New Thermodynamics: Global Warming and Man’s Activities

Kent W. Mayhew

Abstract—A previously published new kinetic theory not only improves the fit with accepted empirical findings, it also means that intermolecular collisions are inelastic. Combined with a previously published new understanding of lost work and the realization that the whole atmosphere acts as a thermal blanket completely changes our understanding, as to how man’s activities relate to global warming.

Index Terms—Global Warming, Lost Work, Atmospheric Gases, Spectrometry, Heat Capacity

I. INTRODUCTION THERMODYNAMICS:

In his 1917 “Treatise on Thermodynamics” [1] Planck acknowledges that there are two ways to formulate thermodynamics. A): “We may take for granted the correctness of the mechanical view of nature, and assume that all changes in nature can be reduced to motions of materials points between which there act forces which have a potential. Then the principle of energy is simply the well-known mechanical theorem of kinetic theory, generalized to include all natural processes.” Or B): As was done; “leave open the question concerning the possibility of reducing all natural processes to those of motion, and start from the fact which has been tested by centuries of human experience and repeatedly verified” “…no way possible to have perpetual motion”.

Adhering to B) has rendered the second law into the supreme postulate with entropy arguably being most fundamental thermodynamic parameter even though it true definition lacks clarity! Even entropy’s association with randomness lack scientific discipline as pointed out by Ben-Naim [2].

This author has challenged thermodynamics by showing that most if not all can be explained in simpler terms by using A) [3]. Moreover, adhering to Occam’s razor allows A) preference over B). However, this requires questioning of the second law as well as entropy’s relevance.

Important to come out of all this is that work done by expanding systems as described by $PdV$ gains clarity through the realization that it is work done onto the surrounding atmosphere [3,4,5]. It should further be pointed out that the second law in its accepted form is restricted to isolated systems and since expanding systems tend to do work onto the surrounding atmosphere then the system is not isolated hence second law should not even apply [4] to such expanding systems. Furthermore, one could readily argue that entropy is a mathematical contrivance that lacks clarity [6] hence its validity must be continually questioned.

Consider an isothermal isobaric expanding system. As with all expanding systems it does work onto the surrounding atmosphere as defined by $W=(PdV)_{atm}$. After expansion, the system and surrounding atmosphere are at same pressure and temperature. Therefore, the atmosphere can return neither work, nor energy back into the expanded system. Hence $(PdV)_{atm}$ represents irreversible work [3,5].

The internal energy change $(dE_{sys})$ being the summation of all the microscopic energies changes of the expanding system is simply the change to the system’s total energy! Therefore, for a system whose expansion is powered by the input of energy $(dQ_{sys})$ one can now write a first law based equation as follows [3]:

$$dQ_{sys} = dE_{sys} + (PdV)_{atm} = dE_{sys} + P_{atm}dV_{sys}$$

(Eqn 1) is applicable to most powered expanding systems, which are systems that often move man and or our machines.

This author has also rewritten kinetic theory providing a new theory that better matches our accepted empirical findings [5,7,8]. Moreover, this is accomplished without any of the many exceptions required by traditional equipartition based kinetic theory in order for it to match empirical findings. E.g. monatomic gases have no rotational energy because of their small radii. The truth is that monatomic gases can have the same rotational energy it is just that they require greater angular velocities in order to do so.

A major point to come out of this author’s new kinetic theory is that intermolecular collisions are inelastic i.e. momentum is conserved in the collision but in order for energy to be conserved then a photon must be released. Not only does this now explain why a fully insulated closed system’s temperature increases with pressure, but it also explains why $P-T$ relationships exist in most systems, including our atmosphere.

When applied to lost work as described by eqn (1), we now realize that expanding systems generally cause a regional pressure increase in the surrounding atmosphere. This leads to a combination of kinetic and/or potential energy increases in the atmosphere, whose total is defined by the lost/irreversible work: $W=(PdV)_{atm}$. Specifically, a kinetic energy increase manifests itself as heat that being an infinitesimal temperature increase to the atmosphere. While the potential energy increase manifests itself as the isobaric lifting of the atmosphere’s mass. It must be emphasized that the atmosphere acts as a heat sink and/or work sink, thus obtaining an immeasurable yet real increase to its energy.

Another consideration of the new kinetic theory [5,7,8] concerns the vibrational energies of gases. Specifically, the...
mean vibrational energy \((E_v)\) of a polyatomic gas molecule is defined by

\[
E_v \approx (n'' - 1)kT
\]  

(2)

Where \(n''\) represents the number of atoms in a molecule. Hence, a diatomic gas molecule \((n''=2)\) has a mean vibrational energy of \(kT\).

Of interest is that numerous theories as to why known/measured heat capacities for diatomic gases do not match traditionally accepted kinetic theory have been presented \([9,10,11,12,13,14]\). These include:

a) Diatomic gases also have no rotational energy

b) Diatomic gases have no vibrational energy

Of course none of the above somewhat illogical exceptions is required for this author’s new kinetic theory to match known empirical findings.

A goal of this paper is to understand how the concept of lost work may apply to global warming. This will include an understanding as to how the atmosphere as a whole may act as thermal blanket, which will be based in part upon the new understanding for vibrational energies of gases.

II. INTRODUCTION GLOBAL WARMING

The insolation (solar input) is such that in 1.5 hrs our Sun shines as much energy onto the Earth, as the human race consumes in a year \([15]\). Global warming involves a couple of degrees of relatively rapid temperature rise from Earth’s average temperature of 288 K. As a rough approximation: 2 degrees/288 degrees vs (1.5 hr/24 hr)/365 days/yr, which becomes: 1 vs 40.

Due to the above, most assert that greenhouse gases are the root cause of global warming i.e. they adsorb infrared photons emanating from the Earth’s surface, and then re-emit a percentage of these photons back towards Earth’s surface, thus maintaining Earth’s elevated temperature e.g. 288 K vs 255 K \([15]\).

Our Sun’s blackbody radiation (5,800 K source) is adsorbed by Earth-bound molecules and then is radially radiated/re-emitted by these molecules. These Earth-bound molecules tend to adsorb higher energy photons than they re-emit, hence conservation of energy tells us that they must also radially radiate more photons than they adsorb. The most likely wavelength of blackbody radiation is temperature dependent as given by Wien’s displacement law, i.e.

\[
\lambda_{\text{max}}T = 2.898 \times 10^{-3} \text{ mK}
\]

(3)

Fig. 1 is a sketch for our Sun’s blackbody radiation \((T=6,000)\) that is often adsorbed by our Earth-bound atmospheric gases and surfaces. The adsorbed energy is then re-emitted as a greater number of photons at longer wavelengths, as illustrated by the blackbody curves for 300 K, 250K and 200 K in Fig.2.

Accepting that the 300 K blackbody curve in Fig. 2 represents the upward radiation from our Earth’s surface, then a minor amount is re-emitted in the visible/near infrared \((730 \mu m < \lambda < 3 \mu m)\) while most of the energy is re-emitted in the thermal \((3 \mu m < \lambda < 8 \mu m)\) and long infra-red \((8 \mu m < \lambda < 15 \mu m)\), with the rest being at longer wavelengths.

A sketch for the irradiance near the top of the atmosphere is shown in Fig 3 along with various adsorptions in the UV, visible and near infrared. Such adsorption spectra can be misleading as they are often shown with the implication that they represent the actual actions of greenhouse gases, as attributed to global warming.
However, it is really the adsorption spectra as measured by John H. Shaw in the 1940’s [16], which is shown in Fig 4 that is really the basis for the accepted greenhouse gas and global warming theory. I.e. acceptance of greenhouse gases being water vapour (H₂O), carbon dioxide (CO₂), nitrous oxide (N₂O), methane (CH₄), and ozone (O₃). Certainly, these gases all adsorb various parts of our 300 K blackbody radiation at various infrared frequencies e.g. CO₂ has sharp adsorption peaks in the near infrared and thermal infra-red at 2.7, 4.3, as well as a broad peak at 15 \( \mu \text{m} \).

![Image](http://dx.doi.org/10.24018/ejers.2019.4.7.1432)

Fig. 4: Shows the infrared adsorption spectra by some so-called greenhouse gases. Interestingly, these actually represent the infrared spectrum not in excess of that which is associated with heat i.e. black body spectrums are subtracted when setting up a spectrometer and measuring the blank.

The concept of greenhouse gases influencing our atmosphere has been confirmed by Earth’s outbound thermal spectrums as measured by satellites between 1970 and 1997, Harries et al [17]. This shows that less long wavelengths of energy are escaping Earth’s atmosphere at the same frequencies/wavelengths as greenhouse gases absorb. Admittedly, the relationship is complex due to several feedback mechanisms such as the hydrological cycle.

A challenge to greenhouse gas based models is given by Holmes [18], Nikolov and Zeller [19] contend that the real impact of greenhouse gases has never really been properly experimentally verified and provide an interesting model. They assert that our witnessed temperature is actually due to solar insolation and our atmosphere’s pressure. Nikolov and Zeller address expected temperatures in a rather broad context hence the few degrees of rapid temperature change associated with global warming was not fully contemplated. Furthermore, they fail to provide an explanation as to why \( P-T \) relations exist.

III. NATURAL \( P-T \) OF OUR ATMOSPHERE

This author’s new kinetic theory where intermolecular collisions are inelastic actually explains why pressure-temperature relations on planets with atmospheres. Accordingly, a pressure increase would result in either:

1) An increase to the number of thermal photons generated, as the mean molecular volumes decreases.

2) An increase to the forces experienced per collision when the mean molecular kinetic energy increases.

Both of the above will increase the amount of thermal energy generated by inelastic intermolecular collisions hence will readily explain why temperatures increase with pressure i.e. natural \( P-T \) relationships. For a full understanding research into what sort of frequencies result from inelastic collisions is required. At this point we can only surmise that there would be some sort of spectrum based upon the colliding molecule’s speeds, masses etc.

Irradiance is the incoming power on a per frequencies basis. Accordingly measured irradiance near Earth’s surface would be a combination of the Sun’s solar output (insolation), reflections from Earth’s surface plus photons due inelastic intermolecular collisions.

IV. NEW INSIGHTS

Diatomic molecules [nitrogen (N₂) and oxygen (O₂)] make up 90% of our atmosphere. It is accepted that neither nitrogen nor oxygen readily adsorbs infrared energy on a per molecule basis to the same extent as the accepted greenhouse gases do. Interestingly, studies have shown that nitrogen and oxygen & nitrogen mixtures do absorb in the infrared [20,21]. The point becomes that although we have accepted (wrongly?) that neither nitrogen nor oxygen contribute to the greenhouse effect, such theorization should be revisited. Especially, based upon their relative abundances and their heat capacities!

V. HEAT CAPACITIES

Most importantly, logic dictates that if diatomic gases do not adsorb and re-emit thermal energy then this would show up by these gases having exceptionally low heat capacities. Specifically a gas’ measured heat capacity is due to a combination of its translational, rotational and vibrational energies. Therefore, a gas that does not adsorb and then re-emit thermal energy as part of its vibrational energy should have a comparatively low heat capacity!

Consider Table 1, which shows the heat capacities of various atmospheric gases (rounded to one decimal place). Clearly the heat capacity of air is similar to that of its main constituent diatomic gases. And these all are a good fit to their theoretical heat capacity values, as based upon this author’s new kinetic theory [7,8]. I.e. their theoretical heat capacities are empirically confirmed! Moreover, they all have vibrational energies as described by eqn 2: \( \frac{E_v}{n!} \approx (n^*−1)kT \). Hence they all adsorb and re-emit thermal radiation, therefore will act as a thermal blanket for thermal energy radiating from Earth’s surface.

| Gas   | \( n^* \) | \( C_v [\text{J/(mol*K)}] \) | THEORETICAL \( C_v \) | \( C_v [\text{J/(mol*K)}] \) | THEORETICAL \( C_v \) |
|-------|------|-----------------|-----------------|-----------------|-----------------|
| H₂    | 2    | 28.8            | 29.1            | 20.5            | 20.8            |
| N₂    | 2    | 29.1            | 29.1            | 20.8            | 20.8            |
| O₂    | 2    | 29.3            | 29.1            | 21.0            | 20.8            |
| AIR   |      | 29.2            |                 | 20.1            |                 |
| CO₂   | 3    | 37.1            | 37.4            | 28.8            | 29.1            |
| H₂O   | 3    | 33.6            | 37.4            | 25.3            | 29.1            |
| CH₄   | 5    | 35.7            | 54.0            | 27.4            | 45.7            |

TABLE 1: Heat Capacities: Empirical vs Theoretical

DOI: [http://dx.doi.org/10.24018/ejers.2019.4.7.1432](http://dx.doi.org/10.24018/ejers.2019.4.7.1432)
Interestingly based upon spectrometry: Five atom methane \((n=5)\) has very strong infrared adsorption, and is said to have 8 times the per molecule greenhouse capability of carbon dioxide. Yet, methane’s empirically determined heat capacity \([c_p=35.72 \text{ J/(mol*K)}]\) is lower than what theory predicts \([c_p=54 \text{ J/(mol*K)}]\). Certainly, this requires some thought and perhaps is best explained by flat-lining, as was discussed in this author’s paper on the subject [8].

Perhaps part of the reason for such an accepted misguided science lay in the fact traditionally accepted equipartition based kinetic theory is a mathematical construct rather than logic based. This has lent itself to outrageous misguided exceptions such as diatomic molecules having little to no vibrational energy, or no rotational energy. This is not to say that greenhouse do not play a role rather it bodes the question as to how much of a role? Certainly as a player in all this, one would still expect the satellite-measured findings, as discussed by Harries et al [17]. More importantly due to the proximately of so-called greenhouse gases to the satellites, there would be little alteration to their absorption spectra by other gases, i.e. irrelevant of greenhouse gases being a primary or secondary cause of global warming, the witnessed decrease in spectral adsorption lines would still be witnessed due to the increasing carbon dioxide concentrations.

VI. DISCONNECT BETWEEN HEAT CAPACITIES AND ADSORPTION SPECTRA

There seems to be some disconnect between measured heat capacities and measured absorption spectra. Why? Prior to measuring an adsorption spectrum one must run a blank so that he/she can subtract any background spectral radiation, which obeys the Stephen-Boltzmann law, i.e. blackbody spectrum.

What is seemingly forgotten is this. The background radiation spectrum represents thermal energy that is adsorbed and re-radiated, within the spectrometer i.e. its walls and contents! In other words, the subtraction of the background blackbody infrared spectrum is the subtraction of the system’s thermal energy signature. Accordingly, Fig. 4 represents what is actually measured inside of the spectrometer that being a spectrum in in excess of the thermal background radiation spectrum!

Consider a homonuclear diatomic gas, i.e. \(N_2\) and \(O_2\). If all that they adsorb and re-emit is the thermal/blackbody radiation spectrum, which is subtracted from their measured adsorption spectrums, then one is left with little to no spectrum. As long as the gas is in thermal equilibrium, this would be irrelevant of the gas’s quantity of such gas i.e. at a given \(T\) over enough time, each gas molecule adsorbs as much thermal/blackbody radiation as it emits!

Not only does the above explain why heat capacities do not correspond with infrared adsorption spectrums, it also explains why the sciences have illogically left \(N_2\) and \(O_2\) out of global warming models. And it also helps explain why the sciences have wrongly limited temperature to the kinematics of matter, but that is for another paper.

VII. RECONSIDER LOST WORK

Accepting that lost work by an expanding system is irreversible/lost work done \([U=\Delta W]\) onto the surrounding atmosphere provides irrefutable clarity that lost work ultimately heats our atmosphere. The issue then becomes, by how much?

A drive to the corner store only puts a relatively small amount thermal energy of into our atmosphere. But what happens if a 100 million people do the same thing? Lost work now gains significance. Even though it remains a pitannce in comparison to the insolation from the Sun, its location on the Earth’s surface renders it much more relevant. Especially when imposing our new understanding that our whole atmosphere is our thermal blanket.

How does one calculate the energy that becomes thermal energy given into the atmosphere, when driving one’s car? Considering all the motions and lost energy involved in driving a car, it may seem like a horrendous task. The simple answer: Assume that a car accelerates hence increases its inertia, representing the energy required to accelerate the car’s mass. Then all other energy directly goes into heating our atmosphere. So if you were driving along a highway at 60 mph, then once you reach that speed, then all energy used to maintain that speed goes directly into heating our atmosphere i.e. drag plus the car’s friction (internal and external). Heck even the inertial energy may eventually be turned into atmospheric heat when one applies the brakes.

Never forget that your car’s motion continually disturbs the air’s equilibrium (thermal and mechanical) e.g. drag is nothing short of the direct heating of our atmosphere via increased intermolecular collisions/ friction. This and other forms of heating such as viscous dissipation can now be attributed to inelastic collisions involving atmospheric gases. The same thing happens but too lesser extend when you ride your bike, or even when a cheetah runs, and to a much greater extent when a jet airplane flies.

What about nuclear energy or any other steam-powered device? Steam, as in any boiling process is about an expanding system performing irreversible/lost work done onto the surrounding atmosphere. So even nuclear power directly heats our atmosphere!

Bear in mind that even traditional thermodynamics accepts that lost work exists although it is rather poorly understood, i.e. wrongly expressed in terms of some isothermal entropy increase within expanding systems. Hence there is a general lack of clarity concerning where the lost work disappears to. One actually may conclude that the work goes into the expanding system, or even into the hands of god i.e. something Enrico Fermi once said at a symposium, concerning lost work of an expanding universe.

VIII. LOCATION OF LOST WORK

The actual amount of atmospheric heating due to lost work may not be as significant as its location. Being close to Earth’s surface means that heat created by man’s activities is close to where global warming is measured. And never forget that the whole overlying atmosphere acts as a thermal blanket. This more than anything may help explain how
man’s activities directly influence the temperatures that we witness.

IX. CONCLUSIONS

Understanding that intermolecular collisions are inelastic explains witnessed P-T relationships e.g. helps explain Earth’s atmosphere’s temperatures. Namely such inelastic collisions release photons/heat in order conserve energy. Hence the more collisions and/or greater forces per collisions, both of which result in pressure increases therefore temperature increases.

Climate change involves greenhouse gases; however, our atmosphere as a whole prevents thermal energy from radiating from our planet into outer space! Specifically, as shown by their heat capacities, most atmospheric gases are capable of adsorbing and re-emitting thermal energy. Hence, Earth’s mean temperature being 33 K higher (15° C instead of -18° C) should now be explained in terms of the whole atmosphere acting as a thermal blanket! Therefore, special emphasis should be given onto the various dynamics that are close to Earth’s surface, where most of man’s activities occur, and where global warming is witnessed.

Why do infrared spectrometry and heat capacities of gases seemingly disagree? The reason is in the methodology in spectrometry i.e. the running of a blank eliminates the system’s thermal energy signature from the output spectrum! I.e. a gas in thermal equilibrium emits as much thermal energy as it adsorbs. Moreover, at a given T, homonuclear diatomic gases should have the same thermal spectrum as the blackbody spectrum inside of the spectrometer hence the subtraction of the blank’s blackbody spectrum results in the removal of the gas’s thermal signature.

An improved understanding is that expanding systems do irreversible lost work onto our atmosphere \[ W_{\text{rev}}=(PdV)_{\text{rev}} \], as well as provide the work required to move man and his machines. All this leads to the heating of our atmosphere. The real question now becomes; can man’s contribution under this thick thermal blanket now explain global warming? Note, when comparing the energy associated with the Sun’s Insolation to the heat associated with man’s activities, there is an approximate 40 to 1 ratio but these two sources of heat are on opposite sides of the atmosphere and the heat tends to be at a much longer wavelength than the insolation.

It is probably the case that we humans must downsize; this certainly includes our activities, and how many of us do it! Sadly, the vast majority of our economy is based upon the suicidal insanity of perpetual growth, which enables fool hearty politicians to pass the buck onto future generations. Our planet’s preservation may require real sanity, scientific and otherwise!

REFERENCES

[1] Planck, Max “Treatise on Thermodynamics” Third edition, London, Logmans, Green and co., 1917 pg 40
[2] Ben-Naim “A Farewell to Entropy: Statistical thermodynamics Based on Information” World Scientific Publishing Co Hackensack NJ 2011
[3] Mayhew, K.W., “Resolving problematic thermodynamics” Hadronic Journal 41(3) 259-272, 2018
[4] Mayhew, K.W. “Second Law and Lost Work” Phys. Essays, 28, 1, 2015 pg 152-155
[5] Mayhew K.W. “New thermodynamics: Say no to entropy” Self-published, 2018
[6] Mayhew K.W. “Entropy: An ill-conceived mathematical contrivance?” Phys. Essays, 28, 3, 2015 pg 252-257
[7] Mayhew, K.W. “A new perspective for kinetic theory and heat capacity” Prog. In Phys. 13, 3, 2017 pg166-173
[8] Mayhew, K.W. “Kinetic Theory: Flattening of Polyatomic Gases:” Prog. In Phys. 14, 2 2018 pg 75-79
[9] Planck M. On the Law of the Energy Distribution in the Normal Spectrum. Ann. Phys., 4 (553): 1-11 (1901)
[10] Einstein A. and Stern O. Einige Argumente Fur die Annahme einer molekularen Agitation beim absolute Nullpunkt (Some Arguments for the Assumption of Molecular Agitation at Absolute Zero). Ann. Phys. 40 551: 551-560 (1913)
[11] Dahl J.P. On the Einstein–Stern model of rotational heat capacities. J. of Chem. Physics 109, 10688 (1998)
[12] Thomson W. (1904). Baltimore Lectures. Baltimore: Johns Hopkins University Press. Sec. 27. Re-issued in 1987 by MIT Press as Kelvin's Baltimore Lectures and Modern Theoretical Physics: Historical and Philosophical Perspectives. (Robert Kargon and Peter Achinstein, editors).
[13] Rayleigh J.W.S. (1900). The Law of Partition of Kinetic Energy. Phil. Mag. 49: 98–118.
[14] Pais A. Subtle is the Lord. Oxford University Press. Oxford UK 1982
[15] Volokin, Den and ReLez, Lark, “On the average temperature of airless spherical bodies and magnitude of Earth’s atmospheric thermal effect” Springer Plus 2014
[16] Gao, Bo-Cai, “Introduction to Atmosphere Spectroscopy and spectrum Matching Technique” Remote Sensing Division, Naval Research Laboratory, Washington DC 2016
[17] Harries, John Edward, Brindley, H.E.Sagoo, Pretty, Bantges Richard “Increases in greenhouse forcing inferred from the outgoing longwave radiation spectra of the Earth in 1970 and 1997” Lett to Nature vol 410 pg 355-357, 2001
[18] Holmes, Robert “Molar mass of ideal gas law points to a very low climate sensitivity” Earth Sciences 6(6) pg 157-163, 2017
[19] Nikolov, Ned and Zeller, Karl, “New Insights on the Physical Nature of the Atmospheric Greenhouse Effect Deduced from an Empirical Temperature Model” Environment Pollut Climate Change 2017 1
[20] Joslin, G.C., Gray C.G, Gburski, Z., “ Far Infrared Adsorption in Nitrogen Gas”, J. Molecu. Phys. 1984, 1
[21] Smith, K.M. and Newnham, D.A. “Near infrared absorption spectroscopy of Oxygen & Nitrogen Gas Mixtures”, Chem Phys. Letters Vol 308 1-2 1999 pg 1