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Communication

On the role of trace gases in the Earth's radiation balance—Thermodynamic treatment

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Abstract: The role of trace gases in the storage of heat in the atmosphere of the Earth and in the exchange of energy between the atmosphere and outer space is discussed. The molar heat capacities of the trace gases water vapor, carbon dioxide and methane are only slightly higher than those of nitrogen and oxygen. The contribution of trace gases carbon dioxide and methane to heat storage is negligible. Water vapor, with its higher concentration and conversion energies, contributes significantly to the heat storage in the atmosphere. Most of the heat in the Earth's atmosphere is stored in nitrogen and oxygen, the main components of the atmosphere. The trace gases act as converters of infrared radiation into heat and vice versa. They are receivers and transmitters in the exchange of energy with outer space. The radiation towards space is favored compared to the reflection towards the surface of the Earth with increasing altitude by decreasing the density of the atmosphere and condensation of water vapor. Predictions of the development of the climate over a century by extrapolation are critically assessed.

Keywords: trace gases; carbon dioxide; water vapour; molar heat capacity; radiation balance; energy of translation; energy of vibration; heat-radiation transmitters

1. Initial situation

With the atmosphere, the surfaces of the continents, the ocean currents and the water cycle, the Earth's surface forms a kind of heat reservoir that provides a favourable climate. A temperature difference of about +15 °C near the Earth's surface and of −18 °C, measured by satellites, is known as the "greenhouse" effect. The greenhouse effect and the causes of its fluctuations are the subject of climate research. Weather and climate form a significant role due to numerous known and other unknown, mutually influencing factors that create a chaotic system whose development is not predictable. Climate predictions over a century have so far been based on largely empirical relationships, i.e., on observations over relatively short periods of time and their extrapolation.

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About half of the electromagnetic radiation of the Sun with ultraviolet (UV), visible (VIS) and infrared (IR) components reaches the Earth's surface. There, a part of surface heat transfers to the atmosphere due to heat conduction and convection. Another part is converted into IR radiation, and it occurs as Earth radiation in the IR radiation region [1]. The IR radiation from Earth is transmitted into the atmosphere, where it is absorbed mainly by water vapor, H_2O, and carbon dioxide, CO_2, the so-called trace gases (or greenhouse gases), and then radiated into all directions, i.e., towards the Earth's surface as well. This process has so far been considered a trigger of a heat build-up in the atmosphere [2].

1.1. The CO_2-T correlation and its uncertainties

According to indirect determination methods, the average global temperatures T were over 20 ℃ during periods of millions of years, and the CO_2 levels were in the range of up to a few 1000 Vppm. Periods with particularly high CO_2 levels and temperatures were times of intense development of new types of life [3,4]. For the time being, we are rather at the lower ends of global temperature and CO_2 scales; in this area, mankind has developed.

Current climate research is strongly oriented towards an empirical relationship between atmospheric CO_2 content and average global temperature. Since the middle of the 19th century, the CO_2 content increased from ca. 280 Vppm to 420 Vppm today. Over the same period, the average global temperature at the Earth's surface rose by about 1.2 degrees [5]. This period was accompanied by the industrial development of mankind on the basis of fossil fuels as energy resources [6]. However, the beginning of this period also coincided with the end of the Little Ice Age. The CO_2-T correlation of the preindustrial age has so far been excluded from considerations.

The concentration of CO_2 in the atmosphere has been measured on Mount Mauna Loa (Hawaii) since the year 1958. This location is at an active volcano far away from human CO_2 emissions. Peaks in the CO_2 concentration curve caused by this are corrected so that they are consistent with measurements from other CO_2 observatories. The CO_2 concentrations show regional deviations of up to ±25 ppm [7].

The increase of the global CO_2 concentration in the atmosphere is due to 96%–97% of natural origin. Only 3%–4% can be allocated to the production of energy and industrial products [8]. The following question remains unanswered: Is the rising CO_2 content of the atmosphere the cause of the temperature increase, or does an increased temperature cause the release of CO_2 from seawater, the CO_2 content of which is much higher than that in the atmosphere?

Measurements of the average global near-surface temperature have been known since 1880. This temperature is given as +15 ℃ to a tenth of a degree. There are legitimate doubts about this accuracy. Over time, the number of measuring stations has increased. An international study on measurements in the northern hemisphere of the Earth [9] shows that the number of measuring stations near cities was ten times greater than those in rural areas. This results in increased values for the average temperature. The temperature differences in the annual average for the atmosphere range from +26 °C at the equator to −35 °C at the poles, sometimes colder. In the "Greenhouse Earth" large temperature differences prevail at the same time of year regionally in different places and latitudes, at different times of the year, and at different times of the day. Unclear ocean and air currents can cause large temperature changes in short periods of time. The vertical T-drop within the troposphere reaches a value of about −50 °C up to its upper end (approx. 8–16 km altitude). Therefore, the calculation of a global average temperature seems to be physically nonsensical [10].

1.2. Global warming potential and radiative forcing of trace gases

The heat accumulation in the "Greenhouse Earth" is attributed to the trace gases H_2O, CO_2 and others (CH_4, O_3, N_2O, mainly) which due to their molecular structure are able to absorb IR radiation in the form of vibrations. The greatest impact, between 36% and 70% depending on climate zones and air temperatures, is based on water vapor, whose concentration among the trace gases is highest at 3% to 6% [11]. As a rule, however, its contribution to the greenhouse effect is not further evaluated, as the release of water vapor is independent of human activities.

The climate impact of the trace gases is weighted according to two variables:

1) The Global Warming Potential (GWP) of a gas is the measure of its contribution to the warming of the Earth's atmosphere usually over a period of time of 100 years (GWP 100) in relation to the effect of the same amount of CO_2 with GWP = 1. The proportion of scientific substance data in the GWP value is low. It is based on the evaluation of the IR absorption spectra. The water vapor, which absorbs the majority of IR radiation, is transparent to IR radiation in small spectral ranges only (water vapor window). The effects of trace gases are judged upon in accordance with their spectral shares in the water vapor window [12]. As a result of extensive calculations, it can be proven that a doubling of the concentration of the most effective trace gases CO_2, N_2O and CH_4 increases their effectiveness for IR absorption by only a few percent.

The proportion of knowledge in the GWP based on experience is a much more extensive value if future developments can be called "experience". This applies, for example, to the quantities in which individual substances will be produced in the future, emitted into the environment and reduced through environmental protection, including the residence times as a result of chemical degradation in the atmosphere. The large numerical values of the parameter GWP, such as for methane 28, nitrous oxide 298 and sulfur hexafluoride 22,800 [2], result from the chemical stability of the compounds as well as from their accumulation in the atmosphere. The GWP values are updated periodically [13].

2) The Radiative Forcing (RF in W/m^2) indicates how the concentration of a substance, starting from an existing background concentration, increases the heat input. Radiative forcing is a measure of the effect of incident solar radiation on warming of the Earth's atmosphere. Gases intensify the effect; aerosols weaken it. For example, in 2019, the IPCC [14] gave the numerical

value of radiative forcing compared to the reference year 1850: After deducting cooling effects due to aerosols, it amounts to 2.72 W/m^2. The contributions of the individual trace gases amount to: CO_2 2.16, CH_4 0.54, O_3 0.47, HCC 0.41, N_2O 0.21 (all data in W/m^2). The RF data are empirically determined comparative values that are reassessed periodically.

The climate forecasts calculated according to various scenarios over a century are based on those two complex and largely empirical parameters by the inclusion of solar and planetary influencing variables.

2. Task definition

The radiation balance between the Sun and the Earth, and thus the climate, is determined by the storage of electromagnetic radiation of the Sun and by the release of it into space. In between lies the transformation of electromagnetic radiation from the sun into heat from solid and liquid surfaces and the gaseous atmosphere and vice versa.

The Earth's surface is neither a "greenhouse" nor a thermostat. The atmosphere is not a closed system in the sense of thermodynamics. The radiation balance between the Earth and the Sun is based on a so-called steady-state equilibrium. The daily inflow is not equal to the daily return flow. As with the water cycle, the inflow is sometimes greater or smaller than the outflow or evaporation losses. An approximate flow equilibrium can only be expected over longer periods of time. Irradiation is influenced, for example, by clouds, changing albedo, etc., while the return radiation (backflow) is influenced by changing humidity, concentration of trace gases and dust, increasing sealing of ground by streets and buildings, or changing vegetation and other factors. What can we contribute to quantifying the balance of energy flows and energy storage between the atmosphere and space in order to get a better sense of the influence of nature and humans on climate change?

2.1. Flows and storage of energy

Of the solar constant, 1361 W/m^2 in space near the Earth, an average of 343 W/m^2 remains as energy flux density at the Earth's surface during day and night [14]. From this follows the daily solar radiation on the entire Earth (cf. **Table 1**, line 2). This is the maximum, 0.8%, of all the energy stored in the atmosphere (**Table 1**, line 1), as calculated from the mass of air in the atmosphere and its specific heat capacity (Section 2.2). The energy production of mankind in 2022 amounted to approx. 6×10^{20} Joule [15]; this is calculated per day (**Table 1**, line 3), 1.5×10^{-4}% of the daily solar radiation (**Table 1**, line 2). The very unevenly distributed heat flow from the Earth's mantle as a result of the decay of radioactive isotopes and chemical reaction heats amounts on average to 87 mW/m^2 [16]. It is, therefore, in the order of magnitude of human energy production.

Changes in the global climate require orders of magnitude higher energy flows than supplied by mankind. Human activity is probably able to influence local and regional climate. Examples are the well-known heat islands in the form of cities or the effect of vegetation and water surfaces on the local climate.

Table 1. Flows of energy.

Energy stored in the atmosphere	1.26×10^{24} Joule
Daily exposure to Sun radiation	1.06×10^{22} Joule
Daily energy production of mankind (in 2022)	1.6×10^{18} Joule
Daily heat flow from the Earth's interior	3.8×10^{18} Joule

2.2. Molar heat capacities of gases in the atmosphere

The molar heat capacity Cp [17] indicates the maximum amount of heat that can be absorbed by one mol of a gas. These experimentally determined energy values are independent of quality and the amount of stimulated degrees of freedom of the individual molecules, which are anyway unknown.

The Cp values of monoatomic gases (see **Table 2**) and diatomic gases (see **Table 2**) are the same regardless of their atomic or molecular weights, as already reported in [18,19]. Monoatomic gases have only degrees of freedom of translation for the absorption of energy. In the case of the diatomic gases N_2 and O_2 with double and triple bonds, respectively, degrees of freedom of rotation are added, which increases the values of the molar heat capacities by approx. 40% compared to those of monoatomic gases.

Table 2. Molar heat capacities of gases.

a) Monoatomic gases		
Element	Atomic weight	Cp (J/mol K)
Helium	4	20.76
Neon	20	20.80
Argon	40	20.96
Xenon	131	20.96
b) Diatomic gases		
Compound	Molecular weight	Cp (J/mol K)
Hydrogen H_2	2	28.72
Nitrogen N_2	28	29.1
Oxygen O_2	32	29.2
Nitric oxide NO	30	30.27
Carbon monoxide CO	28	29.43
0,78 N_2, 0,21 O_2, 0,01 Ar	28.96	28.96
c) Triatomic and polyatomic gases		
Compound	Molecular weight	Cp (J/mol K)
Water vapour H_2O	18	33.4
Carbon dioxide CO_2	44	37.2
Methane CH_4	16	35.4
Ammonia NH_3	14	35.02
Ethane C_2H_6	30	50.01
Propane C_3H_8	44	73.5

The heat capacities of triatomic gases, known as trace gases, are by approx. 20% greater than those of diatomic gases. Due to the activation of valence and deformation vibrations of the molecules [20,21], additional energy is absorbed. According to the values of the heat capacities, however, it is not possible to distinguish how many of the degrees of freedom are excited at the same time.

Multiplied by the low concentrations of the trace gases, less than 0.1% by volume, they cannot contribute significantly to heat storage in the atmosphere. Only H_2O in the form of vapor with concentrations in the percent region of the atmosphere and also due to its phase transformation heats contributes significantly to heat storage.

The main amount of heat in the atmosphere is the kinetic energy E_{trans} of all gas molecules, i.e., mainly N_2 and O_2, stored in the atmosphere. The greenhouse effect is, therefore, distributed among all of the gases in the atmosphere according to their concentration fractions.

The values as reported in [17] were measured at normal pressure and at different temperatures (0 °C, 25 °C or given without an indication of temperature). The Cp values increase slightly with temperature; however, this does not affect the gradations between cases a, b and c.

The examples of ethane and propane show that the molar heat values increase with the number of bonds, i.e., the number of degrees of freedom of the vibrations, by factors that are almost comparable to the number of additional vibrations.

2.3. Heat exchange between Earth and space

Heat in the atmosphere is the kinetic energy, E_{kin}, of all of the gas molecules. It enters the gas molecules through absorption of electromagnetic radiation from the Sun, where it is converted into rotational, E_{rot}, and vibrational energy, E_{swing}, and, through collision mechanisms, as translational energy, E_{trans}, of all molecules in the entire atmosphere:

$$E_{kin} = E_{trans} + E_{rot} + E_{swing} \tag{1}$$

In a space filled with gas, all molecules are constantly in contact with each other due to mutual collisions. This distributes the energy in the form of a Gaussian bell curve. The thermodynamic laws do not allow for permanent hotspots among the molecules. The 2nd Law of Thermodynamics determines the direction of the heat flow from the “warmer” molecules to the “colder” ones.

The energy bound to gas molecules cannot be released into space due to the gravitational force to which the molecules are subject. This can only take place in the form of electromagnetic radiation (IR photons). The trace gases function as energy transducers:

$$E_{trans} \leftrightarrow E_{swing} \leftrightarrow E_{phot} \tag{2}$$

The vibrational energy of the trace gas molecules excited by absorbed IR photons is not only emitted again as an IR photon, but it is also partly passed on to the main components of the atmosphere via collisions. Conversely, thermal energy from the atmosphere can also be converted into vibrations of the trace gas molecules and finally into IR photons. Otherwise, the heat stored in the N_2 and O_2 molecules of the atmosphere would not be able to flow out into space.

In the discussion of IR back radiation to the Earth as the cause of heat accumulation, no difference in radiation intensities in all directions has been seen. With increasing altitude, however, the density of the atmosphere according to the barometric formula and, thus, also to the number of IR-absorbing CO_2 molecules decreases: up to 5 km height to about half, up to 10 km to a quarter. This situation results in a "mean free path length" of the IR photons in the direction of space that will always be greater than in the direction of the Earth's surface. This situation will remain the same even if the CO_2 concentration doubles. With increasing altitude and decreasing temperature, condensation also eliminates water vapor as an IR absorber. Therefore, the exit for IR radiation in the direction of space remains open for Earth radiation.

In the previous remarks, the function of the trace gases as converters and transmitters of energy into space is presumed to explain the energy exchange between the Earth's atmosphere and space on the basis of thermodynamics. According to complicated calculations [22], the share of radiation emitted into space in the real radiation of the Earth's atmosphere originates both from the surface and from the lower layers of the troposphere.

How the uninterrupted exchange of energy according to Equation (2) takes place in detail has not yet been investigated. How long is a "mean free path" of IR photons that could be formulated for the purpose of energy exchange by collision? What would the residence time of IR quanta in the molecules be until the absorbed energy is released as IR photons or as kinetic energy to other molecules?

A qualitative explanation of the steps of energy conversions between electromagnetic radiation and the molecules in the atmosphere has already been given by the Perrin-Jablonski diagram [23,24], which was originally formulated for UV/VIS spectroscopy. However, the discussed energy conversions are also applicable to collisions between molecules with a transfer of kinetic energy into photons or vice versa.

3. Conclusions

A comparison of the molar heat capacities of the gases proves that the heat in the Earth's atmosphere is stored in its main components, i.e., nitrogen and oxygen. The so-called greenhouse gases carbon dioxide, methane, and others contribute to heat storage according to their molar concentrations. Only the greenhouse gas water vapor, thanks to its higher concentration and its conversion energies, contributes significantly to heat storage in the atmosphere.

With the vibrational degrees of freedom of their molecules, trace gases act as converters of IR radiation into heat and vice versa. Therefore, they act as receivers and transmitters in the exchange of energy with space. Radiation towards space is favored over back radiation towards the Earth's surface by the decreasing density of the atmosphere and the condensation of water vapor as the temperature decreases with altitude. There are gaps in quantitative knowledge about the conversion of IR photons into heat and vice versa as well as about the degree of saturation of molecular vibrations, the residence times of the energy in the molecule, the conversion of translational energy into vibrational energy and the release of IR photons through collisions.

The radiation equilibrium between solar radiation and Earth radiation is discussed as a stationary state, without equalization over periods of days or even several years. Temporary climate changes over longer periods of time in limited regions, including those with significant stress factors for the ecosphere, must be expected.

Man-made energy flows are orders of magnitude smaller than natural energy flows. Due to numerous interacting factors, weather and climate are chaotic processes that cannot be predicted. Predicting climate change by extrapolation appears to be very speculative.

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