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NEW THERMODYNAMICS: A SUPERIOR FIT REVISED KINETIC THEORY

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ABSTRACT

The accepted kinetic theory forms a basis for modern thermodynamics and is mathematically based upon equipartition and degrees of freedom. It remains plagued with the necessity of numerous degrees of freedom exceptions for it to explain both empirically determined heat capacities and adiabatic indexes. Furthermore, assuming kT/2 per degree of freedom is to accept that a gas molecule possesses a specified energy without providing any clarity concerning that energy's origins. Energy without an origin contravenes the first law of thermodynamics. This author's previously published superior fit kinetic theory will be clarified and elaborated upon. This includes showing that this revised kinetic theory is a superior fit to both known heat capacities and adiabatic indexes. Not only is it a superior fit that does not rely upon any exceptions, this author's kinetic theory also provides insight into the actual sources of a gas molecule's energy. Furthermore, clarity concerning the difference between isometric (isochoric) and isobaric heat capacities in terms of sensible work will be discussed, along withits likely empirical verification.

KEYWORDS

Adiabatic Index, Kinetic Theory, Degrees of Freedom, Heat Capacity

1. INTRODUCTION

This introduction firstly reviews the currently accepted theories based upon degrees of freedom and equipartition. Secondly, these theories are compared to this author's revised kinetic theory, which is both simpler to comprehend and is a superior fit to known empirical findings for heat capacities. This is necessary before discussing how this revised kinetic theory and resulting heat capacities are also a superior fit to empirically known adiabatic indexes.

Traditionally accepted kinetic theory of gases is based upon a combination of equipartition and degrees of freedom arguments. Specifically, a gas molecule consisting of n" atoms generally possess the following degrees of freedom (*f*):

$$f = 3n" \tag{1}$$

Degrees of freedom is based upon the concept that a molecule (or atom) can:

1) Translate in a given direction
2) Rotate around a given axis
3) Vibrate between atoms in a molecule

Equipartition theory states that the mean energy associated with any given degree of freedom is: $kT/2$, where "k" is Boltzmann's constant and "T" is the absolute temperature. Similarly, for a mole of molecules (or atoms) each degree of freedom results in a molar energy of: $RT/2$, where

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"R" is the ideal gas constant.

The traditionally accepted molar isometric heat capacity (C_v) for an ideal gas is:

$$C_v = fR/2 \tag{2}$$

Combining eq. 1 and 2, one obtains:

$$C_v = 3n''R/2 \tag{3}$$

The difference between the molar isobaric and isometric heat capacity is:

$$R = C_p - C_v \tag{4}$$

Thus, the molar isobaric heat capacity for an ideal gasbecomes:

$$C_p = R(1 + \frac{f}{2}) \tag{5}$$

or

$$C_p = R(1 + 3n''/2) \tag{6}$$

Although each gas molecule has its degrees of freedom defined by eq. 1, there is a difference in the vibrational energies between linear and non-linear molecules. The number of vibrational modes of a linear gas molecule is obtained by:

$$(Vibrational\ Modes)_{linear} = 3n'' - 5 \tag{7}$$

Conversely, non-linear molecules have their vibrational modes determined by:

$$(Vibrational\ Modes)_{non-linear} = 3n'' - 6 \tag{8}$$

The accepted reasoning for the difference is that a linear gas molecule's atoms lie along a solitary axis. As such the molecule can rotate about two different axis that are perpendicular to the stated solitary axis that the atoms lie on. Therefore, linear gas molecules, e.g., O_2, N_2, CO_2, have two rotational degrees of freedom.

Conversely, a non-linear molecule can rotate around any of the three perpendicular axes thus has three rotational degrees of freedom, e.g., H_2O (vapor).

Table 1: Degrees of freedom

	Total degrees of freedom (*f*)	Translational (*f*)	Rotational (*f*)	Vibrational (*f*)
Linear	3*n*"	3	2	3*n*"-5
Non-linear	3*n*"	3	3	3*n*"-6

Table 1 shows that both linear and non-linear molecules have 3 translational degrees of freedom (*f*) but differ in their rotational$f$ and vibrational$f$. Although their explanations differ, generally both linear and non-linear molecules, still have their total degrees of freedom defined by eq. 1.

The ratio of isobaric heat capacity (C_p) to isometric heat capacity (C_v) defines the adiabatic index (γ). In terms of molar heat capacities, one traditionally writes:

$$\gamma = \frac{C_p}{C_v} = 1 + 2/f \tag{9}$$

A monatomic gas is claimed to possess 3 translational degrees of freedom, with no rotational energy. The accepted reasoning is that the solitary atom's radius is too small to have rotational energy. This "Exception 1"enables a monatomic gas to adhere to eq. 1. Hence, based upon eq. 4:

$$\gamma_1 = \frac{5}{3} = 1.66$$

Diatomic gases are claimed to possess 5 degrees of freedom. This is based upon 3 translational degrees of freedom, and 2 rotational degrees with no vibrational energy. This "Exception 2" isdirected at eq. 1. The reasoning for there being no vibrational energy is that when at room temperature, it is too cold for there to be vibrational energy. Based upon Exception 2:$\gamma = \frac{7}{5} = 1.4$. If it were actually based upon eq.1 then:f=6, hence: $\gamma = \frac{8}{6} = 1.33$.

A linear triatomic gas (e.g., CO_2) is also claimed to have 5 degrees of freedom. Thisis also based upon 3 translational degrees of freedom, and 2 rotational degrees. This "Exception 3" is directed at eq. 1. Again, it is asserted that when at room temperature,it is too cold for there to be vibrational energy. Based upon Exception 3: $\gamma = \frac{7}{5} = 1.4$. If it were actually based upon eq.1, then f=9, hence: $\gamma = \frac{11}{9} = 1.22$.

A non-linear triatomic gas [e.g. H_2O (vapor)] is claimed to have 6 degrees of freedom. This is based upon 3 translational degrees of freedom, and 3 rotational degrees. This "Exception 4" is again directed at eq. 1. Again, it is claimed that when at room temperature, it is too cold for there to be vibrational energy e.g., "Exception 5". Based upon these exceptions: $\gamma = \frac{8}{6} = 1.33$. If it were actually based upon eq.1 then:f=9, hence : $\gamma = \frac{11}{9} = 1.22$.

Such a litany of exceptions should raise concern. Furthermore, some exceptions are inherently problematic. Consider Exception 1: A monatomic gas' radius being too small to have rotational energy seems irrational. An object with a smaller radius can have the same rotational energy as a larger object. All that is required is that the smaller object possesses a greater rotational velocity. Moreover, given identical rotational inducing impacts, a smaller atom will always possess a greater rotational velocity than a larger molecule would.

Many exceptions are founded upon whether or not there is a threshold for the thermal energy required for molecules to actually vibrate. Such exceptions have been expressed in terms of quantum arguments, e.g., "*However, as mass increases and the frequency of vibrational modes decreases, vibrational degrees of freedom start to enter into the equation at far lower temperatures than is typically the case for diatomic molecules. For example, it requires a far larger temperature to excite the single vibrational mode for* H_2*, for which one quantum of vibration is a fairly large amount of energy, than for the bending or stretching vibrations of* CO_2 ." [1]

The claim that triatomic gases possess no real vibrational energy can founds any notion of linear

CO_2 being a greenhouse gas. It equally challenges the understanding that non-linear water vapor in our atmosphere can absorb significant quantities of thermal energy. Something is wrong concerning these exceptions.

Kinetic theory was revised on the premise that in a closed system, the larger structured wall molecules impose their kinematics upon the smaller freely moving gas molecules[2]-[4]. Accepting that a molecule will attain a mean energy ($kT/2$) along each degree of freedom warrants a rethink. It would be beneficial to explain the actual origins of the energy, rather than simply claim that it exists. Importantly, this author's revised kinetic theory requires no exceptions in order to explain empirical findings. [2]-[4]

A quick review of this revised superior fit kinetic theory. When a molecule (or atom) collides with a structured wall molecule, that wall molecule imposes a mean kinetic energy of $kT/2$ onto that gas molecule. This kinetic energy consists of the gas molecule's translational plus its rotational energy. An analogy being a bat impacting a ball, where the bat imposes both translational and rotational energy onto the ball.

With there being six walls, the gas molecule (or atom) will attain the above mean kinetic energy along each orthogonal axis (x,y, z). This can be viewed in another context. After numerous collisions with the closed system's walls, each gas molecule possesses a mean component of motion along each orthogonal axis. That component will consist of both the translational motion along that axis, plus any rotational motion.

When it comes to rotation, a molecule (or atom) can only physically be rotating around a given axis (or components thereof) at a given instant of time. Accordingly, rotational energy can be a result of collisions with the three orthogonal walls, but unlike translational energy, the molecule does not necessarily maintain three orthogonal components of rotational motion at all times.

It should be noted that a gas molecule's (or atom's) rotational energy can be transformed back into translational energies in future molecular (or atom) collisions. This applies to gas-wall molecule (or atom) collisions, as well as gas-gas molecule (or atom) collisions. This confronts traditional notions of elastic collisions being limited to translational energy.

As will be discussed, in the revised theory, one attains an inherent understanding concerning the origins of the energy associated with a gas molecule (or atom). This challenges traditional kinetic theory, which places a mean energy of $kT/2$ along all degrees of freedom. This has been done without consideration concerning how the molecule obtains that energy in the first place.

Based upon this author's revised kinetic theory [2],[3],[4] the total thermal energy [$E_{Tk(t,r)}$] of a monatomic gas approximates:

$$E_{Tk(t,r)} \approx \left(\frac{3}{2}\right) NkT \qquad (10)$$

where, "N" is the number of atoms, the subscript "Tk" indicates that it is the gas' total kinetic energy while the sub-subscripts "(t,,r)" indicates that the kinetic energy consists of translational plus rotational energy.

A polyatomic gas molecule has a mean thermal vibrational energy of kT associated with each bond between atoms. Therefore, the total thermal energy of a polyatomic gas, can be approximated by [2]-[4]:

$$E_T \cong \frac{3}{2}NkT + (n'' - 1)NkT = NkT(n'' + 1/2) \qquad (11)$$

where N”represents the number of molecules while “n” ” represents the number of atoms per molecule. When $n'' = 1$, then eq. 11 becomes eq. 10

In terms of the number of moles (n) and the ideal gas constant (R), eq. 11 can be rewritten [2]-[4]:

$$E_T \cong nRT(n'' + 1/2) \qquad (12)$$

If one heated the gas then its temperature would change. In terms ofthermal energy change (dE_T), and temperature change (dT), eq. 12 becomes:

$$dE_T \cong nRdT(n'' + 1/2) \qquad (13)$$

If the heated gas was an isometric (isochoric) System 1, then in terms of the thermal energy in (dq_{1in-v}) and isometric molar heat capacity (C_v) one would write:

$$dq_{1in-v} = nC_v dT \qquad (14)$$

Comparing eq. 14 to eq. 13, one realizes that the isometric molar heat capacity (C_v) is:

$$C_v = R(n'' + 1/2) \qquad (15)$$

Consider that a gas is heated in an isobaric expanding system. One has to heat the gas ($nC_v dT$) plus perform the work. Such work is always external to the system performing that work, e.g., an expanding system.

Our atmosphere has mass therefore all expanding systems must lift the overlying atmosphere’s mass. Thus,the isobaric expanding system performs work onto the overlying atmosphere. This work results in an atmospheric potential energy increase[4]-[9]. This is sensible work.

If a subsystem of the atmosphere contracts, then some atmospheric gas molecules plunge downwards, resulting in potential energy being converted into atmospheric kinetic energy. Atmospheric kinetic energy increases can be viewed as infinitesimal atmospheric temperature increases, which quickly disperse throughout the atmosphere. Therefore, the kinetic energy increase is lost into the atmosphere, which behaves like a heat sink.

Accordingly, whenan expanded system then collapses, the work exerted by the expanding system does not return to the contracting system[1]. Therefore, in terms of the expanding system the work

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[1] True reversibility requires all of the energy exerted by the expanding system to be returned to that system. Situations arise, where a system mechanically returns to its initial state (pre-expansion state) but fails to receive all of its expended energy back. Since the system has mechanically returned to its original state, one witnesses the illusion of reversibility. This is the basis of Loschmidt’s paradox (reversibility paradox) and helps one to understand lost work. state) but fails to receive all of its expended energy back. Since the system has mechanically returned to its original state, one witnesses the illusion of reversibility. This is the basis of Loschmidt’s paradox (reversibility paradox) and helps one to understand lost work.

is lost, hence the name lost work $[W_{lost} = (PdV)_{atm}]$ [4]-[9].

Therefore, in terms of heat in (dq_{1in-p}) and isobaric heat capacity (C_p), one would write:

$$dq_{1in-p} = nC_p dT = nC_v dT + (PdV)_{atm} \qquad (16)$$

In order for the isobaric system to expand then: $P_{Sys1} > P_{atm}$. Consider the process of boiling causing some piston-cylinder to expand.Consider the expanding piston-cylinderis frictionless and thatthe piston is massless. Then the expansion can be isobaric, i.e.,$P_{Sys1} \approx P_{atm}$.

Since the expanding system is a subsystem within Earth's atmosphere then: $dV_{Sys1} = dV_{atm}$.

Therefore: $(PdV)_{Sys1} \approx (PdV)_{atm}$.

Therefore, eq. 16 can be approximated by:

$$dq_{1in-p} \approx nC_v dT + (PdV)_{Sys1} \qquad (17)$$

Defining PdVin terms expanding System 1 is non-sensible work

If the gas can be deemed ideal then one could apply the ideal gas law ($PV = nRT$) and rewrite eq. 17, as follows:

$$dq_{1in-p} \approx (nC_v dT)_{Sys1} + (nRdT)_{Sys1} \qquad (18)$$

Based upon equations 14, 15 and 18, one can now write:

$$C_p \approx R\,(n" + 1/2) + R = R(n" + 3/2) \qquad (19)$$

Comparing eq.19 to eq. 15, one obtains the traditionally accepted relationfor comparing the isobaric (C_p) and isometric (C_v) heat capacities. That being eq. 4.

As previously published in this journal [2], comparison of empirically determined heatcapacities and theoretical heat capacities is given in Fig. 1. It clearly shows that the isometric (isochoric) heat capacity, as defined by this author's eq. 15, is a superior fit to the traditionally accepted isometric heat capacity, i.e., eq. 3 [2],[4].

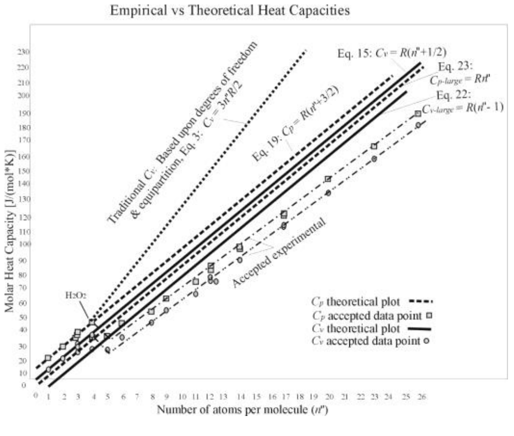

Fig. 1 shows the theoretical isometric based upon eq. 15 and eq. 22. It also shows the theoretical isobaric heat capacities based upon eq. 19 and eq. 23. Note eq. 19 and eq. 23 are for large polyatomic gas molecules that tend to flatline. Data originates from [10].

It must be emphasized that in Fig. 1, the poor fitting traditionally accepted eq.3 does not take into account all those previously discussed exceptions, which tend to be based upon degree of freedom arguments. However, those exceptions have primarily been formulated for smaller gases, e.g., monatomic, diatomic and triatomic gases. Which have been plotted in Fig.1.

Therefore, the slope ($3R/2$) associated with eq. 3 starts at $n''=4$, e.g. data point for H_2O_2. Due to this excessively large slope, the fit of eq. 3 becomes increasingly questionable, as n'' increases.

Small gas molecules, e.g., monatomic, diatomic and triatomic, have the ability to undergo a clean energy transfer when colliding with a wall molecule. Hence, the large structured vibrating wall molecule can impose its energy onto the gas molecule. This is shown at both B and C in Fig. 2. For the case of molecule B, the wall molecule is initially moving in the same direction as the gas molecule. However, at some point in time the wall molecule will reverse it motion, i.e., start moving outwards. At which point, it imposes its kinetic energy onto the colliding gas molecule, resulting in a combination of the gas molecule's translational plus rotational energy, i.e., its kinetic energy. For case C, the wall molecule is moving outward, and therefore immediately imposes its kinetic energy upon the colliding gas molecule.

One can further visualize a larger gas molecule, e.g.,$n'' > 4$, colliding with a group of wall molecules. Some of this group will be moving outwards, while others are moving inwards. Therefore, an elongated/linear gas molecule, as illustrated at point A in Fig. 2, will not cleanly, attain kinetic energy from the wall molecules. This author has previously named this phenomenon, "flatlining" [3],[4].

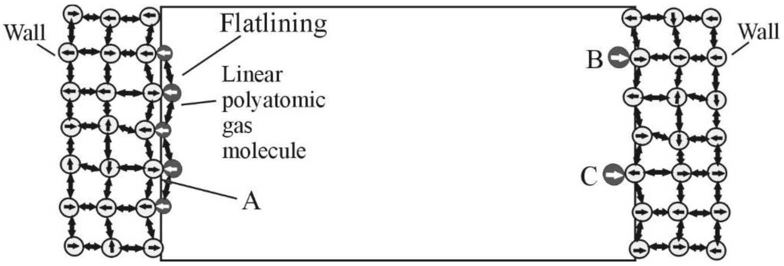

Fig. 2 illustrates two small gas molecules/atoms interacting with the wall at points B and C. It also illustrates a long linear polyatomic gas molecule flatlining at A.

This paper is a continuation of the above discussed realizations.

2. ALL ENERGY HAS AN ORIGIN

A big issue with traditionally accepted kinetic theory is that by assuming a mean energy of $kT/2$ per degree of freedom, one assumes that such energy simply exists. The first law tells us that all energy must have an origin, i.e., energy is never spontaneously created.

Accepting that the structured wall molecules impose their kinematics onto the relatively small gas molecules, provides insight concerning where the gas molecule's kinetic energy originates. Kinetic energy being its translational plus rotational energy, i.e., $3NkT/2$ as defined by eq. 10.

For example, condensed matter absorbs thermal energy from its surroundings. This includes our thermal energy from our Sun. Conductivity ensures that this thermal energy is distributed throughout the condensed matter as vibrational energy. This includes a closed system's walls. That energy is then passed onto the enclosed gas molecules via gas-wall molecule collisions. Thus, providing the gas molecules with combinations of translational and rotational energy.

Simply put, accepted kinetic theory flouts the first law of thermodynamics, when it comes to the acquisition of a gas' kinetic energy.

3. VIBRATIONAL ENERGY ORIGINS

The astute reader may realize that how a polyatomic atomic gas attains its vibrational energy has not been properly addressed. Specifically, if gas molecules (and/or atoms) obtain their translational plus rotational energy through their collisions with wall molecules, then what about a gas molecule's vibrational energy?

If the vibrational energy of polyatomic gases also originated from collisions with the surrounding wall molecules, then that vibrational would be added to translational and rotational energy and the summation of those energies would be equated to eq. 10. This is not the case, whether one considers the revised kinetic theory or the traditionally accepted kinetic theory. Of course, accepted kinetic theory simply states that the vibrational energy exits, a practice that is at best, questionable.

Realizing that eq. 11 is an exact fit to empirical findings, enlightens us to the reality that adding the vibrational energy $[(n"-1)NkT]$ to eq. 10 has a certain rationale. Importantly, it is backed by known empirical findings. Note the question as to how polyatomic gas molecules attain a vibrational energy of $[(n"-1)NkT]$, equally applies to both the revised and accepted kinetic theories.

One may adhere to the notion that certain gas molecules adsorb discrete wavelengths (or, frequencies) of thermal radiation. Such thermal radiation (e,g., sometimes blackbody) is both emitted and adsorbed by a closed system's surrounding walls. The wavelengths are discrete because they are absorbed by electrons and/or charge distributions, such as dipole moments.

What is problematic is that there is a lack of clarity concerning why there is universality when it comes to the heat capacities of gases. A universality based upon the number of atoms (n") in a molecule rather than the molecule's charge distributions, i.e., one must ponder why certain gases are considered transparent to thermal radiation (e.g. homonuclear O_2 and N_2), yet have similar heat capacities to those that are not deemed transparent.

This will take more thought but as a preliminary discussion. Perhaps the adsorption of thermal radiation by polyatomic gases involves a different phenomenon than the absorption of discrete photons. When an electron adsorbs a discrete photon's energy, the electron enters a higher energy state. In a fraction of a second, that electron can drop back down to its original energy state, thus emitting a photon of similar energy to that it adsorbed in the first place.

The adsorption and emission of thermal radiation by electrons is problematic as some complete explanation for heat transfer between photons and gases. This goes beyond the adsorption followed by emission of discrete photons, and the fact that heat capacities have a certain universality. Onto that one must ask how does a gas at a specific temperature, whose electrons are already in an excited state, adsorb more photons, thus further increasing the gas' temperature? In other words, the adsorption of discrete photons by electrons and/or charge distributions is not an accumulative process.

In an attempt to understand what is missing, this author has recently performed an analysis concerning what constitutes thermal energy [11]. Thermal energy can best be described as long wavelength infrared ($\lambda > 10\mu m = 10{,}000\ nm$). That is the part of the EM spectrum that has been considered to be thermal infrared. Although the analysis was preliminary, it clearly shows that the accepted conceptualizations of thermal energy and its density may be misguided. The analysis also gives insights into heat capacities.

What becomes important is that there must be a different mechanism for the absorption of thermal energy by gases. A mechanism that is somewhat universal and involves thermal infrared photons. This author thoughts lean towards the adsorption of the thermal infrared photon's momentum (thermal photons) by atoms within gaseous molecules. Thermal photon adsorption would lead to increases of the vibrational energy within the gas molecules [4], [12]. An adsorption process that would be accumulative, thus explaining the possibility of the continuous increases of a gas' temperature. Note that such adsorptions should primarily occur in the thermal infrared and/or longer wavelengths.

Certainly, the adsorption would involve the scattering cross-section of both the gas molecule (and/or its atoms) and the various photons. This does elicit questions concerning a photon's size and does it vary with wavelength/frequency [4],[12]? Whatever the eventual outcome, accepted theory must be able to explain the universality of n'' in heat capacities and the accumulation of thermal energy.

4. HEAT CAPACITIES OF LONG POLYATOMIC GASES

Based upon Fig. 2, long/large polyatomic gases do not interact cleanly with the wall molecules. Accordingly, such polyatomic gases will tend not to attain net kinetic energy increases from the vibrating wall molecules in a closed system, e.g., most experimental systems. This is not to say that these gas molecules have no kinetic energy. It is to say that these large gas molecules do not necessarily obtain increases in kinetic energy, as the wall molecule's temperature increases.

Hence, the above gas molecules primarily obtain vibrational energy increases, as the system's temperatures increase. As previously stated, at this point the exact mechanism for the adsorption of vibrational energy is unclear. This applies to both traditional and this author's kinetic theory.
Therefore, in context of energy that is readily exchanged, the mean energy for large gas molecules is primarily vibrational. In which case, their thermal energy that can be readily exchanged is approximated by:

$$E_T \cong NkT(n''+1/2)-3NkT/2 = NkT(n''-1) \qquad (20)$$

For n moles of gas, eq. 20 becomes:

$$E_T \cong nRT(n''-1) \qquad (21)$$

The molar isometric heat capacity becomes:

$$C_{v-large} = R(n''-1) \qquad (22)$$

Similarly, the isobaric heat capacity becomes:

$$C_{p-large} = Rn'' \tag{23}$$

It is inarguable that this author's kinetic theory and its determination of heat capacities is a superior fit to known empirical findings. Importantly, it does not require any of the questionable exceptions that have plagued traditionally accepted theories.

5. ADIABATIC INDEX

Based upon eq. 15 and eq. 19, the adiabatic index ($\gamma = C_p/C_v$) can nowbe obtained by:

$$\gamma = \frac{C_p}{C_v} = (n"+\frac{3}{2})/(n''+\frac{1}{2}) \tag{24}$$

Based upon eq. 22 and eq. 23 the adiabatic index for larger polyatomic gases becomes:

$$\gamma_{large} = \frac{C_{p-large}}{C_{v-large}} = n"/(\mathrm{n}"\text{-}1) \tag{25}$$

In Table 2 (end of paper), the adiabatic indexes based upon eq. 24 and eq. 25 are compared to the adiabatic indexes based upon traditionally accepted eq. 9. Eq. 9 is presented in two forms. 1) Based upon degrees of freedom (*f*) with exceptions. 2) Based upon degrees of freedom (*f*) without any exceptions.

These equations are compared to the empirically measured adiabatic indexes. Note that this analysis is based upon specific heats (measured at 25 ^{o}C), i.e., an engineering table[10]. Since the masses cancel out when calculating adiabatic index, the ratios will be identical to the calculations using heat capacities.

Fig. 3 shows the experimentally measured adiabatic index versus theoretical equations 9, 24 and 25. It becomes apparent that traditionally accepted eq. 9 is a poor fit to empirically measured values except for large values of *n"*. Eq. 24 is a superior fit to eq. 9 for all *n"*. Looking at Table 2, one should notice that eq. 24 is even a superior fit to eq. 9, when all the traditionally accepted exceptions are used.

For large gas molecules that tend to flatline, the adiabatic index is best approximated by eq. 25, as illustrated in Fig. 3. It is of interest that even eq. 25 underestimates the empirically obtained adiabatic index for large (*n"*> 4) polyatomic gases

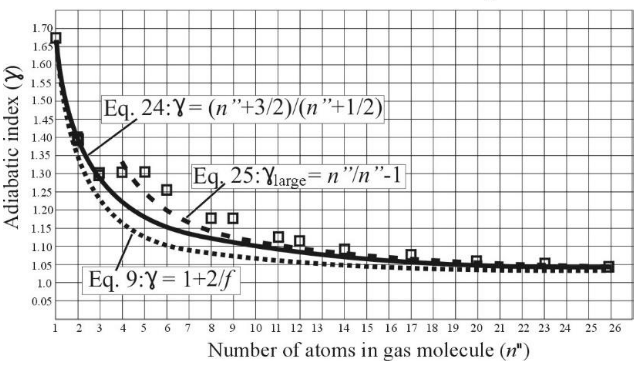

Fig. 3 is a plot of theoretical adiabatic indexes based upon traditionally accepted theory (eq. 9). When compared to this author's theoretical adiabatic indexes (eq. 24 and eq. 25), it is obvious that this author's theory is a superior fit to empirically determined values.

A plausible explanation may be obtained by re-examining Fig. 1. The slope of this author's theoretical equations (15, 19, 22 and 23) is the ideal gas constant (R). However, the empirically measured slope is approximately $0.9R$ for large polyatomic gases. Seemingly the difference must be due to the absorption of energy resulting in the polyatomic gas's vibrational energy.

Accepting that large polyatomic gases primarily absorb and exchange vibrational energies. Then a plausible explanation is that the gas molecules do not absorb 100% of their surrounding thermal photon's energy. Thermal photons/energy that primarily radiates from the closed system's walls. Thermal photons whose energy is also absorbed by the very same walls. In which case one may expect the result of the slope of their heat capacity vs number of atoms per molecule (n'') would be somewhat less than the idealized theoretical values (R). This in turn should help explain the differences in adiabatic indexes between the theoretical and empirically obtained values.

6. A DISCUSSION CONCERNING WORK

It should be stated that although empirically correct, inculcated eq. 17 can be theoretically misleading. Eq. 17 implies that it is logistically correct to express the energy required, as well as the work done, all in terms of the expanding System 1, i.e., work in terms of non-sensible work. Non-sensible work lends itself to questionable considerations of enthalpy [5], e.g., the enthalpy of vaporization (A.K.A., latent heat) is often referred to as non-sensible energy by engineers. This is problematic because as previously stated, sensible work is always external to the system that performs the work [4]-[9].

As previously stated concerning eq. 16, all expanding systems perform sensible work, that being work required to lift the overlying atmosphere's mass [$(PdV)_{\text{atm}}$]. Again, sensible work results in an atmospheric potential energy increase thus, signifying energy that is lost by the expanding system.

Eq. 16 and eq. 17 are two different theories, both backed by the same empirical findings. Thus, one is left with the decision of adhering to the traditionally accepted theory (eq. 17) that is founded on non-sensible work [(PdV)Sys1], or does one endorse eq. 16 that is founded on sensible work [(PdV)atm].

Eq. 17 causes theoretical inconsistencies that eq. 16 does not render [4]-[9]. The traditional use of eq. 17gives insight into why W. Haddad [13] has stated,"no other discipline in mathematical science is riddled with so many logical and mathematical inconsistencies, differences in definitions, and ill-defined notation as classical thermodynamics".

The above also gives one insight into why A. Sommerfield [14] stated,"Thermodynamics is a funny subject. The first time you go through it, you do not understand it all. The second time you go through it, you think you understand it, except for one, or two points. And the third time you go through it, you don't know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore".

7. CONCLUSIONS

An issue with traditionally accepted kinetic theory is that degrees of freedom arguments treat a gas molecule's energies as if that energy's existence is spontaneous. The first law of thermo dynamics informs us that all energy has an origin. The origins of a gas' kinematic energy can not be explained by accepted kinetic theory.

Importantly, this author's superior fitkinetic theory clearly explains the source of a gas molecule's kinetic energy. For example, condensed matter absorbs thermal energy from its surroundings, e.g., the thermal energy from our Sun. Conductivity distributes this energy throughout the matter, thus explaining the origins of a wall molecule's vibrational energy. The structured cohesive vibrating wall molecules then impose their energy onto the smaller, unstructured gas molecules that impact them. This provides clarity concerning how gas molecules attain their kinetic energy.

Enclosed relatively small gas molecules (and/or monatomic gases) undergo clean energy transfers when colliding with wall molecules. Conversely, enclosed long/large gas molecules tend to flatline when colliding with a system's walls. Therefore, the wall's kinematics are not imposed upon them. At least not in the manner that the structured wall molecule's vibrational is imposed onto relatively small gas molecules.

Based upon long/large gas molecule flatlining, such molecules possess a different heat capacity. A heat capacity that may be best explained in terms of their absorption of thermal radiation, rather than the energy imposed upon them by gas-wall collisions. Unfortunately, the universal adsorption of thermal radiation is not properly understood. An understanding that may require new insights. This includes how one envisions thermal energy, its density, as well as its adsorption.

Based upon such logic one obtains a different fundamental formula for the heat capacity of long/large gas molecules ($n''>4$) than has been determined for smaller gas molecules. Interestingly, the heat capacity formulas obtained for both large and small gas molecules based upon this revised kinetic theory, remain a superior fit when compared to the traditionally accepted formulas based upon traditional kinetic theory.

Furthermore, traditional kinetic theory based upon equipartition and degrees of freedom, requires a litany of exceptions for their theoretical formulations to match empirical findings. For example, monatomic gases have been illogically claimed to have no rotational energy because of their small radii. The reality is that the smaller a gas molecule's radius, the greater its rotational velocity will be.

To further emphasize these results, one just has to consider the adiabatic indexes of various gases. The adiabatic indexes of gases can be best explained in terms of this author's kinetic theory, i.e., it provides a superior fit forall known empirical findings. Importantly, as was the case for heat capacities, unlike traditionally accepted theories, no theoretical exceptions are required for this superior fit. Since the adiabatic index is based on the ratio of isobaric and isometric heat capacities, this result was somewhat expected. Even so, this result needs to be enunciated.

The exact mechanism by which gas molecules absorb vibrational energy was speculated to involve the absorption of thermal photons. In all likelihood, thermal photons are predominately in the thermal infrared (and/or longer wavelengths) part of the EM spectrum. Herein, more consideration is warranted

The difference between isobaric and isometric (isochoric) heat capacities was also discussed. The isometric heat capacity involves the energy required to heat a gas, while the isobaric heat capacity involves the energy required to both heat the gas and to perform work. Unfortunately, traditionally accepted notions of work can be non-sensible. Sensible work by an isobaric expanding system involves the energy required to lift the atmosphere’s overlying mass, resulting in an atmospheric potential energy increase. This improved insight into the differences in heat capacities is backed by empirical evidence.

New and improved insights were provided. Insights that challenge our indoctrination.

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Table 2: Empirically Measured Adiabatic Indexes vs Theoretical Relations. [2], [4], [10]

	n”	Isobaric specific heat (25°C) ($C_{p\text{-}\mathbf{m}}$) [kJ/kg*K]	Isometric specific heat (25°C) ($C_{v\text{-}\mathbf{m}}$) [kJ/kg*K]	γ Emper-ical	γ Eq. 24	γ Eq. 25	γ Eq. 9 No “*f*” Except-ions	γ Eq. 9 With “*f*” Except-ions
He	1	5.196	3.117	1.67	1.67		1.67 **	1.67
Ne	1	1.030	0.618	1.67	1.67		1.67 **	1.67
Ar	1	0.521	0.312	1.67	1.67		1.67 **	1.67
Xe	1	0.1568	0.095	1.65	1.67		1.67 **	1.67
H_2	2	14.302	10.178	1.41	1.40		1.33	1.40
N_2	2	1.040	0.743	1.40	1.40		1.33	1.40
O_2	2	0.917	0.657	1.40	1.40		1.33	1.40
NO	2	0.995	0.718	1.38	1.40		1.33	1.40
CO_2	3	0.844	0.655	1.29	1.29		1.22	1.40 *
SO_2	3	0.621	0.491	1.27	1.29		1.22	1.33
NH_3	4	2.096	1.607	1.30	1.22	1.33	1.16	
CH_4	5	2.227	1.708	1.30	1.18	1.25	1.13	
C_2H_4	6	1.552	1.256	1.24	1.15	1.2	1.11	
C_2H_6	8	1.751	1.475	1.19	1.12	1.14	1.08	
C_3H_6	9	1.519	1.279	1.19	1.11	1.13	1.07	
C_3H_8	11	1.667	1.478	1.13	1.09	1.10	1.06	
C_4H_8	12	1.0527	1.374	1.11	1.08	1.09	1.05	
C_4H_{10}	14	1.666	1.523	1.09	1.07	1.08	1.05	

C_5H_{12}	17	1.663	1.548	1.07	1.06	1.06	1.04	
C_6H_{14}	20	1.660	1.564	1.06	1.05	1.05	1.03	
C_7H_{16}	23	1.656	1.573	1.05	1.04	1.05	1.03	
C_8H_{18}	26	1.653	1.581	1.05	1.04	1.04	1.03	
*CO_2 is a linear molecule the other triatomic gases are “v” shaped: ** ignores any rotational energy								

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