omega h \left( \frac{1}{2} \right) \quad (2,2,11) \]

This is the benthic energy particle level, and moreover it cannot be of a particle in the harmonic voltage that his energy is zero, but less energy him half is self-energy \( \omega \) where \( \hbar \) the reduced Planck's constant and self-frequency of the particle (Griffiths, 2004).
2.3 Total energy at temperature T

It stems from the previous result basic result: not possible the oscillator harmonic take continuous energies, but can possess true numbers of energy $\hbar \omega$. And benthic be a situation where the harmonic vibrator has less energy at all are: $E_{0} = 1/2 \hbar \omega$

It is that result conclude that vibrators have harmonic energy (vibrate) also at absolute zero $T = 0 K$ and the amount is energy $E_{0}$, that is the result of quantum mechanics when dealing with the harmonic oscillator at the atomic level.

Even so, the solution offered by quantum mechanics is actually compatible with the description of nature. This is evident also that the probability of the existence of the particle in a privileged position $n=0$ where it has a certain broader and is not zero. This means that the particle does not settle his position at the point $x=0$, as we expect of the solution offered by oscillator classic. This solution is offered by quantum mechanics called absolute zero vibration and thus absolute zero energy (Anderson, 2006).

2.4 Boltzmann Distribution

Consider a gas in a box of fixed volume. The gas consists of particles that are free to move within the box, but cannot penetrate the walls. However, we first need to do some work to identify the energy levels.

We shall use a quantum model for the gas particles: this will ensure that the allowed energy levels within the box occur at our system consists of a low-density gas of particles, which move freely apart from occasional collisions with the (rigid) walls or with each other. To distinguish this gas from others that we will consider later, we refer to the system as a Maxwell-Boltzmann gas (de Podesta, 2013).

The wave function: $(x,y,z,) = A \sin(\pi n x/L) \sin(\pi n y/L) \sin(\pi n z/L)$

If:

$$k_x = \pi n_x / L, \quad k_y = \pi n_y / L, \quad k_z = \pi n_z / L$$

Where $n_x$, $n_y$, and $n_z$ are positive integers,
The wave function (2,4,1) is an energy Eigen function, since it solves the time-independent Schrödinger equation:

\[ H\psi = \varepsilon \psi \]  \hspace{1cm} (2,4,3)

Where \( H \) is the Hamiltonian operator:

\[ H = -\frac{\hbar^2}{2m} \nabla^2 \]  \hspace{1cm} (2,4,4)

and \( \varepsilon \) is a constant, the energy of the particle. Substituting from (2,4,1), we find:

\[ H\psi = -\frac{\hbar^2}{2m} \nabla^2 \psi = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 x + n_y^2 y + n_z^2 z) \psi \]  \hspace{1cm} (2,4,5)

Hence, the energy levels are given by:

\[ \varepsilon = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) = k \Theta (n_x^2 + n_y^2 + n_z^2) \]  \hspace{1cm} (2,4,6)

The parameter \( \Theta \) (with units of temperature) is defined:

\[ \Theta = \frac{\hbar^2 \pi^2}{2mkL^2} \]  \hspace{1cm} (2,4,7)

The partition function \( Z \) plays an important role in calculating quantities such as the total energy and entropy as functions of temperature.

It is defined by:

\[ Z = \sum e^{-\varepsilon_j / kT} J \]  \hspace{1cm} (2,4,8)

Here, the index \( j \) will actually be a triple index, for \( n_x, n_y \) and \( n_z \). But quite apart from that, the summation is now difficult to evaluate.

To make things more convenient, we shall assume that we can replace the summation by an integral, and write:
\[ Z = \sum_j e^{-\frac{\epsilon j}{kT}} \rightarrow \int_0^\infty g(\epsilon) e^{-\frac{\epsilon j}{kT}} d\epsilon \quad (2,4,9) \]

Here, \( g(\epsilon) \) is the density of states: the number of energy states in the (small) energy range \( \epsilon \) to \( \epsilon + d\epsilon \) is \( g(\epsilon)d\epsilon \).

The Boltzmann distribution over a public, it can be changed by the particle density of the influence of gravity to rise above the ground as he gives us the possibility to distribute the energy when the power spectrum ongoing expense (Boltzmann, 1895).

### 2.5 Planck distribution or the Bose-Einstein distribution

This distribution was firstly discovered by Planck in the study of black-body radiation. There, Planck studies the energy carried by light, which is another type of wave (electromagnetic waves) very similar to sound waves.

At that time, before the quantum mechanics is established, people consider light as classical waves. If one assumes that light is a classical wave, one find that the energy carried by these waves (light) is infinite at any temperature, which is obviously wrong. This infinite energy problem is known as the ultraviolet catastrophe. Eventually, it is Planck who pointed out that if we view light as particles (photons) with each particle carrying energy \( \hbar \omega \), then all the problems are solve. This discovery, as well as many other progresses, eventually led to the discovery of the quantum physics.

In fact, the distribution Planck discovered is valid for any waves, not limited to light. For sound waves and phonons, the same physics law applies and the numbers of phonons follow exactly the same distribution.

\[
\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar \omega}{kBT}\right) - 1} \quad (2,5,1)
\]

Later, Bose and Einstein discovered that for any bosonic particles, the average number of particles is:
\[
\langle n \rangle = \frac{1}{\exp \left( \frac{\epsilon - \mu}{k_B T} \right) - 1}
\]  

(2,5,2)

Where \( \epsilon \) is the energy of this particle and \( m \) is the chemical potential. The Planck distribution is a special case of the Bose-Einstein distribution,

Where \( \epsilon = 0 \). (Photons and phonons are both bosonic particles (bosons), so they obey the Bose-Einstein distribution (Maxwell, 1860).

If we assume that the ground state is a state of zero energy, then particles in the Bose-Einstein condensation make no contribution to the total energy of the Bose-Einstein gas. The total energy \( U \) can then be written:

\[
U = \int_0^\infty \epsilon \, n_{\text{ex}}(\epsilon) \, d\epsilon = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} \, d\epsilon}{\text{Be}^{k_T-1}}
\]  

(2,5,3)

Where we have used equation (39) for the density of particles in excited states \( n_{\text{ex}} \). Changing the variable of integration, the total energy can be written:

\[
U = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} (kT)^{5/2} \int_0^\infty \frac{y^{3/2} \, dy}{\text{Be}^y - 1}
\]  

(2,5,4)

Finally, using equation (38) for TB, we can express the total energy as:

\[
U = \frac{2}{\sqrt{\pi} \zeta \left( \frac{3}{2} \right)} NkT \left( \frac{T}{T_B} \right)^{3/2} \int_0^\infty \frac{y^{3/2} \, dy}{\text{Be}^{y/2} - 1},
\]  

(2,5,5)

At low temperature \( T < T_B \), we can take \( \Phi = 1 \), and the total energy becomes (Plank, 1920).

\[
U = \frac{2}{\sqrt{\pi} \zeta \left( \frac{5}{2} \right)} NkT \left( \frac{T}{T_B} \right)^{3/2} \int_0^\infty \frac{y^{3/2} \, dy}{e^y - 1},
\]

\[
= \frac{3 \zeta \left( \frac{5}{2} \right)}{2 \zeta \left( \frac{3}{2} \right)} NkT \left( \frac{T}{T_B} \right)^{3/2}
\]

\[
\approx 0.770 NkT \left( \frac{T}{T_B} \right)^{3/2}.
\]  

(2,5,6)
We see that at low temperature \((T < T_B)\):

\[ U \propto T^{3/2} \tag{2,5,7} \]

At high temperatures, \(B >> 1\), we can make the approximation

\[ B e^y - 1 \approx B e^y : \]

\[ U \approx \frac{2}{\sqrt{\pi \zeta(3/2)}} NkT \left( \frac{T}{T_B} \right)^{3/2} \frac{1}{B} \int_0^\infty \frac{y^{3/2}}{e^y} dy, \]

\[ \approx \frac{3}{2\zeta(3/2)} NkT \left( \frac{T}{T_B} \right)^{3/2} \frac{1}{B}. \tag{2,5,8} \]

we find:

\[ U \approx \frac{3}{2} NkT. \tag{2,5,9} \]

Note that this is the same result as for the Maxwell-Boltzmann gas: as we might expect, since the Boltzmann distribution approximates the Bose- Einstein distribution at high temperature (Plank, 1920).

### 2.6 Heat capacity of Gases

The molar heat capacity of a substance is the quantity of heat required to raise the temperature of a molar amount of it by one degree.

Heat capacity of a body is known as the quantity of heat required to raise its temperature by one degree.

The specific heat capacity of a substance is the quantity of heat required to raise the temperature of unit mass of it by one degree (Warburg, 1876).

The above definitions at first glance seem easy to understand – but we need to be careful. Let us imagine again a gas held in a cylinder by a movable piston.

I choose a gas because its volume can change very obviously on application of pressure or by changing the temperature.
The volume of a solid or a liquid will also change, but only by a small and less obvious amount. If you to a gas that is *allowed to expand at constant pressure*, some of the heat that you supply goes to doing external work, and only a part of it goes towards raising the temperature of the gas. On the other hand, *if you keep the volume of the gas constant*, all of the heat you supply goes towards raising the temperature. Consequently, more heat is required to raise the temperature of the gas by one degree if the gas is allowed to expand at constant pressure than if the gas is held at constant volume and not allowed to expand. Thus the heat capacity of a gas (or any substance for that matter) is greater if the heat is supplied at constant pressure than if it is supplied at constant volume. Thus we have to distinguish between the *heat capacity at constant volume* $C_V$ and the *heat capacity at constant pressure* $C_P$, and, as we have seen $C_P > C_V$.

If the heat is added at constant volume, we have simply that $dU = dQ = C_V d\nu$.

One other detail that requires some care is this. The specific heat capacity of a substance may well vary with temperature, even, in principle, over the temperature range of one degree mentioned in our definitions. Therefore, we really have to define the heat capacity at a given temperature in terms of the heat required to raise the temperature by an infinitesimal amount rather than through a finite range. Thus it is perhaps easiest to *define* heat capacity at constant volume in symbols as follow:

$$C_V = \left( \frac{\partial U}{\partial T} \right)(2,6,1)$$

As with many equations, this applies equally whether we are dealing with total, specific or molar heat capacity or internal energy.

If heat is supplied at constant pressure, some of the heat supplied goes into doing external work $PdV$, and therefore

$$C_P dT = C_V d\nu + PdV \quad (2,6,2)$$

For a mole of an *ideal gas at constant pressure*, $PdV = RdT$ and therefore, for an ideal gas,

$$C_P = C_V + R \quad (2,6,3)$$

Where, in this equation, $C_P$ and $C_V$ are the *molar* heat capacities of an ideal gas.
If we can develop a more general expression for the difference in the heat capacities of any substance, not just an ideal gas.

But let us continue, for the time being with an ideal gas.

In an ideal gas, there are no forces between the molecules, and hence no potential energy terms involving the intermolecular distances in the calculation of the internal energy. In other words, the internal energy is independent of the distances between molecules, and hence the internal energy is independent of the volume of a fixed mass of gas if the temperature (hence kinetic energy) is kept constant. That is, for an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_V = 0 \quad (2.6.4)$$

Let us think now of a monatomic gas, such as helium or argon. When we supply heat to (and raise the temperature of) an ideal mono atomic gas, we are increasing the translational kinetic energy of the molecules. If the gas is ideal, so that there are no intermolecular forces then all of the introduced heat goes into increasing the translational kinetic energy (i.e. the temperature) of the gas. (Recall that a gas at low pressure is nearly ideal, because then the molecules are so far apart that any intermolecular forces are negligible.) Recall from Section 5.5 that the translational kinetic energy of the molecules in a mole of gas is $$\frac{3}{2} RT$$.

The molar internal energy, then, of an ideal mono atomic gas is:

$$U = \frac{3}{2} RT + \text{constan} \quad (2.6.5)$$

From equation 8.1.1, therefore, the molar heat capacity at constant volume of an ideal monatomic gas is:

$$C_V = \frac{3}{2} R. \quad (2.6.6)$$

The molar heat capacities of real monatomic gases when well above their critical temperatures are indeed found to be close to this.
When we are dealing with polyatomic gases, however, the heat capacities are greater. This is because, when we supply heat, only some of it goes towards increasing the translational kinetic energy (temperature) of the gas. Some of the heat goes into increasing the rotational kinetic energy of the molecules. (Wait! Some of you are asking yourselves: "But do not atoms of helium and argon rotate? Do they not have rotational kinetic energy?" These are very good questions, but I am going to pretend for the moment that I haven't heard you. Perhaps, before I come to the end of this section, I may listen.)

When two molecules collide head on, there is an interchange of translational kinetic energy between them. But if they have a glancing collision, there is an exchange of translational and rotational kinetic energies. If millions of molecules are colliding with each other, there is a constant exchange of translational and rotational kinetic energies. When a dynamic equilibrium has been established, the kinetic energy will be shared equally between each degree of translational and rotational kinetic energy. (This is the Principle of Equipartition of Energy.) We know that the translational kinetic energy per mole is \( \frac{3}{2}RT \) - that is, \( \frac{1}{2}RT \) for each translational degree of freedom \( \frac{1}{2}mu^2, \frac{1}{2}mV^2, \frac{1}{2}mw^2 \). There is an equal amount of kinetic energy of rotation (with an exception to be noted below), so that the internal energy associated with a mole of a polyatomic gas is \( 3RT \) plus

a constant, and consequently the molar heat capacity of an ideal polyatomic gas is:

\[
C_v = 3R. \tag{2,6,7}
\]

It takes twice the heat to raise the temperature of a mole of a polyatomic gas compared with a monatomic gas.

The exception we mentioned is for linear molecules. These are molecules in which all the atoms are in a straight line. This necessarily includes, of course, all diatomic molecules (the oxygen and nitrogen in the air that we breathe) as well as some heavier molecules such as CO2, in which all the molecules (at least in the ground state) are in a straight line. (The molecule H2O is not linear.) In linear molecules, the moment of inertia about the inter nuclear axis is negligible, so there are only two degrees of rotational freedom, corresponding to rotation about two axes perpendicular to each other and to the inter nuclear axis. Thus there are five degrees of freedom in all (three of translation and two of rotation) and the
kinetic energy associated with each degree of freedom is \( \frac{1}{2}RT \) per mole for a total of \( \frac{5}{2}RT \) per mole, so the molar heat capacity is: (David, 2004).

\[
C_v = \frac{5}{2}R \tag{2,6,8}
\]

### 2.7 Density of states

The density of states function describes the number of states that are available in a system and is essential for determining the carrier concentrations and energy distributions of carriers within a semiconductor.

The wave function:

\[
\psi(x, y, z) = A \sin(k_xx) \sin(k_yy) \sin(k_zz), \tag{2,7,1}
\]

If:

\[
k_x = \pi n_x/L, \quad k_y = \pi n_y/L, \quad k_z = \pi n_z/L \tag{2,7,2}
\]

Where \( n_x, n_y, \) and \( n_z \) are positive integers. Is an energy Eigen function, since it solves the time-independent Schrodinger equation:

\[
\hat{\mathbf{H}} \psi = \varepsilon \psi \tag{2,7,3}
\]

Where \( \hat{\mathbf{H}} \) is the Hamiltonian operator:

\[
\hat{\mathbf{H}} = -\frac{\hbar^2}{2m} \nabla^2 \tag{2,7,4}
\]

And \( \varepsilon \) is a constant, the energy of the particle. Substituting

from (5), we find:

\[
\hat{\mathbf{H}} \psi = -\frac{\hbar^2}{2m} \nabla^2 \psi = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) \psi \tag{2,7,5}
\]

Hence, the energy levels are given by:
\[ \epsilon = \frac{\hbar^2 \pi^2}{2mL^2} (n^2 x + n^2 y + n^2 z) = k\theta (n^2 x + n^2 y + n^2 z) \quad (2,7,6) \]

The parameter \( \theta \) (with units of temperature) is defined:

\[ \theta = \frac{\hbar^2 \pi^2}{2mkL^2} \]

(2,7,7)

We now run into trouble. If we want to evaluate populations, total energy, heat capacity etc. as functions of temperature, the next step is to evaluate the partition function:

\[ \sum_j e^{-\frac{\epsilon_j}{k\theta}} \quad (2,7,8) \]

Here, the index \( j \) will actually be a triple index, for \( n_x, n_y \) and \( n_z \).

But quite apart from that, the summation is now difficult to evaluate. To make things more convenient, we shall assume that we can replace the summation by an integral, and write:

\[ Z = \sum_j e^{-\frac{\epsilon_j}{k\theta}} \to \int_0^\infty g(\epsilon) e^{-\frac{\epsilon}{k\theta}} d\epsilon \quad (2,7,9) \]

Here, \( g(\epsilon) \) is the density of states: the number of energy states in the (small) energy range \( \epsilon \) to \( \epsilon + d\epsilon \) is \( g(\epsilon) d\epsilon \).

To evaluate the partition function, we need an expression for the density of states, \( g(\epsilon) \). As an intermediate step, we will find the density of states in k-space, \( g(k) \), and then convert to the density of states as a function of energy (Joachain, 2000).

In k-space, states lie on a 3-dimensional rectangular grid of point with spacing \( \pi / L \) between points.

The number of points in the region bounded by \( k \) and \( k + dk \) is:

\[ g(k) dk \approx \frac{4\pi k^2 dk}{8} \times \frac{1}{\left(\frac{\pi}{L}\right)^3} \quad (2,7,8) \]
The first factor is the volume between spherical shells of radius \( k \) and \( k + dk \), and the second factor is the number of grid points per unit volume of k-space. The approximation is valid for large \( k \), i.e. at high energies. (Wange et, 2001)

With the assumption of large \( k \), we have:

\[
g(\kappa) d\kappa = \frac{4\pi \kappa^2}{8 \left( \frac{\pi}{L} \right)^3} d\kappa \tag{2,7,9}
\]

Hence:

\[
g(\kappa) d\kappa = \frac{4\pi}{8 \left( \frac{\pi}{L} \right)^3} \frac{2m\varepsilon}{\hbar^2} \frac{d\kappa}{d\varepsilon} d\varepsilon \tag{2,7,10}
\]

Also, from equation (16), we have:

\[
\kappa = \sqrt{\frac{2m\varepsilon}{\hbar^2}} \implies \frac{d\kappa}{d\varepsilon} = \frac{1}{2} \frac{2m}{\hbar^2 \varepsilon} \tag{2,7,11}
\]

So, writing \( V = L^3 \), we have for the density of states:

\[
g(\varepsilon) d\varepsilon = \frac{4\pi}{8 \left( \frac{\pi}{L} \right)^3} \frac{2m\varepsilon}{\hbar^2} \frac{1}{2} \sqrt{\frac{2m}{\hbar^2 \varepsilon}} d\varepsilon = \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} d\varepsilon \tag{2,7,12}
\]

### 2.8 Debye Model

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. We are interested in determining the number of possible wavelengths or frequencies within a given range.

For quantum waves in a one-dimensional box we saw that the wave function is

$$\Psi = A \sin kx, \text{where}$$

$$K = \frac{2\pi}{\lambda} = \frac{n\pi}{L}, \quad n = 1,2,3,\ldots$$  \hspace{1cm} (2,8,1)

Here $\lambda$ is the de Broglie wavelength, $n$ is the quantum number and $L$ is the dimension of the box. Using the fundamental equation of wave motion, $c \lambda v$, where $c$ is the wave velocity and $v$ the frequency, we obtain

$$n = \frac{2L}{\lambda} = \frac{2L}{c}v$$

If we consider an elastic solid as a cube of volume $V = L^3$ we get

$$n = \frac{v^{1/3}}{c}v$$ \hspace{1cm} (2,8,2)

Where, in this case $n^2 = n^2x + n^2y + n^2z$. The quantum numbers $n_x, n_y, \text{and} n_z$ are positive integers. Thus the possible values that they can assume occupy the first octant of a sphere of radius

$$n = (n^2x + n^2y + n^2z)^{1/2}$$

Let $g(v)dv$ be the number of possible frequencies in the range $v$ to $v + dv$

Since $n$ is proportional to $v$, $g(v) \, dv$ is the number of positive sets of Integers in the interval $n$ to $n+ dn$ that is, within a shell of thickness $dn$ of an octant of a sphere with radius $n$:

$$(v) \, dv = \frac{1}{8} 4\pi n^2 \, dn = \frac{1}{2} \pi n^2 \, dn$$

Substituting Equation (2,8,2) for $n$, we obtain
\[ g(\nu) \, d\nu = \frac{4\pi V}{c^3} \nu^2 \, d\nu \]  

(2,8,3)

In a vibrating solid, there are three types of waves: one longitudinal with velocity \( c_l \), and \textbf{two} transverse with velocity \( c_t \). All are propagated in the same direction. When all three waves are taken into account, Equation (2,8,3) becomes

\[ g(\nu) d\nu = 4\pi V \left[ \frac{1}{c^3l} + \frac{2}{c^3t} \right] \nu^2 d\nu \]  

(2,8,4)

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

\[ \int_0^{\nu_m} g(\nu) \, d\nu = \frac{4\pi V}{3} \left[ \frac{1}{c^3l} + \frac{2}{c^3t} \right] \nu^3 m \]

Combining this result with Equation (2,8,4), we get

\[ g(\nu) d\nu = \frac{9N\nu^2 d\nu}{\nu^3 m} \]  

(2,8,6)

Equation (2,8,5) provides us with some insight into the cutoff frequency and wavelength. Since \( \nu_m \propto (N/V)^{1/3} \) and \( \lambda_{\text{min}} \propto 1/\nu_m \), it follows that

\[ \lambda_{\text{min}} \propto \left( \frac{V}{N} \right)^{1/3} \]

The minimum possible wavelength is determined by the average inter atomic spacing. Thus the structure of the crystal sets a lower limit to the wavelength; shorter wavelengths do not lead to new modes of atomic vibration.

The principal difference between Einstein’s description and Debye’s model is in the assumption about the frequency spectrum of the lattice vibrations.

Now, there is no restriction on the number of phonons per energy level \( jh\nu \), where \( j \) is an integer. Thus phonons are bosons. This means that the occupation numbers must be given by the Bose-Einstein distribution. For the continuum, applies:
\[ \frac{N(\varepsilon)}{g(\varepsilon)} = \frac{1}{e^{(\varepsilon - \mu)/kT} - 1} \]

In this expression the chemical potential \( \mu \) must be set equal to zero. This is because the total number \( N \) of phonons is not an independent variable but rather is determined by the volume and temperature of the particular crystal being considered. Specifically, \( N \) is the number of phonons that causes the Helmholtz function to be a minimum at equilibrium. Since

\[ \mu = \left( \frac{\partial F}{\partial N} \right) \]

It follows that \( \mu = 0 \). With \( \varepsilon = \hbar \nu \), we have

\[ N_d = \frac{g(\nu)d\nu}{e^{\hbar \nu/kT} - 1} \]  \hspace{1cm} (2,8,7)

Where \( d \) is the number of phonons with frequencies in the range \( d \). When we substitute Equation (2,8,6) in this result, we obtain

\[ N_d = \frac{9N}{\nu_m^3} \frac{\nu^2d\nu}{e^{\hbar \nu/kT} - 1}, \quad \nu_m \geq \nu > 0 \]  \hspace{1cm} (2,8,8)

The total energy of the phonons in the frequency range \( d \) is Hence the internal energy of the assembly is

\[ U = \int_0^{\nu_m} \hbar \nu N(\nu)d\nu = \frac{9Nh}{\nu_m^3} \int_0^{\nu_m} \frac{\nu^3d\nu}{e^{\hbar \nu/kT} - 1} \]  \hspace{1cm} (2,8,9)

(We leave out the constant zero-point energy since this term has no effect on the Heat capacity. Its value is calculated in problem 6.2)

The Debye temperature \( \Theta_D \) is defined as

\[ \Theta_D = \frac{\hbar \nu_m}{k} \]  \hspace{1cm} (2,8,10)

That is, the Debye temperature is proportional to the cutoff frequency \( \nu_m \).
To obtain the heat capacity, we need to differentiate Equation (2,8,9) with respect to the temperature. Now

\[
\frac{d}{dT} \left(\frac{1}{e^{hv/VT} - 1}\right) = \frac{hv}{KT^2} \left(\frac{e^{hv/VT}}{e^{VT} - 1}\right)^2
\]

Thus

\[
C_v = \frac{dU}{dT} = \frac{9N}{v^3m} \int_0^{vm} \frac{hv}{KT^2} \left(\frac{e^{hv/VT}}{e^{VT} - 1}\right)^2 v^3 dv
\]

We let \( x = hv/kT \) and \( x = hv/VT = \Theta_D / T \). With the change of variable we have: \( dx = (h/kT) dv \) so:

\[
C_v = \frac{9N}{v^3m} \int_0^{vm} \frac{e^{hv/VT}}{KT^2} e^{x/VT} dx = \frac{9N}{v^3m} \int_0^{x} \frac{e^x}{(e^x - 1)^2} dx
\]

\[
= \frac{9N}{v^3m} \frac{1}{(KT)^2} \frac{\Theta_D}{h} \int_0^{x} \frac{e^x}{(e^x - 1)^2} dx = 9Nk \left(\frac{KT}{hv_{m}}\right)^3 \int_0^{x} \frac{e^{x/VT}}{(e^x - 1)^2} dx
\]

\[
C_v = 9Nk \left(\frac{\Theta_D}{T}\right)^3 \int_0^{x} \frac{x^4 e^x}{(e^x - 1)^2} dx
\]

For high temperatures, \( \Theta_D / T \ll 1 \) and \( x \ll 1 \). So \( e^x - 1 \approx x \) in the denominator and \( e^x \approx 1 \) in the numerator, so the integral becomes

\[
\int_0^{\Theta_D/T} x^2 dx = \frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3
\]

Hence

\[
C_v = 9Nk \left(\frac{T}{\Theta_D}\right)^3 \left\{\frac{1}{3} \left(\frac{\Theta_D}{T}\right)^3\right\} = 3Nk
\]

This is the law of Dulong and Petit. For low temperatures, \( \Theta_D / T \) is large and we can let the upper limit of the integral be infinity. Then
\[
\int_{0}^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx = \frac{4\pi^4}{15}
\]

(2,8,13)

And:

\[
C_v = \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta_D}\right)^3
\]

(2,8,14)

This equation is known as Debye’s \( T^3 \) law. It is valid when the temperature is lower than about \( 0.1\theta_D \) which means for most substances about 10-20 K. The relation gives a better fit to experimental data at very low temperatures than the Einstein model, and is valid for all monatomic solids. When the temperature is above the Debye temperature, the heat capacity is very nearly equal to the classical value \( 3Nk \). For temperatures below the Debye temperature, quantum effects become important and \( C_v \) decreases to zero. Note that diamond, with a Debye temperature of 1860 K, is a “quantum solid” at room temperature. Recent work has centered on the behavior of solids at low temperatures. Experiments suggest that amorphous materials do not follow the Debye \( T^3 \) law even at temperatures below \( 0.01\theta_D \). There is more yet to be learned.

### 2.10 previous studies

#### 2.10.1 Study of the Universal relation for size dependent thermodynamic properties of metallic nanoparticles

In this Study Found that heat capacity is not only a function of temperature, but is also a function of size in Nano scale. The Debye model was developed to estimate the phonon contribution to the special heat capacity in a solid, which give the famous \( T^3 \) law. In Debye model, the molar special heat capacity at constant volume \( C_V \) is expressed as:

\[
C_V = 9R \left(\frac{T}{\theta_D}\right)^3 \int_{0}^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx
\]

(2.10.1.1)

(R refers to the gas constant), where \( \theta_D \) is the only parameter to reveal the magnitude of \( C_V \). Therefore, \( C_V \) can be calculated only if \( \theta_D \) is obtained. (Shiyun Xiong, 2011).
2.10.2 Heat capacity measurements of porous materials at cryogenic temperatures

The main objective of this study is to measure specific heat capacity of porous materials at cryogenic temperature, the working temperature range of hydrogen adsorption storage system. The heat distribution in the sorption materials used in adsorption processes plays a significant role during charging and discharging of the storage system, it is therefore necessary to measure the heat capacity at their temperatures; In addition there are very little published data for the materials under investigation in this study. (Thea Ragna, 2005).

2.10.3 Determining the phonon density of state from specific heat measurements via maximum entropy methods:

The maximum entropy and reverse Monte Carlo methods are applied to the computation of the phonon density of state (DOS) from heat capacity data.

The approach is introduced and the formalism is described. Simulated data are used to test the method, and its sensitivity to noise.

Heat capacity measurements from diamond are used to demonstrate the use of the method with the experimental data. Comparison between maximum entropy and reverse Monte Carlo result shows that the form of entropy used here is correct, and that results are stable and reliable.

Major features of the (DOS) are picked out, and acoustic and optical phonons can be treated with the same approach. The treatment set out in this work provides a cost-effective and reliable method for studies of the phonon properties of materials. (JP Haguy, 2005).

2.10.4 Thermodynamics and lattice vibrations of minerals: 1.Mineral heat capacities and their relationships to simple lattice vibrational models:

The thermodynamic properties of minerals are interpreted in terms of lattice vibrational spectra. In this work, measured heat capacities for minerals are examined in terms of the
Debye theory of lattice vibrations, and it is demonstrated that heat capacities of silicates show large deviations from the behavior expected from Debye theory.

The underlying assumption of Debye theory are critically reviewed, and it is shown that the observed thermodynamic deviations in minerals probably arise from four effects not included in the Debye model: anisotropy of elastic parameters, disoperation of acoustic waves toward Brillouin Zone boundaries, optic vibrations in excess of the Debye spectrum at low frequency, and optic vibrations at frequencies much greater than the Debye cutoff frequency predicted by acoustic measurements. Each of the four effects influences the heat capacity in a particular temperature range: anisotropy, dispersion and low-frequency optic vibrations are important at low temperatures; high-frequency vibrations are important at higher temperatures. It is necessary to include all four effects in a generalized lattice vibrational model for minerals. (Reviews of Geophysics, 2010).
CHAPTER THREE

MATERIALS AND METHOD

3.1 Introduction

For each atom in a solid or gas phase, three coordinates have to be specified to describe the atom’s position – a single atom has 3 degrees of freedom for its motion. A solid or a molecule composed of N atoms has 3N degrees of freedom. We can also think about the number of degrees of freedom as the number of ways to absorb energy. The theorem of equipartition of energy (classical mechanics) states that in thermal equilibrium the same average energy is associated with each independent degree of freedom and that the energy is $\frac{1}{2} kBT$. In an ideal gas of molecules only internal vibrational degrees of freedom have potential energy associated with them. For example, a diatomic molecule has 3 translational + 2 rotational + 1 vibrational = 6 total degrees of freedom. Potential energy contributes $\frac{1}{2} kBT$ only to the energy of the vibrational degree of freedom, and $U_{\text{molecule}} = \frac{7}{2}kBT$ if all degrees of freedom are “fully” excited.

Heat capacity of gas, solid or liquid tends to increase with temperature, due to the increasing number of excited degrees of freedom, requiring more energy to cause the same temperature rise.

Most notably in the gas heat capacity depends on the surrounding circumstances. That is a distinction between the heat capacity of the gas when the pressure stability of CP and the heat capacity of the gas when the stability of CV size. When the stability of volume status change occurs via the supply of gas from abroad warmly working to the high temperature of the gas and this means increasing the gas molecules kinetic energy. As in the case of gas supply heat from the outside while maintaining the stability of the pressure, we find that the performance of gas filled as increasing the volume of gas. This occurs because of gas extends under the impact of the heat and because of that we maintain the stability of the pressure.

The measure of heat capacity, or the quantity of heat needed to raise the temperature of one gram of a substance by one degree Celsius, is termed specific heat and is represented by the symbol C.
3.2 Experiment Theory

\[ \Delta V = \frac{NR}{P} = \frac{V}{T} \Delta T \quad (3.3.1) \]

Where:

\( \Delta V \equiv \text{Change in volume} \)

\( N \equiv \text{Number of moles} \)

\( R \equiv \text{Gas constant} \)

\( P \equiv \text{Pressure} \)

\( V \equiv \text{Volume} \)

\( T \equiv \text{Temperature} \)

\( \Delta T \equiv \text{Change in temperature} \)

Molecules within gases are further apart and weakly attracted to each other. Heat causes the molecules to move faster, (heat energy is converted to kinetic energy) which means that the volume of a gas increases more than the volume of a solid or liquid.

However, gases that are contained in a fixed volume cannot expand - and so increases in temperature result in increases in pressure.

3.3 Material and Method

Figures (3.1) show a simple form of laboratory apparatus. They used a sample of three gases (oxygen - nitrogen - carbon dioxide) and placed in a gas cylinder connected to a bottle Registrar Pro belted with a computer to monitor the key is pressed (T). The system has been cleansed of any other gases and then allowing the gas to sweep the flask for five minutes. The objectives of this experiment are measurements heat capacity of (oxygen), (nitrogen) and (carbon dioxide) at deferent temperature T
Fig (3-3-1): laboratory apparatus Measurement of Specific Heat Capacity

Fig (3.1): laboratory apparatus Measurement of Specific Heat Capacity
CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Introduction

This chapter includes the data analysis that collected to achieve the objective of the research, beside the most important findings of the study.

4.2 Results:

Table (4.1): Heat capacity of samples gases (O₂-N₂-CO₂) at temperature from 1 °C to 100 °C

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Table (4.2): the statistics of temperature applied (°C) and heat capacity of sample gas (O₂)

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<th>Maximum</th>
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Fig.(4-2-1): The relationship between the temperature and heat capacity of O₂
Table (4.3): the statistics of temperature applied (°C) and heat capacity of sample gas (N₂)

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<td>64.66793</td>
</tr>
</tbody>
</table>

Fig.(4-2-2): The relationship between the temperature and heat capacity of CO₂
Table (4.3): the statistics of temperature applied (°C) and heat capacity of sample gas (CO₂)

<table>
<thead>
<tr>
<th>Descriptive Statistics Data</th>
<th>Mean</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>51.5</td>
<td>3</td>
<td>100</td>
</tr>
<tr>
<td>CO₂</td>
<td>10.3545</td>
<td>0.60114</td>
<td>19.99526</td>
</tr>
</tbody>
</table>

Fig.(4-2-3): The relationship between the temperature and heat capacity of CO₂
4.3 Discussion

The basic objective of this chapter is to present and discuss the results obtained from the experimentalist work of this study. Some of the results were measured and the others were calculated to determine heat capacity of samples gases (O\textsubscript{2}–N\textsubscript{2} and CO\textsubscript{2}), the following experiment investigates the relationship between temperatures applied and heat capacity of samples gases (O\textsubscript{2}–N\textsubscript{2} and CO\textsubscript{2}), gases (O\textsubscript{2}–N\textsubscript{2} and CO\textsubscript{2}), using the Equation (3-3-1).

The measured heat capacity of samples gases (O\textsubscript{2}–N\textsubscript{2} and CO\textsubscript{2}) are tabulated in table (4-2-1).

The effect of temperature on the heat capacity of was increases by the read

\[ (O_2 = 0.22 \text{ Kcal} \cdot \text{k}^{-1} ) \]

\[ .\text{kg}^{-1} \cdot N_2 = 0.25 \text{ Kcal} \cdot \text{k}^{-1} \cdot \text{kg}^{-1} \text{ and CO}_2 = 0.2 \text{ Kcal} \cdot \text{k}^{-1} \cdot \text{kg}^{-1} ) \] for °C. These different values of three gases because CO\textsubscript{2} are lightest gas then O\textsubscript{2} and N\textsubscript{2} are heaviest gas.
By noting to calculate the statistics of temperature applied (°C) and heat capacity of samples gases (O₂- N₂- CO₂) following low in table (4-2-2). Show on the table (4-2-2) the mean values of heat capacity for the samples (O₂) is 11.29 at mean temperature 51.5 °C. But the mean values of heat capacity for samples (N₂) is 12.77 at temperature 51.5 °C. At last the mean values of heat capacity for the samples (CO₂) is 10.35 at mean temperature 51.5 °C.

In figure (4-2-2) shows the relation between temperature and heat capacity of samples gases (O₂- N₂- CO₂). The effects of temperature applied (°C) on the samples, while the temperature value increased the heat capacity of samples (O₂-N₂-CO₂) increase. Due to the change in substance structure, more precisely, it depends on how many degree of freedom are available in the substance particles, where a degree of freedom is a form of energy stored in the particles.

When we compare these study with other studies for the heat capacity we found the heat capacity of gas, solid or liquid tends to increase with temperature, due to the increasing number of excited degrees of freedom, requiring more energy to cause the same temperature rise.

4.4 Conclusions

In this work, the specific heat capacity for O₂, N₂ and CO₂, have been measured using an Eq (3-3-1). The heat capacity of samples at different temperatures varies with temperature at 1°C and at 100 °C. At temperatures 25 , 50 , 75 °C , the heat capacities (CP) of O₂ , N₂ , and CO₂ were (5.49 , 6.22 , 5.04 , 10.99 , 12.44 , 10 08 , 16.44 , 18.60 , 15..08 Kcal.k⁻¹ .kg⁻¹ ) for O₂ , N₂ , and CO₂ respectively.

The primary intention of this work is to investigate the heat capacity of gases (O₂ , N₂ ,and CO₂). And discussing the effect of temperature on the heat capacity of gases (O2 , N2 and CO2). The theoretical background for studying this dependency is Einsteins model for determining the heat capacity. Consequently, the report illustrates use of quantum theory and statistical mechanics and how they relate to macroscopic observables.

The effects of temperature applied (°C) on the samples, while the temperature value increased the heat capacity of samples gases (O₂ , N₂ and CO₂) increase.
These results were found to fit Debye relation for the heat capacity of solids. Therefore this work shows that Debye relation is suitable for measurement of heat capacities of gases.

4.5 Recommendations

This work recommends future studies for other gases, and using other suitable methods to find heat capacity such as measuring radiation and convection.
References


Reviews Geophyscis (2010). Volume 17, Issue 1, Version of Record online.


