Role of heat reservation of N_2 and O_2 and the role of heat dissipation of CO_2 and water vapour

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Abstract: There is a fallacy dominating the way of our thinking in current climate research that radiative gases such as carbon dioxide and water vapour are regarded greenhouse gases that trap heat and warm up the atmosphere. This article will show it is non-radiative nitrogen and oxygen gases that award the Earth a warm liveable near surface atmosphere. Radiative gases such as carbon dioxide are cooler than, gain heat by molecular collision from, and dissipate heat by radiation for nitrogen and oxygen.

1. Introduction

The universal misconception originates from our daily experience of the Sun, heaters and ovens that radiate infrared and warm up our body. This has established a notation that infrared absorption leads to an object to trap heat and warm up. Carbon dioxide and water vapour do absorb infrared thus are unanimously thought greenhouse gases (*1-6*). Terminology of radiative forcing has been widely employed as a quantitative measure of the greenhouse effect of a radiative gas (*7-9*). The following will show absorption and emission are the two inseparable equivalent identities of the same physical essence, radiative gases such as carbon dioxide do not trap heat but function as a half-mirror hanging on the sky.

2. Radiative equilibrium temperature of carbon dioxide

Figure 1 shows the spectral irradiances derived from radiative transfer code Modtran that examines each spectral line for atmospheric conditions for a detector facing down at 20 km altitude under standard US atmosphere conditions. Clearly, the absorption band centred at 667 cm^{-1} (15 μm) is due to carbon dioxide.

However, absorption of thermal radiation is only half of the story for CO_2. The Kirchhoff's law states that spectral emissivity, $\varepsilon_\lambda(\lambda, T)$, equals spectral absorptivity, $a_\lambda(\lambda, T)$, at any given wavelength, λ, and temperature, T, for an object. This can be translated into a plain language that an object that absorbs emits, or an object that emits absorbs. Absorption and emission are two inseparable equivalent identities of the same physical essence. The Kirchhoff's law permits calculation of the equilibrium temperature of carbon dioxide in terms of radiation.

From the irradiance spectrum shown in Figure 1, one obtains a mathematical expression of the 15 μm adsorption band as the first approximation:

$$a_{\lambda co2}(\lambda, T) = \varepsilon_{\lambda co2}(\lambda, T) = \begin{cases} 1 & 13.04\mu m \le \lambda \le 17.64\mu m \\ 0 & \lambda < 13.04\mu m \ \ or\ \ \lambda > 17.64\mu m \end{cases} \quad (1)$$

Thus, the absorbing radiant flux of a carbon dioxide molecule, Q_{aco2}, reads:

$$Q_{aco2} = \overline{A}\,\Delta E_{Gsurf} \tag{2}$$

where, ΔE_{Gsurf} is the component over the wavelength range from λ_1 to λ_2 (13.04-17.64 μm or 767-567 cm^{-1}) of the earth ground surface radiation, and equal to 77.95 W/m^2 as determined by numerical integration of the spectrum shown in Figure 1.

According to the Planck's law the emitting radiant flux, Q_{eco2}, is written:

$$Q_{eco2} = A_s \int_0^\infty \varepsilon_{\lambda co2}(\lambda,T)\,\frac{2\pi c^2 h}{\lambda^5}\,\frac{1}{e^{\frac{ch}{k\lambda T_{co2}}}-1}\,d\lambda = A_s \int_{\lambda_1}^{\lambda_2} \frac{2\pi c^2 h}{\lambda^5}\,\frac{1}{e^{\frac{ch}{k\lambda T_{co2}}}-1}\,d\lambda \tag{3}$$

where, the symbols $\overline{A}$ and A_S represent the average cross sectional area and the surface area of carbon dioxide molecules, respectively; c is the speed of light in vacuum (2.99792458 x 10^8 m/sec), h is the Planck constant (6.62606957 x 10^{-34} J ·sec) and k the Boltzmann constant (1.3806488 x 10^{-23} J/K).

When Eq. (2) equals Eq. (3), carbon dioxide reaches its radiative equilibrium temperature. The equations were solved using a numerical method to obtain T_{co2} = 195.32 K (≅ -77.8°C, appendix shows $\overline{A}/A_s$ = 4.726).

The bottom curve segment near 667cm^{-1}(15 μm) shown in Figure 1 is the irradiance of carbon dioxide. The spectra curves were fitted with the Planck's law. The top envelop 285.04 K (11.89°C) is the temperature of the earth's ground surface, and the bottom envelop measures the actual temperature of carbon dioxide being determined 216.50 K (-56.65°C), 21.2°C higher than its radiative equilibrium temperature. The reason follows.

Nitrogen and oxygen gases constitute of around 99% air of the atmosphere. They are nearly transparent-body gases in terms of thermal radiation – absorb nothing, emit nothing, keeping their own temperature without losing or gaining heat by thermal radiation. The average air temperature is around 15°C close to the Earth's ground surface; and decreases as the altitude increases. Carbon dioxide constantly gains heat leading to temperature rising by colliding with warmer nitrogen and oxygen molecules.

Gases are well mixed in the atmosphere. Air flow or molecular collisions tend to homogenise the temperature of different gases; however, radiative absorption and emission tend to differentiate it. Depending on the source of radiation, the absorption and emission properties, gases in the atmosphere could have different temperatures from each other. In other words, although air is well mixed, carbon dioxide, water vapour and nitrogen and oxygen may differ in temperature from each other due to difference in radiation.

At high altitude space, e.g. at the 50-85km altitude mesosphere where the air temperature is around -100°C, there is no more thermal radiation over the band with wave number 667cm^{-1} from the earth ground surface but from comrade molecules at the lower altitude for carbon dioxide to absorb. As such carbon dioxide at high altitude is expected to have an even lower equilibrium temperature. A more precise quantitative analysis can be achieved by establishing a differential equation. However, this is omitted in this article to focus on concepts.

This finding reveals the true colour of the roles of carbon dioxide. Although it absorbs thermal radiation from the Earth, it emits more. Carbon dioxide is in thermal deficit in terms of radiative balance. Nitrogen and oxygen constantly feed CO_2 with heat so that it maintains a temperature higher than its radiative equilibrium.

3. A thinking experiment

To generalise this notion into a practicable conception, however, there is a need to carry out a thinking experiment to show that there are two different domains according to the strength of radiation. Radiative species trap heat and are hotter than non-radiative species in the high domain with strong radiation sources; but dissipate heat and are cooler in the low domain with weak radiation sources.

The thinking experiment starts with two basic equations: one describes how much heat energy, I, an object with temperature, T, absorbs; the other expresses how much heat energy, J, the same object emits per unit area and unit time.

$$I = a I_0 \tag{4}$$

$$J = \varepsilon \sigma T^4 \tag{5}$$

where, a and ε are absorptivity and emissivity of the surface of the object, σ is the Stefan-Boltzmann constant equal to 5.670373x 10^{-8} (W/m^2K^4), and I_0 represents the radiation source.

An important message from Eqs (4) and (5) is that absorption of heat energy relies on external radiation source, I_0, whilst emission is determined by its own temperature, T, of the object.

Literally $a = 0$ for nitrogen and oxygen gases, therefore $\varepsilon = 0$ according to the Kirchhoff's law; $a \neq 0$ for carbon dioxide, water vapour and any other radiative gases, thus $\varepsilon \neq 0$. Figure 2 illustrates the thinking experiment by taking nitrogen, oxygen and CO_2 as an example. One obtains:

A) If nitrogen (or oxygen) and carbon dioxide are placed separately in space without any radiation source, nitrogen and oxygen keep their initial temperature; CO_2 continues to emit and drop its temperature until reaching -273.15°C (0°K) because emission loses heat.

B) Now, we apply a low radiation source to the both. Nitrogen and oxygen keep unchanged; however, CO_2 will approach to a temperature higher than -273.15°C, at which the amount of emission heat equals the amount of absorption heat.

C) Intensifying the radiation source to a level equivalent to the Earth's Ground Surface radiation at 12°C, nitrogen and oxygen still keep unchanged; whereas CO_2 will approach to -78°C to reach its radiative equilibrium.

D) Further intensifying the radiation source to a level equivalent to radiation by the Earth Ground Surface at 145°C will lead CO_2 to reach 15°C.

E) When the radiation source is strong enough, radiative gas begins to be hotter than non-radiative gases.

This thinking experiment, though simple, illustrates that because the earth ground surface is a weak radiation source for CO_2, the ability of infrared absorption is a manifestation that CO_2

dissipates rather than traps heat energy. This is why CO_2 is far cooler than atmospheric nitrogen and oxygen.

All the other so called greenhouse gases follow the same physical principles. However, the numbers specified above would be different because their absorption/emission bands of the gases are different from that of CO_2.

4. Conclusion

In summary, if there is no radiation source, CO_2 approaches 0 K because of its emission; absorption of the thermal radiation from the earth ground surface rises CO_2 temperature from -273.15°C to -78°C only. Carbon dioxide gains heat by molecular collision from nitrogen and oxygen, and dissipate the gained heat by radiative emission. Considering gases are far more effective than bulky objects in heat dissipation by emission, one would not surprise to realise that it is non-radiative nitrogen and oxygen gases that award the Earth a warm liveable near surface atmosphere.

Appendix: Ratio of the surface area and the average cross sectional area of a prolate spheroid

Carbon dioxide has a linear molecular shape as such it can be approximated a prolate spheroid rugby with its polar radius being 3 times as long as its equatorial radius. The surface area, *S*, and volume, *V*, of a prolate spheroid read:

$$S = 2\pi a^2 + \frac{2\pi ac^2}{\sqrt{c^2 - a^2}} \sin^{-1}\left(\frac{\sqrt{c^2 - a^2}}{c}\right) \tag{A1}$$

$$V = \frac{4}{3}\pi a^2 c \tag{A2}$$

where, *a* and *c* are the equatorial radius and the polar radius of the prolate spheroid, respectively.

One obtains the radius of a sphere that has the same volume as that of the prolate spheroid,

$$r = \sqrt[3]{a^2 c} \tag{A3}$$

Thus the average cross sectional area of the prolate spheroid is written;

$$\overline{A} = \pi\left(a^2 c\right)^{2/3} \tag{A4}$$

Therefore

$$\frac{S}{\overline{A}} = \frac{2\pi a^2 + \frac{2\pi ac^2}{\sqrt{c^2 - a^2}} \sin^{-1}\left(\frac{\sqrt{c^2 - a^2}}{c}\right)}{\pi\left(a^2 c\right)^{2/3}} \tag{A5}$$

If c=3a, one obtains:

$$\frac{S}{A} = \frac{2a^2 + \dfrac{2a \times 9a^2}{\sqrt{9a^2 - a^2}} \sin^{-1}\left(\dfrac{\sqrt{9a^2 - a^2}}{3a}\right)}{\pi\left(3a^3\right)^{2/3}} = \frac{2 + \dfrac{18}{\sqrt{8}} \sin^{-1}\left(\dfrac{\sqrt{8}}{3}\right)}{(3)^{2/3}} = 4.725960 \qquad \text{(A6)}$$

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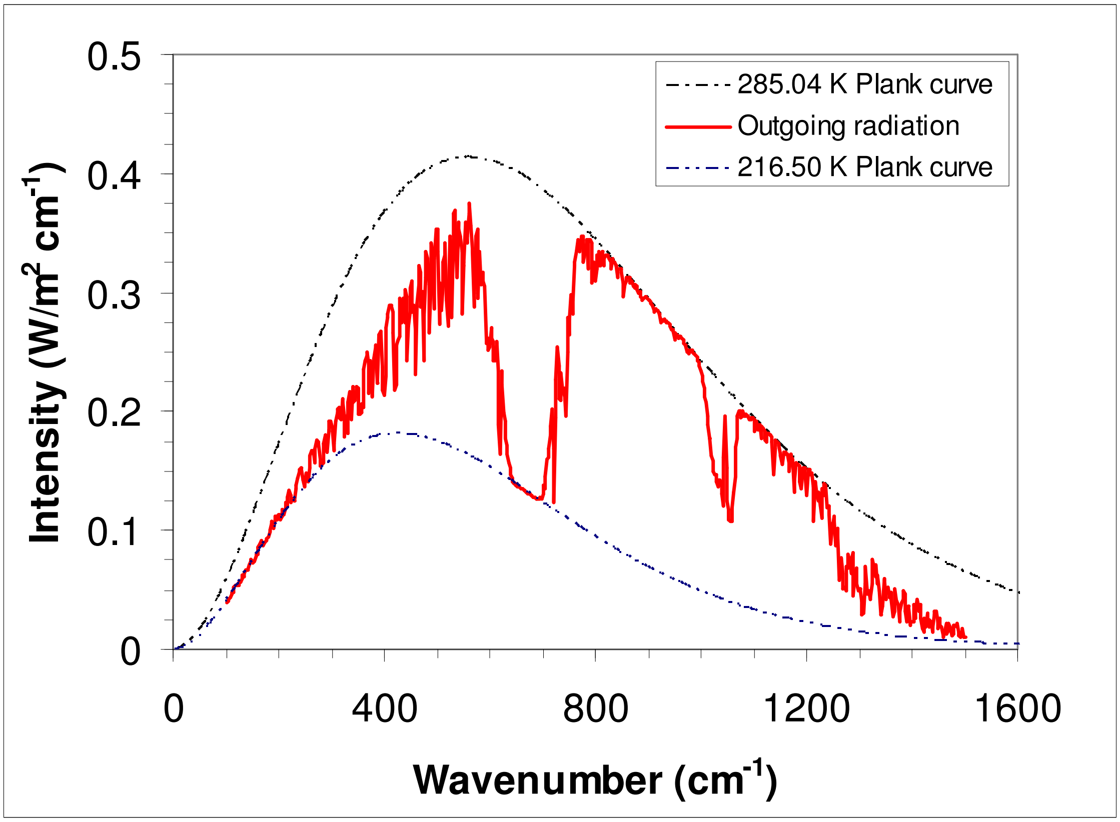
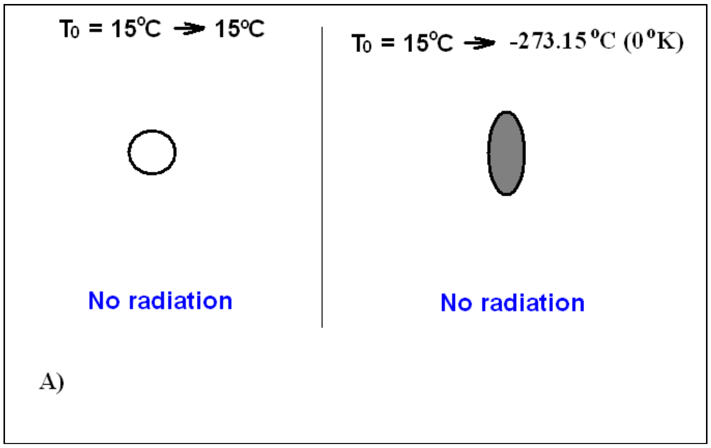
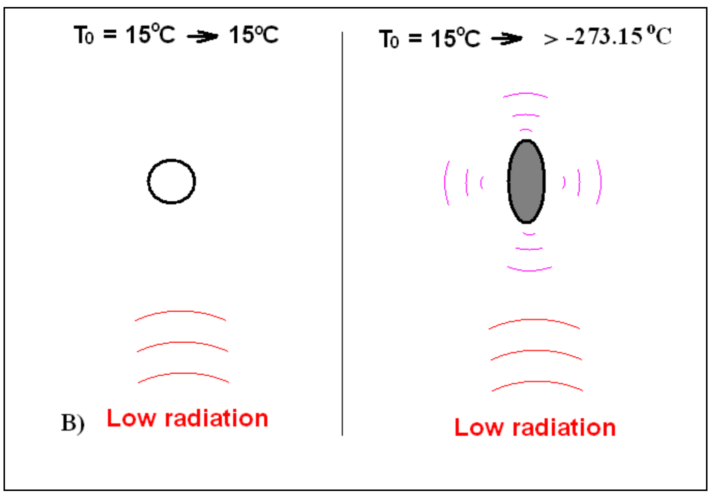


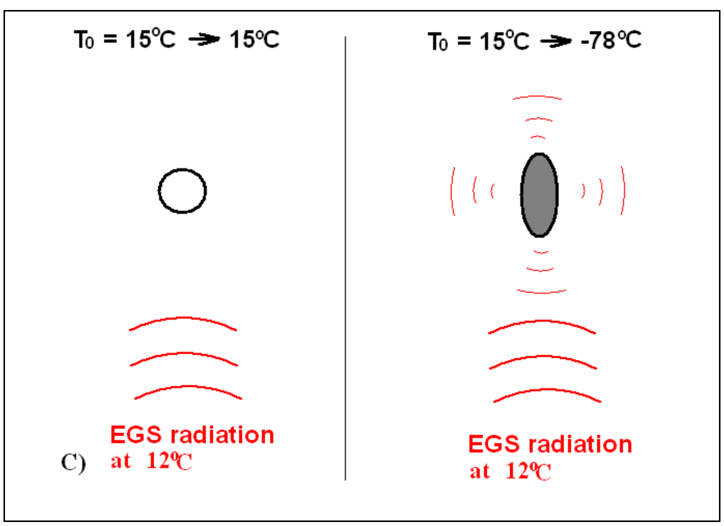
Fig. 1. The upward irradiance spectrum of the Earth as measured at 20 km high altitude with detector facing down under standard US atmosphere conditions with 400 ppm of CO_2



T0 = 15°C → 15°C
T0 = 15°C → -273.15°C (0°K)
No radiation
No radiation
A)



T0 = 15°C → 15°C
T0 = 15°C → > -273.15°C
B)
Low radiation
Low radiation



T0 = 15°C → 15°C
T0 = 15°C → -78°C
EGS radiation
C) at 12°C
EGS radiation
at 12°C

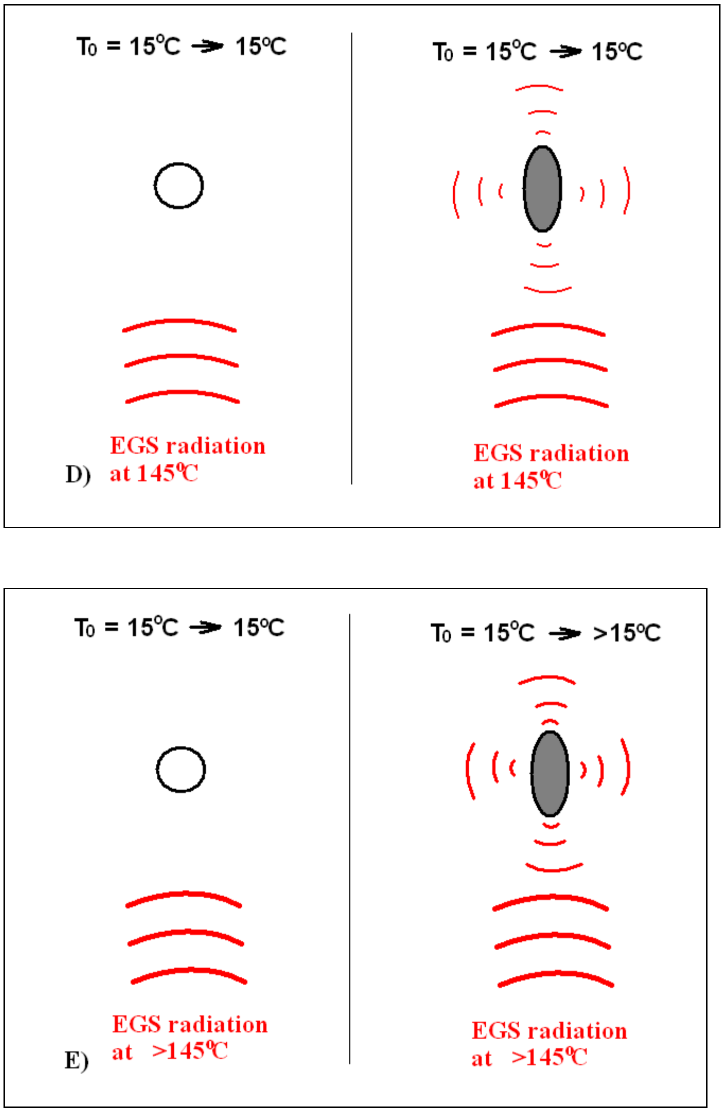


Fig. 2. A thinking experiment illustrating the absorption and emission roles of radiative and non-radiative gas molecules.