Translator's note: The translation has not been made by a native speaker or by a specialist in physics and thermodynamics, but special attention has been paid to respect the integrity of the author's content and to avoid misinterpretations.

Thermal Radiation and Thermodynamics

Summary

Among the mechanisms for regulating the temperature of the atmosphere and the Earth's surface, thermal radiation and its carriers, the so-called greenhouse gases, play an essential role.

Heating causes an increase in the concentration in the atmosphere of water vapor, carbon dioxide, methane, etc. These gases, in turn, cause an increase in the transfer between thermal radiation and the atmosphere, and consequently, a reduction in the differences in temperature gradients which exist between them. This results in a cooling of the lower atmosphere and the surface of the Earth.

Interpretation

The exchanges of energy between electromagnetic radiation and matter can be described in a very simple way in being consistent with our intuition of thermal phenomena.

These exchanges occur at frequencies characteristic of the material elements. According to the work of Max Planck, we can assign a temperature to a thermal radiation whose frequency is given.

Consequently, the description of the exchanges between radiation and matter is expressed in an obvious way. Cold radiation heats up (absorbs energy) by cooling a hotter material element. A hot radiation warms a cold element by transferring energy to it.

The need to introduce the notions of hot radiation and cold radiation is due to the fact that there can be no direct exchange between two electromagnetic waves; their coupling can only be done by their interaction with matter.

However, in all cases, the heat transfers take place from hot bodies to cold bodies and with the production of entropy. These exchanges show the tendency to equalize temperatures between hot elements and cold elements in accordance with the second law of thermodynamics.

This point of view on exchanges allows to better understand the role of "greenhouse" gases in the transfer of heat in the atmosphere. A hot radiation passing through a layer of atmospheric gas whose temperature is lower, transfers energy to it. Its temperature decreases during its passthrough, tending to thermal equilibrium with the gas. In an analogous way, a cold radiation, passing through a warmer atmospheric layer, borrows energy from it and also tends to reach equilibrium with it. This tendency to equalize temperatures depends on the concentration of greenhouse gases, it increases when the concentration increases.

The atmosphere

The Earth's atmosphere can be described as formed by successive horizontal layers of decreasing temperatures from the Earth's surface to the top of the troposphere.

The temperature of radiation coming from the Earth and passing through the atmosphere is, whatever the incidence, always higher than that of the layers crossed: the radiation constantly gives up energy to them.

Radiation from space (4°K) and directed towards the Earth passes through warmer layers, which transfer energy to it. Its temperature near the earth's surface is at most equal to that at the bottom of the atmosphere. It is cold radiation which cools the Earth which absorbs it (the Earth indeed transfers energy to the radiation so that it reaches thermal equilibrium with it).

Thus, the radiations which pass through the atmosphere from the Earth towards space or from space towards the Earth tend to equalize the temperatures between the various parts of the atmosphere and between the Earth's surface and the atmosphere.

In this sense, this mechanism does not differ in its effects from the phenomena of conduction, convection, or others, which govern the heat transfers of the atmosphere.

Temperature gradient

An "Earth" and an "atmosphere" contained in an adiabatic enclosure must, according to the above, be at the same temperature, whether or not the whole is under the action of a gravitational field.

But the Earth and the atmosphere obviously do not constitute a closed system. The Earth receives short wavelength energy from the sun by radiation. An equal quantity of energy, on average, is re-emitted in infrared towards space, directly by the Earth for a small part, and for the most part, at the top of the troposphere. The temperature in this region is determined by the level of energy to be emitted.

But there can be no net transfer of energy in an atmosphere at thermal equilibrium. Therefore, the temperature of the lower layers and of the earth must be higher than the temperature of the emission zone to ensure the necessary energy transfer there.

When the concentration of greenhouse gases increases, the temperature gradient of the atmosphere decreases. The temperature of the top of the troposphere remaining constant, the temperature of the lower atmosphere and the surface of the Earth must drop.

Conclusion

It is widely accepted that the increase in the concentration of molecules of greenhouse gases causes a warming of the earth's surface.
The preceding presentation leads to the opposite conclusion: increasing the concentration of these gases must reduce the temperature difference between the top of the atmosphere and the earth's surface and, consequently, lowers the temperature of the latter.

On the greenhouse effect

The following observations are intended to identify the reasons for the obvious disagreement that appears between the previous conclusions and those most widely accepted on the “greenhouse effect”.

The transfer equation

The most comprehensive calculations on energy exchanges between radiation and greenhouse gases use, with some variations, the same “radiative transfer equation”. This equation establishes the balance of the exchanges in each direction of space and for each of the interaction frequencies. It is suitable for describing phenomena in a "clear sky" atmosphere, where scattering is negligible.

The energy balance is presented there in the form of a sum of two terms. One concerns the incident radiation at the entrance to the interacting atmospheric layer: it is presented as absorbed by greenhouse gases. The other term relates to the layer's own radiation, emitted at the output. This formulation is in accordance with Kirchhoff's law which expresses that the “absorptivity” and “the emissivity” of a system at thermal equilibrium are equal to each other. It makes it possible to calculate the energy exchanged with radiation passing through the thickness of the entire atmospheric layer; but, in doing so, it erases the “local” physical reality of the interaction.

To describe a complex thermodynamic system, a volume of gas (composed of molecules and atoms), or even radiation (composed of elementary electromagnetic waves), it is not enough to know its total energy, but it is also necessary to know the distribution of this energy between its different elementary components. It is necessary to know either the temperature or the entropy.

The notion of radiation temperature allows a better understanding of the physics of exchanges at the local level. Between thermal radiation and the atmosphere, the temperature differences are relatively small. Over a short distance, the amount of heat transferred from one to the other, at a given frequency, can be considered proportional to the temperature difference and the concentration of greenhouse gases. The energy exchanged naturally goes from the hot body to the cold body.

The above is not inconsistent with the transfer equation. A simple rearrangement of the terms of this equation suffices to reveal the exchange at the local level. However, the notion of temperature is missing.

The atmosphere balance

Calculations of current energy transfers between thermal radiation and the atmosphere assume that greenhouse gas molecules remain locally in thermal equilibrium with other molecules and atoms. There are schematically several temperature profiles of the atmosphere: equatorial regions, temperate regions, polar regions.

In an average profile, the temperature of the earth's surface is 15°C. The temperature of the atmosphere, which is lower, decreases slowly in the lower layers, more rapidly at altitude (around 6 to 7°C per km) down to the tropopause. The sky there is cloudless. For the calculations, a distinction is made between upward radiation and downward radiation.

Upward radiation is composed of all the elementary waves coming from the surface and which cross the atmosphere under various incidences. In the most often accepted hypothesis where the earth's surface is assimilated to a blackbody, all these waves initially have the same temperature, that of the surface. As they pass through the atmosphere, they constantly release energy. Their temperatures cease to be identical, but they remain higher than that of the top of the atmosphere. The energy radiated into space is thus less than the energy emitted by the earth's surface. The difference between these two quantities, the energy transmitted to the atmosphere, generally denoted by G, is given as a measure of greenhouse effect.

Downward radiation, from space, is a “cold radiation”. As it passes through the atmosphere, it heats up by constantly absorbing energy, but its temperature always remains lower than that of the layers it passes through. This radiation cools the earth's surface warmer than it. The energy it receives from the atmosphere is greater than the energy supplied by the upward radiation. The balance of energy exchanges between thermal radiation and the atmosphere is clear: the atmosphere provides more energy to the radiation than it receives from it. The order of magnitude is around one hundred W/m^2. The heat capacity at constant pressure of an atmospheric column with a section of one square meter is of the order of 10^7 J/°K; without external energy input, the average temperature of the atmosphere would drop by around one degree in 24 hours.

The temperature of the atmosphere is maintained at its level by an energy input essentially coming from two distinct sources. On the one hand, the return of the ozone molecules to the state of normal oxygen molecules, for approximately $70W/m^2$; and, on the other hand, the contribution by the terrestrial surface of energy by thermal conduction and especially by convection and latent heat of water vapor. It is difficult to accurately assess these different contributions. The calculations of energies brought into play in the exchanges where the radiation intervenes are, on the contrary, it seems, capable of being made with great precision. As we know that the atmosphere has to be in a balanced energy balance, clearly, the quantification of these different effects can be done accurately.

Growth of carbon dioxide concentration

The increase in the concentration of greenhouse gases in the atmosphere promotes the transfer of energy between the atmosphere and thermal radiation. More precisely, at each point of their interaction regions, the temperature differences between radiation and atmosphere must decrease.

Particular attention is focused on carbon dioxide because of the positive feedback mechanisms associated with it.

It is clear that, if we assume that the temperature of the atmosphere and its profile remain constant when the concentration of carbon dioxide increases, the energy transferred by the upward radiation, always warmer than the atmosphere in its passthrough, increases. This is what the calculation shows; the coefficient G, given as measuring greenhouse effect, increases, the energy radiated at the top of the atmosphere decreases. According to widely accepted reasoning, the temperature of the earth's surface must increase in order for the energy emitted to increase.

However, when the concentration of carbon dioxide increases, the downward “cold radiation” is more closely coupled to the atmosphere, and, in the calculation hypothesis of the preceding paragraph, the energy which it receives from it increases. Locally, the temperature difference between upward and downward radiation decreases, showing the tendency of temperatures to become uniform. All in all, the energy deficit of the atmosphere in its exchanges with radiation increases, contributing to its cooling.

Under these conditions the transfer of energy from the earth's surface to the atmosphere by conduction, convection, and latent heat must increase, thus contributing to a decrease in the surface temperature. The final equilibrium of the whole must be achieved in a decrease in the temperature gradient of the atmosphere and the temperature of the earth's surface.

The calculation of this new equilibrium is a complex problem. Radiation, atmosphere, conduction, convection are coupled. For example, one cannot treat separately the interaction between radiation and atmosphere, the distribution of the temperature of the atmosphere being an unknown factor of the problem.

But, although it may seem difficult, perhaps, to obtain a precise quantified evaluation, one conclusion remains: an increase in the concentration of carbon dioxide leads to a cooling of the atmosphere and of the earth's surface.

Scientific arguments

The purpose of the previous note is to identify some essential notions on the mechanism of so-called greenhouse gases. We have tried to make it as simple as possible. But it is perhaps useful, for a better understanding of the note and to support some of its arguments, to recall here some basic notions. Here again, this simple presentation neglects many technicalities, but without altering the fundamental aspects.

Greenhouse-effect gas

Molecules in the atmosphere, such as water vapor, carbon dioxide, methane, which play an active role in greenhouse effect, can find themselves in an "excited state" where they are the site of complex oscillatory movements, at defined frequencies, characteristic of each type of molecule. These states of excitation can be caused by collisions with other molecules in the atmosphere, oxygen, nitrogen, for example, but also by interaction with electromagnetic radiation.

The transition, at the frequency ν, from the normal state to the excited state of an active molecule is made by absorption of a quantum of energy *h*ν. The passage from the excited state to the normal state is done by emission of the same quantum of energy.

There can be, in fact, several levels of excitation whose energies are measured in multiples of the same quantum. Thus, a molecule of carbon dioxide, at the wavelength of 15µ, exhibits deformation oscillations (the linear molecule O—C—O undergoes transverse bending when it is excited). These oscillations are harmonic: they correspond to a series of excitation states with energy *nhc/λ.*

We will confine ourselves in what follows, for the simplicity of the presentation, to consider that greenhouse molecules are only capable of two states; one normal, the other excited at an energy level *hν.*

The collisions between molecules contribute, in a gas, to the establishment of a thermal equilibrium. Under the action of these collisions, active molecules can pass from the excited state to the unexcited state, or vice versa, from the unexcited state to the excited state. However, at thermal equilibrium, and in the absence of any other type of interaction, the numbers N_1 and N_2, respectively unexcited molecules and excited molecules, are, on average, a constant ratio given by Gibbs' formula, where T is the gas temperature:

$$(1) \qquad \frac{N_2}{N_1} = \exp - \frac{h\nu}{kT}$$

Interaction with an electromagnetic field

Thermal radiation can be considered as formed by a beam of plane electromagnetic waves, or elements of plane waves, each of them characterized by its direction in space, its frequency and the energy it carries. At the frequency ν, this energy is measured in number of photons. The energy density is $nh\nu$ and the energy flux per unit area is cnh ν where c is the speed of the wave, equal to the speed of light in a sparse gas such as the atmosphere.

In the study of greenhouse effect, much attention is paid on the two thermal energy flows transported by electromagnetic radiation, one from the surface of the earth to space, the other from space to the surface of the earth. Each of these radiations results from the superposition of elementary electromagnetic waves passing through the atmosphere under different incidences and for each of the specific frequencies of the molecules of greenhouse gases.

Studying the interaction of these complex radiations means, first of all, to examine the interaction of an elementary wave of a given direction, at a frequency of one of the different gases.

Consider therefore a plane electromagnetic wave passing through an “atmospheric” layer comprising, per unit volume, N_1 and N_2 unexcited and excited molecules, at the frequency ν.

The balance of the energy exchanged over the distance *dl* can be expressed, according to quantum mechanics, by the equation:

$$(2)\qquad \frac{dn}{dl} = -K(N_1 n - N_2 n - N_2)$$

where n is the number of photons per unit volume of the wave.

Three basic mechanisms are involved:

- Absorption, described by the first term of the second side of the equation. The electromagnetic field transfers photons, excitation energy, to unexcited molecules.

- Stimulated emission, the second term in the equation. Under the action of the field, excited molecules lose their excitation energy by transmitting photons to it.

- Spontaneous emission, described by the third term. Excited molecules return to the non-excited state, giving up their energy to the field, independently of the energy it already carries.

The constant K is expressed as a function of the specific electrical characteristics of the molecules. It measures the strength of the coupling between field and molecules.

We observe that in the questions concerning thermal radiation, (eq.1), the density of the non-excited molecules is always greater than the density of the excited molecules. As a result, we can use an always positive net absorption coefficient: $\alpha = K(N_1 - N_2)$

Tendency to temperature equalization

Suppose that the gas is in thermal equilibrium with the electromagnetic wave at the same temperature. The exchange of energy between gas and wave must be nil, on average. From the Gibbs equation and the exchange equation $N_1 n - N_2(n+1) = 0$, we obtain the photon density at thermal equilibrium:

$$(3)\qquad \bar{n} = \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

This is the value given by M. Planck in his theory of blackbody. It depends only on frequency and temperature.

The function $\bar{n}(T)$ is monotonous. n increases when T increases. As a result, we can assign a defined temperature to any wave carrying a density of photons n, and any body at that temperature can be considered to be in thermal equilibrium with that wave.

Energy exchanges between a wave carrying a density n of photons and an atmospheric layer at temperature T are given by the local radiative transfer equation (2). By introducing Planck's equilibrium density (3), this equation takes the simple form:

$$(2b)\qquad \frac{dn}{dl} = -\alpha(n - \bar{n})$$

Its interpretation is expressed in terms of exchange of energy, quantity of heat, between hot body and cold body.

A wave whose density of photons is lower than that of Planck, whose temperature is, consequently, lower than that of the gas, absorbs energy; it cools the gas as it passes through it. A wave whose temperature is higher than that of the gas, heats it, giving it energy as it passes.

In the two cases, one observes in these transfers of quantity of heat the tendency to the equalization of the temperatures between radiation and gas in accordance to the Second law of Thermodynamics.

The exchanges between radiation and gas therefore modify the temperatures, both of the radiation and of the gas. The equilibrium density $\overline{n}$ therefore varies with the temperature of the greenhouse molecules which, themselves, are coupled with the other molecules of the atmosphere.

To simplify the calculations of energy transfer between radiation and atmosphere, it is assumed that the local temperature of the atmosphere is not modified by the interaction. The results obtained under these conditions show that the balance of exchanges by radiation is deficient: the atmosphere supplies energy to the radiation. It is assumed that thermal conduction and convection compensate this deficit. In this hypothesis, the local transfer equation integrates immediately:

$$(4) \quad n(l) - \overline{n} = (n(0) - \overline{n}) \exp - \alpha l$$

This equation shows that the density of photons transported by the wave tends towards the Planck equilibrium value during its passage through the atmosphere. In other words, the temperature difference between the wave and the atmosphere decreases as the wave progresses. Depending on the sign of the result, the wave transfers or receives energy from the atmosphere, heats it up or cools it down. The absorption coefficient increases proportionally to the density of greenhouse gases. Equality of temperatures between atmosphere and wave is reached more quickly when the density of greenhouse gases is higher.

The temperature of the lower layers of the atmosphere is little different from that of the earth's surface. Radiation from the earth exchanges photons by absorption and emission when crossing these lower layers, but its energy content, its number of photons, remains little modified.

If the number of photons transported by a wave is much greater than the number of photons corresponding to the temperature of the gas, the previous equation takes the form:

$$(5) \quad n(l) = n(0) \exp - \alpha l$$

It is to an equation of this type that we refer in order to 'explain' the greenhouse effect: "opacity of the atmosphere" to infrared radiation, "trapping" of the radiation emitted by the surface of the earth.

The “classical” radiative transfer equation

A change in the order of its terms allows to write the equilibrium equation (4) in the form:

$$(6) \quad n(l) = n(0) \exp(-\alpha l) + \overline{n}(1 - \exp(-\alpha l))$$

It highlights Kirchhoff's law, according to which absorptivity is equal to emissivity, both represented by the quantity: $(1 - \exp - \alpha l)$.

Absorption and emission are clearly separated; leading to the interpretation of the phenomena of infrared radiation, incorrect from the physics perspective, already identified in the preceding paragraph. The temperature differences between the radiation and the atmospheric layer that it passes through remain small, and the emission cannot be considered negligible in comparison with the absorption.

By iteration, on successive layers, we get:

(7) $$n(l)=n(0)e^{-\int_0^l \alpha(x)dx}+\int_0^l \alpha(x)\overline{n}(x,T)e^{-\int_{x'=x}^{l}\alpha(x')dx'}dx$$

$n(x)$ is the photon density of the wave, and $\alpha(x)$ the net attenuation at a point x in its travel.

It is a transfer equation relating to an elementary wave of given direction and frequency. It can be considered as forming the backbone of the classical radiative transfer equation.

However, the latter does not relate to a single elementary wave, but considers radiation formed by a beam of elementary waves. We need to transpose the equation by introducing a simple multiplicative factor. The following reminder develops this point.

The complete description of an electromagnetic field in a given volume involves all the elementary waves, the modes, likely to propagate inside this volume. It is shown that, at a given frequency ν, and in the frequency band dν, the density of these modes in a volume V is equal to:

(8) $$pd\nu=\frac{8\pi\nu^2 d\nu}{c^3}$$

In a solid angle dΩ their density is:

(9) $$p_\Omega d\Omega=2\frac{\nu^2}{c^3}d\Omega$$

If we assume that these modes are at the same temperature, which is plausible when it comes to radiation emitted by an isothermal body, the energy flux transported in this solid angle is:

(10) $$dI_\nu=2\frac{nh\nu^3}{c^2}d\Omega$$

It suffices to multiply the two sides of the transfer equation applicable to an elementary wave by the factor $2\frac{h\nu^3}{c^2}$ to end up with the classical radiative transfer equation.

Blackbody radiation

The energy emitted in an element of solid angle, on the surface of an atmospheric layer, by radiation in thermal equilibrium with it at the frequency ν is given by formula (10). The total flux of energy emitted perpendicular to the layer is expressed in this equation:

(11) $$\Phi_\nu=2\frac{h\nu^3 n}{c^2}\int_0^{\frac{\pi}{2}}\cos\theta.d\Omega_\theta$$

The integral has the value π, n is defined by Planck's relation (3). The radiation emitted by a black body is obtained by calculating the integral: $\Phi=\int_0^\infty \Phi_\nu d\nu$

Hence the Stefan-Boltzmann formula: $\Phi = \sigma.T^4$ with $\sigma = 5,67.10^{-8}\, W.m^{-2}$