The role of greenhouse gases in radiative equilibrium – Thermodynamic evaluation

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Abstract: The significance of greenhouse gases for climate change is assessed in the case of carbon dioxide on the basis of thermodynamic data. According to the values of the molar heat capacity, no increased heat-storing property of this greenhouse gas can be determined. The absorption and desorption of infrared radiation by the greenhouse gases is seen as a reversible dynamic process, which on the one hand reduces the IR radiation from the Sun, and on the other hand, delays the re-radiation from the Earth. As converters of heat into IR photons and vice versa, the greenhouse gases play an important role in balancing the radiation. The direction of heat transport in the atmosphere is determined by the 2nd Law of Thermodynamics. The range of IR radiation is determined according to the gradation of air pressure in the atmosphere.

Keywords: carbon dioxide; greenhouse gases; molar heat capacity; radiation balance; IR absorption/desorption; heat/radiation transmitter

Zusammenfassung: Die Bedeutung von Treibhausgasen für den Klimawandel wird im Fall von Kohlendioxid anhand thermodynamischer Daten beurteilt. Anhand der Werte der molaren Wärmekapazität kann keine erhöhte Wärmespeichereigenschaft dieses Treibhausgases festgestellt werden. Die Absorption und Desorption von Infrarot-Strahlung durch die Treibhausgase wird als ein reversibler dynamischer Prozess angesehen, der einerseits die Infrarot-Strahlung der Sonne reduziert und andererseits die Rückstrahlung von der Erde verzögert. Als Wandler von Wärme in IR-Photonen und umgekehrt spielen die Treibhausgase eine wichtige Rolle beim Ausgleich der Strahlung. Die Richtung des Wärmetransports in der Atmosphäre wird durch den 2. Hauptsatz der Thermodynamik bestimmt. Die Reichweite der IR-Strahlung wird durch die Abstufung des Luftdrucks in der Atmosphäre bestimmt.

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1 Initial situation and task

An air envelope prevents the planet Earth from becoming too hot during the day and too cold at night. The radiated solar energy reaches the Earth's surface in a filtered form and is released from it with a delay. This creates a climate in the lower layers of the atmosphere like in a greenhouse, GH, in which life could develop. The temperature difference of 33° between the upper edge of the greenhouse and the Earth's surface is called the greenhouse effect, GH effect. Disturbances in the function of the greenhouse could severely affect a globally and digitally networked population of billions on Earth.

Due to their ability to absorb IR radiation energy, the so-called GH gases such as water vapour, H_2O, and the trace gases carbon dioxide, CO_2, methane, CH_4, nitrous oxide, N_2O, ozone, O_3 and others are held responsible for the GH effect. Climate research evaluates the contributions of the individual gases to the overall GH effect according to two parameters: the Global Warming Potential, GWP, and the Radiative Forcing RF (W/m^2). In addition to IR absorption data, cf.,[1] time-varying data such as the emission of individual gases into the atmosphere as well as their long-term residence time therein are also included in the calculation of those parameters. Due to the temporal variability of some output variables, the GWP and RF values are periodically updated by the IPCC[2,3].

The heat absorption and transfer properties of water and water vapour are well-known. Additionally, the water of oceans is an essential part of climate control.[4] However, since the hydrological cycle is largely unaffected by human impacts, the main blame for global warming is placed on CO_2 – and here even on the anthropogenic contribution, although this - summed up over the years of the Industrial Revolution – is estimated at only a fraction of the 0.042 vol %.

Climate research is currently focused to a correlation between the concentration of GH gases, especially CO_2, in the atmosphere and a rise in temperature over the last 150 years. In contrast to this, palaeoclimatological results show within some time intervals reverse dependencies of CO_2 increase after global temperature rise.[5] Thus, the GH effect became the subject of uncertain temperature extrapolations with the prediction of a climate catastrophe by the end of this century. However, a number of questions remain unanswered.

In the present work, molecular and physicochemical data concerning the properties of GH gases with regard to heat storage as well as to IR absorption/desorption processes are considered. Thereby, CO_2 as a representative of a group of GH gases is the focus of the considerations. Following thermodynamic considerations, the contribution of GH trace gases to the GH effect is estimated using GWP- and RF-based results.

2 Solar radiation

At the outer air envelope of the Earth, at an altitude of about 20 km, solar radiation has a power density of 1.361 kW/m^2 (solar constant). On its way through the atmosphere the solar radiation is weakened by reflection and absorption, depending on the path length and the angle of incidence. At the Earth's surface, the power of the solar radiation amounts to a maximum of 1 kW/m^2. This value depends on the latitude, altitude, weather conditions, time of day and season. At higher latitudes, the peak value is limited to midday and the months of June and July. At latitude 60°, for example, this is up to 900 W/m^2 in summer and 200 W/m^2 in winter.

The spectrum of solar radiation ranges with increasing wavelength from ultraviolet, UV, through the visible range of light to infrared, IR. According to various data[6,7], on average about 50–70 % of the irradiated energy reaches the Earth's surface, whereby the spectral distribution shifts in favour of the long-wave components. The figures fluctuate over a wide range depending on weather, humidity and regional air pollution.

The most energetic UV radiation is already absorbed in the stratosphere via chemical reactions with the formation and decay of ozone.[8] Only about one 10th of the original UV radiation reaches the Earth's surface.

Visible light is reflected by clouds and fine dust in the atmosphere; only about one half reaches the Earth's surface.

IR radiation is absorbed by water vapour, aerosols and other trace gases, e.g., CO_2, CH_4, etc., in the atmosphere. Only about half of the original IR radiation reaches the ground. Table 1 shows the absorption losses of solar radiation in the atmosphere.[6]

At the Earth's surface, the solar radiation is absorbed in water and solids and converted into heat via molecular or lattice vibrations. The heat is transferred from heated roof surfaces, concrete highways, house walls, arable land, waters, etc., to the molecules of the atmospheric gases. Heated air with a lower density than cold air rises. It spreads through the atmosphere by convection, air currents, high and low pressure areas. A part, about 15–30 % of the radiated energy, is re-radiated from the Earth's surface as IR radiation.[3]

Table 1: Absorption of parts of the solar radiation in the atmosphere.

Type	Wavelength	Before atmosphere (100 %)	At ground (58 %)
Ultraviolet rad.	0.38–0.10 µm	9 %	1.5 %
Visible light	0.78–0.38 µm	49 %	45 %
Infrared rad	1000–0.78 µm	42 %	53.5 %

3 Greenhouse gases – Molecular consideration

Heat energy in the atmosphere is the kinetic energy of the gas molecules. The molar heat capacity of air (78 vol % N_2, 21 vol % O_2, 1 vol % Ar) amounts to 28.96 J/mol K (at 20 °C).[9] From this, the energy values per molecule are calculated in milli-electron volts (meV) with

1 mol = 6.02×10^{23} molecules1 eV = 1.602×10^{-19} J.

The average heat energy per gas molecule of the air is then: $28.96/(6.02 \times 10^{23}) \times 293$ J/molecule = 1.41×10^{-20} J/molecule = approx. 100 meV/molecule.

Table 2 lists the photon energies of the IR radiation. With increasing altitude, the temperature in the atmosphere decreases. The energy per molecule should then fall into the wavelength range of the far IR.

The main amount of energy is stored in the air molecules in form of kinetic energy, E_{trans}, in space. In the case of the diatomic gases N_2 and O_2 and polyatomic gases such as H_2O and CO_2, the rotational energy, E_{rot}, is added.

In contrast to the molecules of the diatomic gases nitrogen and oxygen, triatomic and polyatomic gas molecules such as H_2O (up to 5 % in the atmosphere), and trace gases such as CO_2, CH_4, and others (in total less than 0.1 % by volume in the atmosphere) exhibit the possibility of oscillation and deformation vibrations due to their molecular structures. These vibrations are excited by IR radiation of certain frequencies, especially in the wavelength range from 1 to 15 µm, and thereby they convert absorbed IR photons into heat.[10] Thus, in addition to the translational and rotational energy, they can absorb vibrational energy, E_{swing}, in the molecule according to the number and size of the resonance frequencies.[11]

$$E_{\text{kin}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{swing}}$$

Therefore, the polyatomic gases are considered the drivers of the GH effect and are referred to as GH gases. Among the GH gases, the atmospheric part of the water cycle provides the largest contribution to the GH effect because of the high concentration of water vapour in the atmosphere. In addition, the transformation heats have an effect of heat storage, cooling or heating:

Table 2: Energies per IR photon.

IR spectrum	Wavelength	Energy $\varepsilon = h\nu$
Far IR	15–6 µm	>1.2 meV
Mid IR	6–3 µm	>25 meV
Near IR	3–0.78 µm	>500 meV

$$\text{Heat of melting: } 6.0 \quad \text{kJ/mol}=62\,\text{meV/molecule}$$

$$\text{Heat of evaporation: } 40.7 \quad \text{kJ/mol}=422\,\text{meV/molecule}$$

4 The greenhouse effect – Thermodynamic consideration

The stored heat is distributed statistically in the form of a *Gaussian* bell curve over all gas molecules in the Earth's atmosphere. The temperature is always an average value. The measure for the maximum heat energy that can be absorbed by a gas is the specific or molar heat capacity Cp[9,12] (Table 3).

Table 3: Molar heat capacities of gases.

Element	Atomic weight	Cp (J/mol K)	Spec. Cp (J/g K)
a) Monoatomic gases			
Helium	4	20.76	5.190
Neon	20	20.80	1.030
Argon	40	20.96	0.524
Compound	**Molecular weight**	**Cp (J/mol K) spec.**	**Cp (J/g K)**
b) Biatomic gas molecules			
Hydrogen H_2	2	28.72	14.36
Nitrogen N_2	28	29.1	1.04
Oxygen O_2	32	29.2	0.912
Nitric oxide NO	30	30.27	1.009
Carbon monoxide CO	28	29.43	1.051
Compound	**Molecular weight**	**Cp (J/mol K) spec.**	**Cp (J/g K)**
c) Polyatomic gas molecules			
Carbon dioxide CO_2	44	37.2	0.846
Methane CH_4	16	35.4	2.21
Ammonia NH_3	17	35.02	1.56
Sulphur dioxide SO_2	64	39.94	0.624
Water vapour H_2O	18	33.4	1.85

Some of the tabulated values were measured at different temperature (O °C, 25 °C or without specifying a temperature). However, the T dependencies of values are small and do not change the gradations between the cases a, b and c. All values apply at normal pressure.

The differences between the molar heat capacities of mono-, di- and polyatomic gases in the atmosphere were related to the degrees of freedom of movement of the molecules.[13]

The Cp values for monatomic (Table 3a) and diatomic gases (Table 3b) are independent of the atomic or molar weights. The monatomic gases have only translational degrees of freedom to absorb energy. In the cases of diatomic, double- and triple-bonded O_2 or N_2 molecules, the degrees of freedom of rotation and of oscillation are added to those of translation. This leads to an increase in the heat capacity by about 40 % compared to the translational energy of monatomic gases. Their excitation requires higher temperatures or higher-energy radiation outside the IR range.

The heat capacities of polyatomic gases, H_2O and the trace gases such as CO_2, CH_4 and SO_2 are a further approx. 20 % greater than those of O_2 and N_2 molecules due to the excitation of valence and deformation vibrations in the molecules. These degrees of freedom are activated by IR photons.[14] Multiplied by the low concentration of trace gases, they cannot noticeably increase heat storage in the air. Only H_2O by its phase transformations is able to store great amounts of heat.

According to the values of the molar heat capacities of the gases, most of the energy in the atmosphere is stored as translational energy (motion of the gas molecules in space). The heat retention in the greenhouse Earth is caused by all gas components according to their molar heat capacities and concentrations in the atmosphere, i.e., mainly by nitrogen and oxygen. It is not permissible to exclusively assign the GH effect of 33° to water vapour, CO_2 and the other trace gases.

5 The radiation equilibrium

What would the amounts of energy in the atmosphere be? The enthalpy of the atmosphere has been estimated to be $\Delta H = 1.26 \times 10^{24}$ J. The energy of daily solar irradiation is 1.06×10^{22} J. This corresponds to 0.8 % of the stored energy.[15] For example, the global "energy production" of mankind, 80 % of which is fossil energy, was about 600×10^{18} J, in the year 2022,[16] which is 1.6×10^{18} J/day, a modest 1.5×10^{-4} % of daily solar irradiation. All values are medium, neglecting changes by solar parameters, weather, and others, as discussed in Dübal and Vahrenholt.[17]

To balance the radiation daily, the energy irradiated by the Sun in 12 h would have to be re-emitted mainly as IR radiation within 24 h. Apart from the reflection of visible radiation, almost half of the irradiated energy is converted into heat.

Within a space filled with gas, all molecules are in contact with each other via mutual collisions and exchange of energy. The thermodynamic laws do not allow for static behaviour of individual molecules or molecule types. Permanent hotspot molecules are not conceivable under the *Gaussian* bell curve of statistical energy distribution. The 2nd Law of Thermodynamics specifies the direction of heat flow: Heat distributes from hot to colder molecules. The Earth's atmospheric GH exists within the troposphere. According to the equation of state for ideal gases and the barometric altitude formula, temperature and pressure decrease with increasing altitude, to about – 50 °C up to an altitude of about 10 km.

Heat is bound to molecules as kinetic energy; molecules cannot leave the Earth because of the Gravitation Force. The exchange of energy between the Earth and the Universe takes place exclusively via electromagnetic radiation. Electromagnetic radiation is not subject to the 2nd Law of Thermodynamics.

The GH gases do not distinguish between solar IR radiation and Earth IR radiation. Since they absorb the solar IR radiation (see Table 1), the solid Earth surface is heated less, and consequently less heat can be transferred from the Earth surface to the air by convection. Part of the radiated energy is reflected as IR radiation from the Earth's surface back to the Universe. The energy of this re-radiation is absorbed by polyatomic gas molecules, especially CO_2 and H_2O, and re-radiated in all directions. The proportion of IR radiation in the direction of the Earth has so far been regarded as the reason for the increase in mean global surface temperature.

IR photons are absorbed by converting their energy into vibrational energy of the molecules. When they cool down, they emit the IR photons again. As a result of barometric air density graduation, one can assume that the radiation from the GH gas molecules in the direction of the Earth's surface is hindered by increasing density of "absorber molecules" in air. An analogous effect must occur for the IR re-radiation from the Earth: The range of IR photons in the direction of outer space – as the density of "absorbers" decreases – should be longer than that in the direction of Earth. With decreasing temperature corresponding to increasing height above the Earth's surface, the IR radiation emitted by the GH gas molecules shifts to longer and longer wavelengths. What would the effect of an increase in CO_2 concentration be? It increases the concentration of "absorber molecules" as well as "transmitter molecules" for both IR radiation and IR re-radiation.

It should also be possible to both generate and stop resonance oscillations in the GH gas molecules and convert them into photons by collisions with non-GH gas molecules of certain energy:

$$E_{\mathrm{trans}} \leftrightarrow E_{\mathrm{swing}} \leftrightarrow E_{\mathrm{phot}}$$

Thus, nothing stands in the way of heat exchange between nitrogen and oxygen molecules and the Universe as well. This part accounts for about 40 % of the molar heat capacity of the main components of the atmosphere (Table 3). In such a reversible process, the GH gas molecules would be able to convert heat stored in the atmosphere into IR radiation and vice versa. This view is closer to the experience from the thermodynamics of gases and more convincing than the specific position of the CO_2 molecule as an energy store postulated by official climate research.

Water vapour and carbon dioxide, as well as other trace gases, would then act as energy transmitters and IR emitters, without which the process of energy exchange between the Earth's atmosphere and the Universe, and vice versa, cannot take place.

6 Conclusions

The basic constituents of the atmosphere, nitrogen and oxygen, are the main contributors to heat storage in the Earth's GH. The gases known as GH gases – water vapour, carbon dioxide, methane, mainly – act with their molecular vibrational degrees of freedom as transmitters and emitters that regulate the energy flow between Earth and Universe, thanks to their property of converting heat into IR photons and vice versa. In a reversible exchange process, they can thus achieve great effects even at low concentrations.

According to the 2nd Law of Thermodynamics, heat is distributed from hot to colder molecules; there are no hotspots among molecules or types of molecules in the atmosphere. A special role of carbon dioxide cannot be confirmed. Only H_2O by its phase transformations is able to store great amounts of heat.

A number of questions remain unresolved and are probably not accessible experimentally. The degree of saturation and the residence time of heat in the GH gas molecules are unknown. With decreasing temperature corresponding to increasing height above the Earth's surface, the IR radiation emitted by the GH gas molecules shifts to longer and longer wavelengths. None of the transformations has to be complete, i.e., the wavelength of the IR quantum decreases with increasing height, the rest can remain as kinetic energy (heat). It is not possible to determine whether the energy radiated in and the energy radiated out per unit of time is equal in the sense of radiative equilibrium. This could result in an energy accumulation in the atmosphere over certain periods of time.

Even with constant solar and planetary parameters, the radiation balance does not appear to be equalised either daily or over the course of one or more years. Sometimes this occurs only over millennia. The Earth's greenhouse is working slowly, and the Mankind should be prepared for climate changes.

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