Determination of the Total Emissivity of a Mixture of Gases Containing 5% of Water Vapor and 0.039% of Carbon Dioxide at Overlapping Absorption Bands.

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Abstract

This assessment is a review of the common AGW argument on the carbon dioxide increasing the potential of the water vapor for absorbing and emitting IR radiation as a consequence of the overlapping absorption/emission spectral bands. I have determined the total emissivity of a mixture of gases containing 5% of water vapor and 0.039% of carbon dioxide in all spectral bands where their absorptivities/emissivities overlap. The result of these calculations is that the carbon dioxide attenuates the total absorptivity/emissivity of the water vapor, working like a coolant, not a warmer of the atmosphere and the surface.

Introduction

Since the popularization of the information about a hypothetical anthropogenic global warming (AGW) in 1988, AGW proponents have been arguing that the carbon dioxide causes an increase in the total absorptivity of the atmosphere[1, 2, 3].

For example, the anonymous author of the essay at Environmental Defense[1] argues that:

"*As humans emit greenhouse gases like CO2, the air warms and holds more water vapor, which then traps more heat and accelerates warming*."

The second anonymous author at Science Daily[2] assures that:

"*Climate warming causes many changes in the global carbon cycle, with the net effect generally considered to be an increase in atmospheric CO_2 with increasing temperature -- in other words, a positive feedback between temperature and CO_2*."

Masato Sugi and Jun Yoshimura assure in their article[3] that:

"*By the overlap effect of CO2 and water vapor absorption bands, the existence of CO_2 significantly reduces the cooling rate of water vapor…*"

The authors of the arguments above these lines assure that by increasing the concentration of carbon dioxide in the atmosphere would increase also the warming of the atmosphere.

However, according to results from experimentation made by H. C. Hottel[11], B. Leckner[12], M. Lapp[13], C. B. Ludwig[14], A. F. Sarofim[15] and their collaborators[14, 15] on this matter, the combined effect of overlapping absorption bands causes a reduction on the total absorptivity of a mixture of gases[4, 5, 6].

My assessment reinforces the argument made by H. C. Hottel[11], B. Leckner[12], M. Lapp[13], C. B. Ludwig[14], A. F. Sarofim[15] and their collaborators[14, 15] because my calculations coincide with the results obtained from the algorithms derived from their experiments.

In 1954, Hoyt C. Hottel conducted an experiment to determine the total emissivity/absorptivity of carbon dioxide and water vapor[11]. From his experiments, he found that the carbon dioxide has a total emissivity of almost zero below a temperature of 33 °C (306 K) in combination with a partial pressure of the carbon dioxide of 0.6096 atm cm.

17 year later, B. Leckner repeated Hottel's experiment and corrected the graphs[12] plotted by Hottel. However, the results of Hottel were verified and Leckner found the same extremely insignificant emissivity of the carbon dioxide below 33 °C (306 K) of temperature and 0.6096 atm cm of partial pressure.

Hottel's and Leckner's graphs show a total emissivity of the carbon dioxide of zero under those conditions.

The results of Hottel and Leckner have been verified by other researchers, like Marshall Lapp[13], C. B. Ludwig[14], A. F. Sarofim[15], who also found the same physical trend of the carbon dioxide.

On the other hand, in agreement with observations and experimentation carried out by the same investigators[11, 12, 14, 15, 16], the atmospheric water vapor, in a proportion of 5% at 33 °C, has a total emissivity/absorptivity of 0.4.[5, 6]

The total emissivity/absorptivity of water vapor combined with its high specific heat capacity and its volumetric mass fraction makes of the water vapor the most efficient absorbent and emitter of Infrared Radiation among all gases forming the Earth's atmosphere.

In contrast, the carbon dioxide has negligible total emissivities and partial pressures as a component of the atmosphere (the partial pressure of the carbon dioxide at the present atmosphere is 0.0051 atm cm); that's why it is very important to make some precisions about what the effect of a combination of water vapor and carbon dioxide could be at their current conditions of partial pressure, temperature and mass densities in the atmosphere.

Methodology

The whole range of spectral absorption of both gases and an effective path length (L_e) of 7000 *m* were considered for calculating the total emissivity of a mixture of water vapor and carbon dioxide in the atmosphere. I have made use of formulas on radiative heat transfer taken from the references numbered as 4, 5 and 6; however, I made use of the main formula to calculate the total emissivity of a mixture of gases in the atmosphere, where their absorption bands overlap, that was derived by H. C. Hottel[11], B. Leckner[12], M. Lapp[13], C. B. Ludwig[14], A. F. Sarofim[15] and their collaborators[14, 15], and enhanced by contemporary authors as Michael Modest[5], as from the results of observations, as from the results of experimentation.

The effective path length is the length of the radiation path through the atmosphere. It differs from the geometrical distance travelled because the radiation is scattered or absorbed on entering and leaving the atmosphere. In a vacuum there is no difference between the effective path length and the geometrical path length. As this assessment deals with the atmosphere, I considered the effective path length into my calculations.

The volumetric mass fraction of water vapor in the atmosphere fluctuates between 10000 *ppmV* and 50000 *ppmV* [10]. This variability allows the water vapor to show a wide range of high total absorptivities and total emissivities which may vary according to the temperature of the molecule of water vapor. For this reason, I considered the maximum mass fraction of the water vapor in the atmosphere.

The water vapor potential to absorb shortwave infrared radiation from the solar photon stream makes of it the most efficient absorbent of Infrared Radiation. In quantum physics, a photon stream is a current of photons emitted by a source that behave as particles and waves and have a specific directionality, i.e. from the source towards the surroundings.

At the very moment of concluding this article, **Dr. Charles R. Anderson, PhD** called my attention over the observation that these calculations constituted further evidence on his theory about the cooling effect of the carbon dioxide on the Earth's surface. When Dr. Anderson and I examined the calculations, we found that the carbon dioxide not only has a cooling effect on the surface, but also on the molecules of other gases in the atmosphere.

The total emissivities of the atmospheric carbon dioxide, water vapor and oxygen were obtained by taking into account the mean free path length of the quantum/waves through those gases, taken individually, and the time lapse rate that a quantum/wave takes on leaving the troposphere after colliding with molecules of carbon dioxide, water vapor and oxygen. This set of calculations will be described in a future article.

Symbols:

ζ Equilibrium partial pressure

pH_2O Partial pressure of water vapor in current atmosphere

pCO_2 Partial pressure of carbon dioxide in current atmosphere

$(pabsL)_0$ Absolute pressure of a column of air of length L

ε Total emissivity

$\Delta\varepsilon$ Emissivity of a mixture of gases on overlapping absorption spectral band

Le Effective length L of the column of air

Total Emissivity of a Mixture of Water Vapor and Carbon Dioxide in the Current Atmosphere of the Earth

On July 3, 2010, at 10:00 hr (UT), the proportion of water vapor in the atmosphere at the location situated at 25º 48´ N lat. and 100 º 19' W long., at an altitude of 513 m ASL, in San Nicolas de los Garza, Nuevo Leon, Mexico, was 5%. The temperature of the air at an altitude of 1 m was 310.95 K and the temperature of the soil was 330 K. I chose this location, near my office, because it is an open field, far enough from the city and its urban effects.

From this data, I proceeded to calculate the following elements:

1. The *correction factor* for the overlapping emissive bands of H_2O_g and CO_{2g}.
2. The *correction factor of the total emissivity* of carbon dioxide where the *radiative emission bands* of both gases overlaps, considering that the partial pressure of the carbon dioxide is 0.00039 atm.
3. The *total emissivity* of the mixture of water vapor and carbon dioxide in the atmosphere.
4. The *total normal intensity* of the mixture of water vapor and carbon dioxide in the atmosphere.
5. The *change of temperature* caused by the mixture of water vapor and carbon dioxide in the atmosphere.

Obtaining the correction factor for the overlapping emissive bands of H_2O_g and CO_{2g}:

To obtain the total emissivity of the mixture of water vapor and carbon dioxide in the atmosphere, we need to know the *equilibrium partial pressure* of the mixture of water vapor and carbon dioxide. The formula for obtaining the *equilibrium partial pressure* (ζ) of the mixture is as follows:

$$\zeta = \frac{pH_2O}{(pH2O + pCO2)} \quad (Ref. 5)$$

Where p_{H2O} is the partial pressure of water vapor in a proportion of 5% in the atmosphere –which is an instantaneous measurement of the water vapor, and p_{CO2} is the partial pressure of the carbon dioxide.

Known values:

p_{H2O} = 0.05 atm

p_{CO2} = 0.00039 atm

Introducing magnitudes:

$$\zeta = \frac{pH2O}{(pH2O + pCO2)} = \frac{0.05\ atm}{(0.05\ atm + 0.00039\ atm)} = 0.9923$$

Therefore, ζ = 0.9923

Obtaining the total emissivity of a mixture of water vapor and carbon dioxide in the atmosphere:

Now let us proceed to calculate the magnitude of the overlapped radiative emission bands of the water vapor and the carbon dioxide. To do this, we apply the following formula:

$$\Delta\varepsilon = \left[\left[\frac{\zeta}{(10.7 + 101\,\zeta)}\right] - 0.0089\,(\zeta)^{10.4}\right]\left(log10\,\frac{[(pH2O + pCO2)L]}{(pabsL)_0}\right)^{2.76} [Ref. 5]$$

Known values:

$\zeta = 0.9923$

$pH2O = 0.05\ atm$

$pCO2 = 0.00039\ atm$

$(pabsL)_0$ $(absolute\ pressure\ of\ the\ mixture\ of\ gases\ on\ the\ Earth's\ surface) = 1\ atm\ m$

$Le = (2.3026)(\frac{Aas}{\mu a}) = 7000\ m$

Introducing magnitudes:

$$\Delta\varepsilon = [\left(\frac{0.992}{110.892}\right) - (0.0089 * (0.992)^{10.4}] * \left(\frac{log_{10}\,[(0.05\,atm + 0.00039\,atm)7000\,m]}{(1\,atm\,m)_0}\right)^{2.76} \quad (Ref.2)$$

$$\Delta\varepsilon = [0.00076] * (13.21) = 0.01$$

Therefore, the *correction addend* for the overlapping absorption bands is 0.01

Consequently, the *total emissivity of the mixture water vapor and carbon dioxide* is as follows:

$$\varepsilon_{mixture} = \varepsilon_{CO2} + \varepsilon_{H2O} - \Delta\varepsilon = 0.0017 + 0.4 - 0.01 = 0.3917$$

Total Normal Intensity of the energy radiated by the mixture of gases in the air:

Therefore, the total normal intensity (*I*) (or the spectral radiance over wavelength) caused by the mixture of water vapor and carbon dioxide in the atmosphere is:

$$I = \frac{(\varepsilon_{mix}\,(\sigma)(T)^4)}{\pi} \quad (Ref.5\ and\ 6)$$

$$I = \frac{\left(0.3997\ \left(5.6697\,x\,\frac{10^{-8}W}{m^2K^4}\right)(310.95)^4\right)}{3.1416} = 67.44\frac{W}{m^2sr}$$

By way of contrast, the spectral irradiance over wavelength caused by the surface (soil), with a total emissivity of 0.82 (*Ref. 1 and 5*), is as follows:

$$I = \frac{\left(\varepsilon_{surface}\,(\sigma)(T)^4\right)}{\pi} \quad (Ref.5\ and\ 6)$$

$$I = \frac{\left[0.82\ \left(5.6697\,x\,10 - 8\frac{W}{m^2K^4}\right)(330\,K)^4\right]}{3.1416} = 203\frac{W}{m^2sr}$$

Following Dr. Anderson's recommendation (which I mentioned above in the abstract) I calculated the overlapping bands of a mixture of water vapor (4%), carbon dioxide (0.039%) and Oxygen (21%).

The calculation for a mixture of atmospheric Oxygen (O_2), Water Vapor (H2O) and Carbon Dioxide (CO_2) is as follows:

$$\zeta = \frac{pO2}{(pO2 + pCO2)} = \frac{0.21\,atm}{(0.21\,atm + 0.00039\,atm)} = 0.9981$$

$$\zeta = \frac{(pO2 + CO2)}{(pHO2 + pO2 + CO2)} = \frac{0.9981\,atm}{(0.9981 + 0.05\,atm)} = 0.9523$$

Consequently, the equilibrium partial pressure of the mixture of Oxygen, Water Vapor and Carbon Dioxide in the atmosphere is 0.9523

And the change of the total emissivity of the mixture is:

$$\Delta\varepsilon = \left[\left(\frac{\zeta}{10.7 + 101\zeta}\right) - (0.0089\,(\zeta)^{10.4})\right] * \left(Log10\,\frac{[(pH2O + pCO2 + pO2)L]}{(pabsL)_0}\right)^{2.76} \qquad [Ref.5]$$

$$\Delta\varepsilon = [(\frac{0.9523}{10.7 + (101 * 0.9523)} - (0.0089\,(0.9523\text{^}10.4))] * [(3.261)^{2.76}]$$

$$\Delta\varepsilon = [0.00891 - (0.00535)] * [(3.261)^{2.76}]$$

$$\Delta\varepsilon = [0.00356] * [26.1] = 0.092916$$

And the total emissivity of the mixture of gases in the atmosphere is:

$$\varepsilon_{mixture} = \varepsilon_{CO2} + \varepsilon_{H2O} - \Delta E = 0.0017 + 0.4 + 0.004 - 0.0.092916 = 0.3128$$

The emissivity of the water vapor decreased by 0.0872 units. Evidently, the mixture of oxygen, carbon dioxide and water vapor, at current conditions of temperature and partial pressures, causes a sensible decrease of the total emissivity of the mixture of air.

The general conclusion is that by adding any gas with total emissivity/absorptivity lower than the total emissivity/absorptivity of the main absorber/emitter in the mixture of gases makes that the total emissivity/absorptivity of the mixture of gases decreases.

In consequence, the carbon dioxide and the oxygen at the overlapping absorption spectral bands act as mitigating factors of the warming of the atmosphere, not as intensifier factors of the total absorptivity/emissivity of the atmosphere.

Conclusions

This assessment demonstrates that the effect of an increased warming caused by an increase of absorptivity of infrared radiation (IR) by water vapor due to overlapping spectral bands with carbon dioxide does not happen in nature.

On the overlapping absorption spectral bands of carbon dioxide and water vapor, the carbon dioxide propitiates a decrease of the total emissivity/absorptivity of the mixture in the atmosphere, not an increase, as AGW proponents argue [1, 2, 3].

Applying the physics laws of atmospheric heat transfer, the Carbon Dioxide behaves as a coolant of the Earth's surface and the Earth's atmosphere by its effect of diminishing the total absorptivity and total emissivity of the mixture of atmospheric gases.

Dr. Anderson and I found that the coolant effect of the carbon dioxide is stronger when Oxygen is included into the mixture, giving a value of $\Delta\varepsilon = 0.3814$, which is lower than the value of $\Delta\varepsilon$ obtained by considering only the mixture of water vapor and carbon dioxide.

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http://www.amazon.com/Slaying-Sky-Dragon-Greenhouse-ebook/dp/B004DNWJN6

References

1. http://www.edf.org/documents/5596_GlobalWarmingWaterVapor_onepager.pdf
2. http://www.sciencedaily.com/releases/2010/01/100127134721.htm
3. http://journals.ametsoc.org/doi/pdf/10.1175/1520-0442(2004)017%3C0238%3AAMOTPC%3E2.0.CO%3B2
4. Manrique, J. A. V. *Transferencia de Calor*. 2002. Oxford University Press. England.
5. Modest, Michael F. *Radiative Heat Transfer-Second Edition*. 2003. Elsevier Science, USA and Academic Press, UK.
6. Pitts, Donald and Sissom, Leighto*n. Heat Transfer*. 1998. McGraw-Hill, NY.
7. Van Ness, H. C. *Understanding Thermodynamics*. 1969. General Publishing Company. Ltd. Ontario, Canada.
8. Engel, Thomas and Reid, Philip. *Thermodynamics, Statistical, Thermodynamics & Kinetics*. 2006. Pearson Education, Inc.
9. Anderson, Charles R. *Slaying the Sky Dragon-Death of the Greenhouse Gas Theory.* 2011. Chapter 20. Page 313.
10. http://www.eoearth.org/article/Atmospheric_composition
11. Hottel, H. C. *Radiant Heat Transmission-3rd Edition*. 1954. McGraw-Hill, NY.
12. Leckner, B. *The Spectral and Total Emissivity of Water Vapor and Carbon Dioxide*. Combustion and Flame. Volume 17; Issue 1; August 1971, Pages 37-44.
13. http://thesis.library.caltech.edu/2809/1/Lapp_m_1960.pdf
14. Ludwig, C. B., Malkmus, W., Reardon, J. E., and Thomson, J. A. L. Handbook of Infrared Radiation from Combustion Gases. Technical Report SP-3080.NASA. 1973.
15. Sarofim, A. F., Farag, I. H., Hottel, H. C. Radiative Heat Transmission from Nonluminous Gases. Computational Study of the Emissivities of Carbon Dioxide. ASME paper No. 78-HT-55.1978