Greenhouse effect

Aims of the experiment

- To understand the physical principles of the greenhouse effect
- To compare the greenhouse effect of various gases based on their absorption properties
- To understand the principles of IR absorption in terms of quantum chemistry

Principles

The greenhouse effect was discovered in 1824 by Joseph Fourier. He recognised that the Earth was warmer than it should be based on the radiation laws known at that time. He attributed this to the observation, that the Earth's atmosphere is transparent to visible light, but largely opaque to infra-red radiation. This, in his opinion, leads to heat being stored at ground level. Even at that time, he pointed out the possibility of human influence on the Earth's climate. Then in 1862, John Tyndall identified water vapour and CO_2 as the gases mainly responsible for the greenhouse effect. The first quantitative calculations of the greenhouse effect of CO_2 were performed in 1896 by Svante Arrhenius. The global warming caused by CO_2 emissions from humans was not yet seen by Arrhenius as a problem. Instead, he hoped for better climate conditions and higher harvest yields.

In 1958, Charles D. Keeling began systematic research on the anthropogenic greenhouse effect. Through Keeling numerous stations were set up for monitoring carbon dioxide levels in the atmosphere. The Keeling Curve measures the progressive CO_2 concentration since 1958. Keeling proved that the concentration of CO_2 in the atmosphere is increased through human activities.

The negative consequences of a possible global warming caused by greenhouse gas emissions was not recognised until the second half of the 20th century. In 1988, the United Nations founded the IPCC (International Panel on Climate Change) with the aim of collecting the results of research from all leading climate researchers world-wide to provide recommendations for policies. Meanwhile, the IPCC considers it extremely likely that human influence has been the main cause of the global warming observed since the middle of the 20th century. The negative consequences of global warming that are predicted by the IPCC are the decline in ice volumes, particularly in the Arctic, the increase in ocean levels as well as changes in the global water cycle and the increase in extreme weather events associated with this, such as heavy rainfall and drought.

The influence of the greenhouse effect on the average temperature of the Earth's surface can be explained through the balance between incoming and emitted radiation. Solids and liquids with a temperature greater than 0 Kelvin emit heat radiation, the spectrum of which depends only on the temperature. The spectrum resembles a distorted Gaussian bell curve, whose maximum is shifted towards shorter wavelengths with an increase in temperature (Planck distribution curve). The radiation emitted from a body therefore becomes richer in energy with an increase in temperature.

The Sun has a temperature of about 5,777 K. Its radiation maximum corresponds to the light that is visible to us. The effective radiation power acting on a body per surface area decreases with the square of the distance to the Sun. The average radiation power density reaching the spherical Earth's surface is 342 W/m^2. A proportion of this is reflected by clouds, aerosols and by the Earth's surface itself. A large proportion of the UV and infra-red radiation is already absorbed in the upper atmosphere by the ozone layer and by water vapour and emitted again. On the other hand, the atmosphere is largely transparent to visible light (the atmospheric window). It arrives unhindered at the Earth's surface and warms it up. Without the greenhouse effect, a net radiation power density of about 205 W/m^2 would be absorbed by the Earth.

Fig. 1: Set-up of the experiment.

FS-2014-10

Absorption of electromagnetic radiation leads to warming of the absorbing body. In terms of a radiation balance, a body will continue to heat up until the absorbed radiation power equals the radiation power emitted by the body. Without taking the greenhouse effect into account, the Earth would have a temperature of -28 °C (245 K). According to the Planck distribution curve, the radiation peak of a body at this temperature lies in the infra-red area. The radiation emitted by the Earth is therefore IR light.

Greenhouse gases, like the roof of a greenhouse, have at certain wavelengths the property of absorbing infra-red radiation and emitting it again. The emission of radiation takes place in all spatial directions, so that a large proportion of the IR radiation is radiated back towards the Earth (atmospheric counter-radiation). This part of the radiation warms up the Earth additionally, so that the radiation balance is shifted. Taking the greenhouse effect into account results in an average temperature of the Earth's surface of +15 °C.

According to this model, an increase in concentration of greenhouse gases leads to an increase in the average temperature of the Earth's surface.

In the experiment presented here, the IR absorption properties of various gases will be determined in order to estimate their greenhouse effect based on these. The experiment is also intended to contribute towards understanding why greenhouse gases absorb infra-red radiation.

Risk assessment

Appropriate hazard statements and precautionary statements must be observed, depending on the gases one wishes to investigate. The hazard statements and precautionary statements presented in the following relate to the example measurements to be performed.

Argon	
 **Signal word:** **Caution**	**Hazard statements** H280: Contains gas under pressure; may explode if heated. **Precautionary statements** P403: Store in a well ventilated place.
Carbon dioxide	
 **Signal word:** **Caution**	**Hazard statements** H280: Contains gas under pressure; may explode if heated. **Precautionary statements** P403: Store in a well ventilated place.

Ethane	
  **Signal word:** **Hazard**	**Hazard statements** H220: Extremely flammable gas. H280: Contains gas under pressure; may explode if heated. **Precautionary statements** P210: Keep away from heat/sparks/ open flames/hot surfaces. No smoking. P377: Leaking gas fire: Do not extinguish unless the leak can be stopped safely. P381: Eliminate all ignition sources if safe to do so. P403: Store in a well ventilated place.
Isobutane	
  **Signal word:** **Hazard**	**Hazard statements** H220: Extremely flammable gas. H280: Contains gas under pressure; may explode if heated. **Precautionary statements** P210: Keep away from heat/sparks/ open flames/hot surfaces. No smoking. P377: Leaking gas fire: Do not extinguish unless the leak can be stopped safely. P381: Eliminate all ignition sources if safe to do so. P403: Store in a well ventilated place.
Oxygen	
  **Signal word:** **Caution**	**Hazard statements** H270: May cause or intensify fire; oxidizer. H280: Contains gas under pressure; may explode if heated. **Precautionary statements** P244: Keep pressure reducer free of fat and oil. P220: Store away from combustible materials. P370+P376: In case of fire: Stop a leak if this can be done safely. P403: Store in a well ventilated place.

Equipment and chemicals

1 IR Gas Experimental Kit 666 2652
1 Pocket-CASSY 524 018
1 CASSY Lab 2 ....524 220
1 µV Box..524 040
1 DC power supply, 2 x 0...16 V / 2 x 0...5 A 521 535
2 Connecting leads 19 A, 50 cm, R/B, pair..........500 45
2 Crocodile clips, polished, set of 6 ....501 861
1 Moll's thermopile..557 36
1 Manual vacuum pump 375 58
1 Fine regulating valve for Minican cans.............660 980
1 PVC tubing 6 mm diam., 1 m............................604 500
1 Silicone tubing 5 mm diam., 1 m.......................604 431
1 Silicone tubing 4 mm diam., 1 m.......................667 197
1 Connector, straight PP, 4 ... 8 / 8 ... 12 mm......604 520
1 Minican pressurised gas can, argon 661 0010
1 Minican pressurised gas can, ethane 660 988
1 Minican pressurised gas can, isobutane...........661 0011
1 Minican pressurised gas can, carbon dioxide ...660 999
1 Minican pressurised gas can, oxygen..............660 998
Also required:
1 Ruler
1 USB cable
1 PC with Windows XP or higher

Set-up and preparation of the experiment

Insert the retaining clip into the holes provided on the tray (see Fig. 1).

With the help of rubber rings provided, close off both openings of the cuvette using PE film. Attach the black caps to the gas inlets and screw a GL end cap onto the screwed opening.

Insert the cuvette into the two central retaining clips. Mount the coiled filament behind the cuvette using fibreglass tape for heat protection. Insert the Moll's thermopile into the retaining clip in front of the cuvette.

The protective cap is removed from the thermopile when making measurements, as this absorbs a large amount of the infra-red radiation.

Place the power supply to the right of the apparatus and connect it to a mains socket.

Using two connecting leads and two metal crocodile clips, connect the coiled filament to the positive and negative terminals of the left-hand output of the power supply. By pressing both adjustment knobs, the right-hand output is switched in additionally. Turn the current control to maximum and then set a constant voltage of 2 V.

Using connecting leads, connect the positive (red) and the negative (black) terminals of the thermopile to the microvolt box. Insert the microvolt box into the Pocket-CASSY and connect the Pocket-CASSY via a USB cable to the computer. Start CASSY Lab 2.

Shorten the tubing used for delivering the gases and for the vacuum pump each to the required length. For delivering the gases, use the 4 mm diameter tubing. The 6 mm diameter tubing is joined to the 5 mm diameter tubing using a straight connector and then attached to the vacuum pump.

Performing the experiment

Start the measurement. Wait until the value displayed remains constant. This can take 10 - 15 minutes, as the coiled filament takes some time to heat up and the radiation power it emits thus increases. Screw the fine regulating valve to the CO_2 Minican, attach the 4 mm diameter tubing to the valve and carefully connect it to the gas delivery tube. Remove the end cap from the second opening.

As soon as a constant voltage value has been reached, introduce CO_2 gas at a moderate pressure for about 1 minute. Then close the valve and carefully replace the end cap. The measurement can be started by inserting a vertical line in CASSY Lab (right click → place mark → vertical line) (see Fig. 2).

Do not remove the tubing after the measurement. Instead, remove the valve from the Minican and screw it onto the next can. Proceed for every following gas as for CO_2. It is recommended to investigate a greenhouse gas alternately with a non-greenhouse gas, so that the difference is more clearly visible. For a better overview, the name of the gas can be entered into CASSY Lab (right click → place mark → ABC Text) (see Fig. 2).

Using the manual vacuum pump, aspirate air again at the end of the measurements to obtain a second reference value, as the measurements can be subject to slight variations.

Observation

A different radiation power will be recorded on the Moll's thermopile, depending on the gas delivered (see Fig. 2).

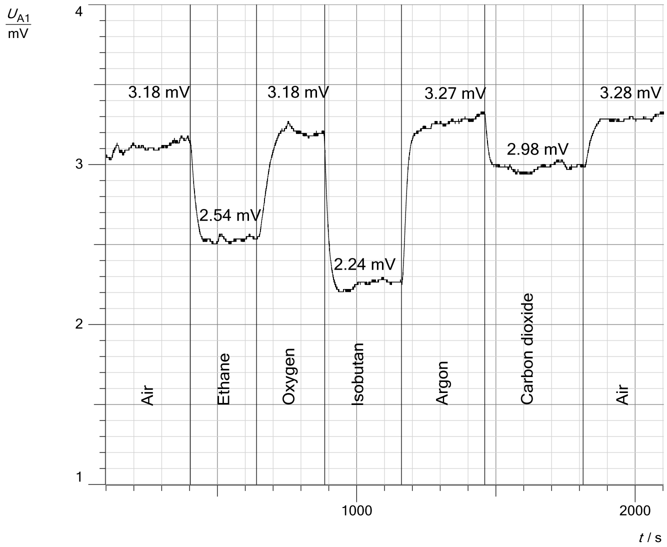

Fig. 2: Example measurements of various gases.

Evaluation

Moll's thermopile measures the radiation power of the incident radiation. It can measure in the range of 0.15 µm to 15 µm. The polished metal funnel of the thermopile deflects the incident infra-red radiation onto the blackened disc in the centre of the funnel. This makes contact with the measurement junctions of 16 thermoelements connected in series. The incident radiation heats up the blackened disc until an equilibrium is reached. This creates a temperature gradient across opposite junctions of the thermopile. According to the Seebeck effect this creates a thermoelectric voltage which is proportional to the incident radiation power. An incident radiation power of 1 mW produces a voltage of 0.16 mV. The associated radiation power can be calculated from the voltage measured by cross multiplication. (see Tab.1).

Tab. 1: Radiation power to measured voltage.

Gas	Voltage	Radiation power
Air 1	3.18 mV	19.9 mW
Ethane	2.54 mV	15.9 mW

Oxygen	3.18 mV	19.9 mW
Isobutane	2.24 mV	14.0 mW
Argon	3.27 mV	20.4 mW
Carbon dioxide	2.98 mV	18.6 mW
Air 2	3.28 mV	20.5 mW

In the above measurement examples, air was measured twice for verification purposes (see Fig. 2). The second value is 0.1 mV greater than the first. The reasons for this could be an increase in the intensity of the source of radiation, a decrease in the room temperature or a slight shift in the angle of the thermopile. To take this discrepancy into account, the mean of the start and end values was used in all calculations.

$$\text{radiation power air} \quad \text{mean} \ = $$
$$= \frac{19{,}9\ \text{mW} + 20{,}5\ \text{mW}}{2} = 20{,}2\ \text{mW}$$

From the values in Table 1, the percentage reduction in the radiation power relative to air can be calculated.

Example: air and ethane

$$\frac{\text{radiation power ethane}}{\text{radiation power air (mean)}} = \frac{15{,}9\ \text{mW}}{20{,}2\ \text{mW}} \cdot 100\ \% = 78{,}7\ \%$$

$$78.7\ \% - 100\ \% = -\,21{,}3\ \%$$

On introducing ethane, the measured radiation power fell by 21.3 %. The percentage change in the radiation power passing through for the various gases is shown in Table 2.

Table 2: Percentage reduction in the radiation power

Gas	Reduction in the radiation power
Ethane	-21.3 %
Oxygen	-1.49 %
Isobutane	-30.7%
Argon	+0.99 %
Carbon dioxide	-7.92 %

Result of the experiment

The observations can be summarised as follows:

1. Noble gases and diatomic gases of homoatomic structure, such as oxygen, show no reduction in the radiation power relative to air.

2. The more complex the structure of multiatomic gases and the more atoms they consist of, the more the measured radiation power is reduced (carbon dioxide < ethane < isobutane).

The absorption properties of molecules can be explained by quantum theory. The energies associated with the states of motion of a molecule are quantised. This means that the transition between the various rotational and vibrational motions of a molecule can only take place with the absorption or release of discrete energy packets corresponding to a multiple of Planck's constant *h*. A molecule can obtain the energy required for excitation to rotational or vibrational motion by absorbing light quanta, the energy of which corresponds exactly to the energy difference between the two energy states. Particularly the energies of vibrational transitions of molecules correspond to light quanta whose wavelengths are also in the infra-red region.

For the excitation of vibrational transitions it is the case that transitions are only IR active if the dipole moment of the molecule changes during the transition. Noble gases and diatomic homoatomic molecules such as N_2 and O_2 do not absorb IR radiation, as they do not possess a permanent dipole moment and therefore there is no vibrational transition in which the dipole moment changes. In our example measurements, oxygen and the noble gas argon, in agreement with the theory, show no stronger absorption than air does.

The more complex the construction of a molecule, the more vibrational states exist in which the dipole can change. Complex molecules that consist of many atoms therefore absorb more infra-red radiation and are more powerful greenhouse gases than molecules that consist of just a few atoms.

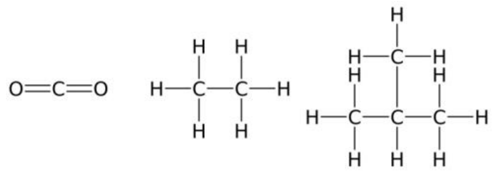

Fig. 3: Substances investigated. From left to right: CO_2, ethane and Isobutane.

Of the three molecules in our example measurements that show an absorption in the infra-red region, CO_2, which consists of only three atoms, has the least complex structure (see Fig. 3). In agreement with the theory, it also shows the smallest reduction in radiation power, as it displays fewer IR-active vibrational states in comparison with the more complex molecules ethane and isobutane.

Ethane is made up of eight atoms. It shows a greater reduction in radiation power than carbon dioxide, but a lower reduction in radiation power than isobutane, which is made up of 14 atoms. This result also agrees with the theory.

Although CO_2 is not the most powerful greenhouse gas, it is the most important for the anthropogenic greenhouse effect, as it results from the combustion of carboniferous materials. Humans release about 32 gigatons of CO_2 into the atmosphere, with an upward tendency.

Cleaning and disposal

Empty Minican cans can be disposed of in the household waste if it is ensured beforehand that they are completely empty. To do this, open the valve to allow the gas to escape. Remove the hazardous substance label before disposal.