

# On the Physical Chemistry of the Greenhouse Effect

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## Abstract

In the present, a looming catastrophe is feared due to climate change. People are looking for ways to prevent the anticipated warming of the climate. The primary approach promoted is the reduction of carbon dioxide, CO<sub>2</sub>, emissions from human activities. This would require a major transformation of existing ways of life and production. There are legitimate doubts about the reasoning that human-generated CO<sub>2</sub> is the main cause of global warming. We examined the physico-chemical properties of CO<sub>2</sub> and the so-called greenhouse gases to determine their influence on the heat exchange between the Earth's atmosphere and space. Their role as converters of infrared radiation from the sun into heat is a fact; conversely, they are equally indispensable as transmitters of heat from the Earth's atmosphere into infrared radiation to balance the Earth's radiation equilibrium. The balances of CO<sub>2</sub> exchange with the plant world and the oceans, in comparison with anthropogenic emissions, are critically assessed. The anthropogenic energy flow is four orders of magnitude smaller than that of daily solar radiation. The planetary regulatory system of ice ages and warm periods, which has been operating for hundreds of thousands of years, is being discussed. It must be taken into account in the climate discussion of the past centuries. The CO<sub>2</sub> as the driving force in the CO<sub>2</sub>-T correlation is being questioned.

**Keywords:** Greenhouse gases, heat capacity, energy transmitters and emitters, radiation balance, exchange of energy and CO<sub>2</sub>

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## 1. Introduction

No other chemical compound is currently attributed with as much harmful impact as carbon dioxide. The basis of climate predictions is the correlation between CO<sub>2</sub> concentration and global temperature rise, which has been observed since the beginning of the Industrial Revolution around 1850 (IPCC 2014 & WMO 2024). During this period, CO<sub>2</sub> levels increased from about 280 to 480 vppm (volume parts per million). By extrapolating this relationship, a climate catastrophe is predicted. Climate research recognizes numerous sources and sinks for CO<sub>2</sub> as well as amplifications or reductions of solar radiation. Some of them can be quantified, others cannot, and additional as -yet- unknown influences are suspected. Climate predictions are evaluated more or less critically. The sensitivity of the climate to anthropogenic CO<sub>2</sub> is excluded from any doubt by modern climate research. The significant climate impact of water in its three states of matter in the atmosphere usually goes unmentioned, because it cannot be influenced by humans. However, a good correlation does not necessarily imply causality. Causal relationships could only be deduced from results of the exact natural sciences. Studies of the physico-chemical properties of CO<sub>2</sub>, which would explain its high climate sensitivity, have so far been patchy; existing partial results tend to contradict this.

The Swedish chemist and physicist Svante Arrhenius was the first to suspect an effect of atmospheric CO<sub>2</sub> levels on global warming (Arrhenius 1896). He assumed that the ice ages were primarily controlled by CO<sub>2</sub> concentrations. No mention is made of measurements by the Swiss scientist N. de Saussure (De Saussure 1830), which he carried out in the city of Geneva and its surroundings before the beginning of the Industrial Revolution, from 1827 to 1829. The numerous measurements, day and night, at various wind speeds, before and after rainfall, resulted in atmospheric CO<sub>2</sub> levels of 400 to 500 ppm (Marten 2025). CO<sub>2</sub> levels have been measured automatically since 1960 at a measuring station on the Mauna Loa volcano of Hawaii; previous measurements were taken from ice cores (Grassl 1993). The accuracy of recent CO<sub>2</sub> measurements and global temperature reported by climate researchers is rightly criticized: CO<sub>2</sub> is distributed very differently regionally. Estimating a global temperature to within tenths of a degree is physically questionable given the enormous temperature differences that exist on planet Earth simultaneously regionally distributed and within an annual cycle (Ullmann *et al.* 2024).

Atmosphere CO<sub>2</sub> concentrations have a long history. In the Earth's prehistoric era, which was characterized by intense volcanism, the atmosphere likely consisted of a high proportion of CO<sub>2</sub>. At the time of the dinosaurs

(approx. 200 to 100 million years ago), its concentration was still a few thousand vppm (Rae *et al.* 2021 & Hönisch *et al.* 2023). During the Pleistocene (ca. 1 million years ago), CO<sub>2</sub> levels were about 180 vppm, and during the interglacial periods, approx. 300 vppm. The difference between ice ages and interglacial periods is explained by outgassing from the oceans, which can occur with a delay of centuries.

## 2. Physico-chemical Properties of CO<sub>2</sub>

### 2.1 Interaction of photons with gas molecules

According to quantum theory, during absorption and emission of a photon in a molecule, the entire energy of the quantum,  $\varepsilon = hv$ , is transferred or released to the molecule. The molecule receives an energy pulse of the same magnitude in the direction of the incident quantum upon absorption, and in the opposite direction upon emission (Einstein 1917). The fundamentals of photon absorption in atmospheric gas molecules describe which photon wavelengths resonate with which rotational and vibrational degrees of freedom of the molecules (Schrader 1995 & Hug 2000).

As mentined already, heat is the kinetic energy of gas molecules. The molecules are set in motion by collisions with other gas molecules, by contact with the heated Earth's surface, or by radiation. The second law of thermodynamics determines the direction of heat flow from warmer to colder molecules. This results in a dispersion of energy, which leads to the *Gaussian* Bell curve of temperature distribution among all molecules in the atmosphere. Heat from gas molecules is composed of translational, rotational, and vibrational energy, depending on the structure of the molecules. All molecules of the air absorb kinetic energy,  $E = mv^2$ , with doubly (O<sub>2</sub>) and triply bonded (N<sub>2</sub>) molecules additionally absorbing rotational energy, and multiply bonded molecules further additionally absorbing vibrational energy of the bonds:

$$E_{kin} = E_{trans} + E_{rot} + E_{vibr}. \quad (1)$$

As a rule, vibrational energy  $E_{vibr}$  is labeled as  $E_{swing}$  - matching standard physics notation.

Thermal energy corresponds to the energy of photons in the infrared range of electromagnetic radiation. Only tri- and polyatomic gases possess the ability to absorb radiation in the IR range, which led to the designation "greenhouse gases".

### 2.2 Greenhouse gases as heat storage medium

The measure of the maximum absorbable heat energy of a gas is its specific or molar heat capacity, Cp. It has been recorded in tables for decades (Kortüm 1981 & WIKIBOOKS 2023). If one compares the Cp values of monatomic gases with those of diatomic and triatomic gases found in the atmosphere, the Cp values for monatomic gases - helium, neon, argon - and diatomic ones - N<sub>2</sub>, O<sub>2</sub>, NO, CO - are the same, regardless of their atomic or molecular weight (Table 1).

**Table 1.** Molar heat capacities of gases.

<i>a) Monoatomic gases</i>		
Element	Atomic weight	Cp (J/mol K)
Helium	4	20,76
Neon	20	20,80
Argon	40	20,96
<i>b) Diatomic gases</i>		
Compound	Molecular weight	Cp (J/mol K)
Hydrogen H <sub>2</sub>	2	28,72
Nitrogen N <sub>2</sub>	28	29,1
Oxygen O <sub>2</sub>	32	29,2
Nitric oxide NO	30	30,27
Carbon monoxide CO	28	29,43
Air: 0,78N <sub>2</sub> , 0,21O <sub>2</sub> , 0,01Ar	28,96	28,96
<i>c) Tri- and polyatomic gases</i>		
Compound	Molecular weight	Cp (J/mol K)
Water vapour H <sub>2</sub> O	18	33,4
Carbon dioxide CO <sub>2</sub>	44	37,2
Methane CH <sub>4</sub>	16	35,4
Ammonia NH <sub>3</sub>	17	35,02
Ethane C <sub>2</sub> H <sub>6</sub>	30	50,01
Propane C <sub>3</sub> H <sub>8</sub>	44	73,5

Diatomic gases have a heat capacity about 40 % higher than that of monatomic gases. The heat capacity of air corresponds to that of its diatomic main components N<sub>2</sub> and O<sub>2</sub>.

The heat capacities of triatomic gases such as H<sub>2</sub>O, and trace gases CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and SO<sub>2</sub> are approx. 20 % higher than those of diatomic gases (Ullmann *et al.* 2023). The increase in heat capacity in this order is explained by the larger number of energy-absorbing degrees of freedom according to equation (1). Monatomic gases possess only translational degrees of freedom for absorbing energy. In the case of diatomic, doubly- or triple-bonded O<sub>2</sub> and N<sub>2</sub> molecules, rotational and oscillatory degrees of freedom are added to the translational degrees of freedom. However, their excitation requires higher-energy radiation outside the IR range. Tri- and polyatomic gases can absorb further energy and convert it into heat by exciting stretching and deformation vibrations with IR photons.

The molar heat capacities of gases show that the majority of the energy in the atmosphere is translational energy. The heat in the greenhouse Earth is stored by all gas components according to their molar heat capacities multiplied with their concentrations in the atmosphere. The heat is located primarily in its main components, nitrogen and oxygen. Viewing the CO<sub>2</sub> molecule as an energy storage medium cannot be justified based on the measured molar heat values. Only water vapor can make a significant contribution at the appropriate concentration and additionally taking into account the phase transition enthalpies. The concentration of water vapor - up to approx. 6 % in the atmosphere - cannot be influenced by humans. Therefore, CO<sub>2</sub> remains as the molecule with the second highest concentration among greenhouse gases at about 0.04 vppm and a human-generated share as the main culprit for global warming.

### 2.3 Greenhouse gases as converters between electromagnetic radiation and heat

In climate research, the role of greenhouse gases is characterized by two properties: Global Warming Potential (GWP) and Radiative Forcing (RF). Both quantities are empirical values based on experience and estimation. Climate forecasts calculated over a century according to different scenarios are based on these two complex empirical parameters, which are periodically reassessed. The GWP100 value is intended to indicate the contribution of a gas to the warming of the Earth's atmosphere over the next hundred years in relation to the same amount of CO<sub>2</sub>. In doing so, future developments in production, emission, accumulation, and depletion must be taken into account.

The value of Radiative Forcing (RF in W/m<sup>2</sup>) is intended to indicate how the concentration increase of a substance from anthropogenic sources, starting from an existing natural background concentration, increases the heat input into the atmosphere. The RF quantity is also determined empirically and periodically reassessed. It is

critical to note that anthropogenic sources, or the green energy sources recommended as substitutes, can be easily evaluated subjectively regarding their CO<sub>2</sub> balances. Natural sources of CO<sub>2</sub> and methane can also only be determined with great uncertainty, as shown in Section 3. Empirical climate research attributes the effect of greenhouse gases solely to the input of heat into the atmosphere, whereas from a physical-thermodynamic perspective, they are equally responsible for the heat release from the atmosphere into space.

The heat energy bound to gas molecules cannot be released into space due to the force of gravity to which the molecules are subject. This can only occur in the form of electromagnetic radiation (IR photons). For this to happen, the heat energy of the atmosphere must be converted through collisions into vibrations of the greenhouse gas molecules and ultimately into IR photons, as shown in equation (2):

$$E_{trans} \leftrightarrow E_{vibr} \leftrightarrow E_{phot} \quad (2)$$

Water vapor and carbon dioxide, as well as other trace gases, would act as transmitters and photon emitters, without which the process of energy exchange between the Earth's atmosphere and space would not be possible in both directions. Only in this function can trace gases have a significant effect, even in low concentrations (Hönisch *et al.*2023).

Whether this energy conversion can be fully reversible would depend on the residence time of the photon energy in the molecule. So far little is known about residence times. Greenhouse gases absorb a portion of the IR radiation from the sun, thus generating the life-sustaining greenhouse effect in the Earth's atmosphere. The energy radiated in the IR range by the heated Earth's surface is also absorbed by greenhouse gases. The subsequent radiation is re-radiated in all spatial directions. The assumption is that the same radiation intensities are radiated both toward space and back to Earth, which according to the opinion of climate researchers should lead to a heat build-up near the Earth's surface.

However, with increasing altitude, the density of the atmosphere decreases according to the barometric altitude formula, and thus also decreases the number of IR-absorbing CO<sub>2</sub> molecules. With increasing altitude and decreasing temperature, water vapor also ceases to act as an IR absorber due to condensation. As a consequence of this, it follows, the exit for the IR radiation toward space thus remains open for Earth's radiation. For the absorption of electromagnetic radiation of a certain wavelength by absorbing molecules, the following relationship applies:

$$\log(I_0/I_1) = \epsilon c d \quad (3)$$

$\epsilon$  - absorption coefficient,  $c$  - molar concentration,  $d$  - layer thickness.

The intensity of irradiation  $I_0$  to the intensity  $I_1$  after that, the layer thickness  $d$ , and, thus, the absorbed energy, increases logarithmically with concentration. In the case of CO<sub>2</sub> in the atmosphere, this relationship must be considered in a differentiated manner: In the main absorption range, the 15- $\mu$ m-band, saturation already occurs after a small layer thickness at high absorption coefficients. In the adjacent regions of shorter and longer wavelengths, the layer remains permeable at low energy absorption coefficients. Thus, even with saturation in one part of the spectrum, there is still permeability for other IR wavelengths with low energy input.

### 3. Balances of CO<sub>2</sub> and Energy at the Earth's Surface

#### 3.1 CO<sub>2</sub> emissions and exchange processes

Carbon dioxide is subject to exchange processes between the hydrosphere, the atmosphere, and the living and fossil biospheres. These exchange processes lead to a fractionation between C<sup>13</sup>-CO<sub>2</sub> and C<sup>12</sup>-CO<sub>2</sub>, with the lighter C<sup>12</sup>-CO<sub>2</sub> is preferentially released from the oceans and also preferentially absorbed into the living biosphere. The gradation of the concentration ratio of these isotopes has been demonstrated; it is present in the least amount in fossil biomass (Koutsyiannis 2024). Estimates of annual CO<sub>2</sub> emissions and exchange quantities of the year 2021 can be found in Table 2 (IPCC 2021).

**Table 2.** Comparison of CO<sub>2</sub> exchange amounts.  
 (t C/a - tonnes of carbon per annum.  
 One ton of C corresponds to 3.67 tons of CO<sub>2</sub>.)

Emission and exchange of CO <sub>2</sub>	in t C/a
(1) Anthropogenic emissions	9,4 x 10 <sup>9</sup>
(2) Land use	1,6 x 10 <sup>9</sup>
(3) Atmosphere → Biosphere	-142 x 10 <sup>9</sup>
(4) Biosphere → Atmosphere	137 x 10 <sup>9</sup>
(5) Atmosphere → Oceans	- 80 x 10 <sup>9</sup>
(6) Oceans → Atmosphere	78 x 10 <sup>9</sup>
(7) Emissions from volcanoes	> 0,1 x 10 <sup>9</sup>
CO <sub>2</sub> -Inventories of the spheres	in t C
(8) Hydrosphere	37 000 x 10 <sup>9</sup>
(9) Atmosphere *	< 120 x 10 <sup>9</sup>

\* at 480 Vppm CO<sub>2</sub> content, (Ullmann *et al.*, this paper)

Extensive studies (Resplandy *et al.* 2018, Friedlingstein 2019 & IPCC 2021) showed the difficulties of quantifying the contributions of individual sources and sinks. The amounts vary like crop yields from year to year.

The majority of anthropogenic annual CO<sub>2</sub> emissions come from energy production (1), still more than 80 % based on fossil fuels, and land use (2), approximately 3 %. The contribution of volcanoes (7) fluctuates widely and has likely been underestimated. Annual anthropogenic and volcanic CO<sub>2</sub> emissions are significantly smaller than the exchange processes between the atmosphere and the biosphere (3), (4) or the oceans (5), (6), but the differences between absorption and emission must be taken into account. Little is known about the time constants in this carbon cycle. Doubts about the accuracy of such estimates are justified, with the exception of the data for (1) and (9).

Oceans and inland waters, with their vast inventory of CO<sub>2</sub> and their more than 70 % share of the Earth's surface, play an important role in the exchange with the atmosphere. Mixing processes of the air with the moving water surface of the oceans play a role in balancing the CO<sub>2</sub> concentration in the atmosphere and the ocean. The transport of CO<sub>2</sub> to deeper water layers or from them to the surface proceeds through global ocean currents, but also through the precipitation or dissolution of solid carbonates, all of which are time-consuming processes (Resplandy *et al.* 2018).

Regardless of all discussions about these exchange processes, the question of the driving force in the observed CO<sub>2</sub>-T correlation remains open. It is blamed on anthropogenic CO<sub>2</sub> by modern climate researchers, although this contributes a comparatively small amount.

### 3.2 Radiative equilibrium and climate

Radiative equilibrium means that the magnitudes of energy flows from space to Earth and back are balanced. This is determined by comparing the average daily energy flows of solar radiation, geothermal energy, and human energy production (Table 3). Human energy flow is by four orders of magnitude lower than sunlight exposure. Human “energy production” is comparable to the small energy flow from the Earth's interior through radioactivity and reaction heat (Ullmann *et al.* 2025).

**Table 3.** Comparison of natural and anthropogenic energy flows.

Energy flows	Joule	Source
Daily sunlight exposure	1,06 × 10 <sup>22</sup>	(IPCC2021, Trenberth 2009)
Anthropogen. energy production, daily	1,6 × 10 <sup>18</sup>	(Statista 2024)
Daily heat flux from the Earth's interior	3,8 × 10 <sup>18</sup>	(Pollack 1993)
Energy stored in the atmosphere	1,26 × 10 <sup>24</sup>	(Ullmann 2025)

Radiation equilibrium is therefore essentially established by solar radiation and the reflection of the incoming solar radiation from the Earth's surface and the atmosphere. The balance between solar radiation and Earth's

reflection is understood here as a so-called flow equilibrium, comparable to a lake that is temporarily filled by stronger inflow, but also temporarily empties more rapidly. An equilibrium within days or years would not be expected. There are too many periodic events (solar activity, pole shifts, ocean currents, etc.) or random events (volcanism, particle radiation, cloud formation, dust emissions *etc.*) for this to happen. Climate changes over longer periods in limited regions, including those with significant stress factors for the ecosphere, are therefore to be expected. Due to the large number of influences, the climate is described as a chaotic process that cannot be predicted or extrapolated.

#### 4. The Climate History of the Earth

Current discussions about the Earth's climate are limited to roughly the past 200 years and 100 years of the future. Attempts to create a climate model based on this period, valid until the end of our century, have failed. Looking back at the history of our planet's climate could provide new explanations. The analysis of ice cores from Antarctica (Petit *et al.* 1999) and Greenland (Dansgaard *et al.* 1992) yielded results going back 800 000 and 500 000 years, respectively. In this process, temperatures as well as CO<sub>2</sub> and CH<sub>4</sub> levels were recorded through gas analyses over the course of multiple ice ages and warm periods. A periodic alternation between warm and ice ages in cycles of approx. 100 000 years has been observed. One hypothesis attributes this to periodic changes in the gravitational relationships within the planetary system, with changes in the eccentricity of Earth's orbit and shifts in the tilt of Earth's axis, the so-called Milanković cycles (Petrovic *et al.* 2009). In addition, the Earth's climate is influenced by a number of geophysical and cosmic cycles (Bülow 2020).

Ice ages last significantly longer than warm periods. The rise from the temperature minimum of the ice age to the new warm period occurs within a few thousand years, whereas the transition to a new ice age happens much more slowly, over tens of thousands of years. Similar to the temperature-time patterns, CO<sub>2</sub> and CH<sub>4</sub> concentrations behaved in the same way. Peak values during warm periods reach up to 300 ppm, and minimum values around 190 ppm CO<sub>2</sub> during cold periods were analysed (Lindzen *et al.* 2025). A more detailed analysis of the last 11 000 years, starting after the last ice age, reveals that around 8 000 years ago, the maximum temperature of the current warm period had already been surpassed, and the slow decline toward a new ice age had begun. Peaks downward and upward of up to 2 °C for several decades occurred multiple times. The Little Ice Age of the Middle Ages in Europe is an example of this.

Some phenomena of this extraterrestrial regulatory mechanism of Earth's climate could be of interest for clarifying the mechanisms of climate change. The authors of (Petit *et al.* 1999) claim to have found that the CO<sub>2</sub> peaks lagged behind the temperature peaks by several thousand years. They did not provide an explanation for this. This would mean that the temperature of the ocean is the driving force, which, when increased, releases more CO<sub>2</sub> from the seawater. With this insight, the framework of current climate research would be turned upside down.

What is the mechanism for the slower transition from warm periods to low temperatures? It could be the significantly slower change in ocean water temperature due to its high heat capacity compared to that of the atmosphere, as well as the high energy transformations occurring in the water cycle. Added to this would be the incoming and reflected solar radiation with a changed *Albedo*. Changes in CO<sub>2</sub> concentrations in the range of 100 ppm could rather be seen as a secondary effect and not as a driving force.

#### Conclusions

The observed relationship between CO<sub>2</sub> levels and global temperature rise in the Earth's atmosphere since the beginning of the Industrial Revolution cannot be confirmed as a causal relationship by physical and chemical results. Water vapor has the highest concentration among the IR-absorbing greenhouse gases. The temperature can be assumed to be the driving force for the increase in CO<sub>2</sub> concentration. In contrast, climate research currently focuses on human-made CO<sub>2</sub>. The heat of gas molecules is composed - depending on the structure of the molecules - of translational, rotational, and vibrational energy. The heat in the "Greenhouse Earth" is stored by all gas components according to their molar heat capacities and concentrations in the atmosphere, thus being located primarily in its main components, nitrogen and oxygen. Viewing the CO<sub>2</sub> molecule as an energy storage medium cannot be justified by the molar heat values. Only water vapor can make a significant contribution at appropriate concentrations and taking into account the transformation enthalpies of water.

Greenhouse gases are considered as transmitters and transducers between translational, rotational, and vibrational energy, corresponding heat on the one hand, and photon energy on the other, without which the process of energy exchange between the Earth's atmosphere and Space cannot proceed in both directions.

The CO<sub>2</sub> exchange between the atmosphere and the plant world, as well as the oceans, is estimated to be several times greater than annual anthropogenic emissions. The oceans, with their vast inventory of CO<sub>2</sub>, play an important role in this exchange. The ocean has so far been predominantly assumed to be a CO<sub>2</sub> sink; however, it should also be a CO<sub>2</sub> source with rising temperatures.

Human “energy production” is four orders of magnitude smaller than solar radiation and comparable to the small energy flow from the Earth's interior. The Earth's “greenhouse” atmosphere is an open system; the existing flow equilibrium establishes the climate changes.

The history of the Earth's climate should be included in the climate discussion. A planetary regulatory system with ice ages and warm periods occurring in cycles of a hundred thousand years overrides short-term climate forecasts, so the next ice age is certain to come.

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