

## **Historical Review:**

### **Measurement methods concerning the thermal behaviour of gases under the influence of IR-radiation, especially focussing the greenhouse assumption**

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#### **Abstract**

With respect to the current climate discussion focussing the scientific background, it is necessary going back to the roots critically reviewing the original experimental methods which are usually alleged, particularly concerning the interaction between infrared radiation and gases, and hence the greenhouse assumption. The review was made in view of authors own research which has been published separately, and which is not referred here. It is not confined on simple quotations but it also delivers graphical drafts of the given results being at that time unusual. In addition, a critical discussion is appended. The hitherto known basic measuring methods being carried out with gases and/or in the vacuum trace back to ancient work made in the 19<sup>th</sup> century, particularly to that one of Tyndall which has been widely quoted with respect to the greenhouse assumption. Besides simple heat conduction, they solely concerned medium-wave IR-radiation ( $\lambda = 3 - 50 \mu\text{m}$ ), i.e. thermal radiation occurring at comparatively low temperatures, instead of near IR ( $\lambda = 0.8 - 3 \mu\text{m}$ ) meanwhile being clear as the relevant factor. Moreover, they ever involved the spectroscopic principle where the intensity loss of a radiation beam is measured but not the temperature increase of the involved gas. Thus no empirical data are yet available whether, and to which extent, a gas is warmed-up under the influence of IR-radiation. Furthermore, very weak absorbance could not be detected since the intensity loss is too low. Such measurements would afford an apparatus exhibiting a very low heat capacity and a perfect thermic isolation which were not available at that time, and which are not given at the equipment being usually employed for demonstration and education purposes at schools, too.

**Keywords:** Lambert, Dulong/Petit, Stefan, Langley, Tyndall, Arrhenius, Ångström, Beer

## 1. Introduction

The starting point of this investigation was the generally accepted greenhouse assumption assuming that the recent climate change would be predominantly due to the growing content of the so-called greenhouse gases in the atmosphere, particularly of carbon dioxide. This theory traces back to the comparison of the Earth atmosphere with the glass of a hot house, made by M. Fourier 1827, first promoted by Tyndall 1863 and later by Arrhenius 1896/1901.

The herewith implied question of the infrared radiation (IR) and of its interaction with matter, particularly with gases, is one of the most delicate problems in physics being connected with the question of the nature of light. It goes back to the beginning of natural science, and has been investigated over a long period of time, starting with Newton's discovery of the light spectrum in 1672, followed by Huygens' wave propagation principle in 1678, and resulting in Planck's quantum law in 1900 about the black-body radiation, Einstein's relation about the photo-effect in 1905, Bohr's atom model in 1913, and De Broglie's electronic wave hypothesis in 1924 which lead to the modern quantum mechanics. During this wide period, the comprehension of matter has considerably changed, too. And insofar as heat and temperature are affected, further physical scopes are involved, in particular thermodynamics and the kinetic gas theory. Regarding IR-radiation, it is important to distinguish between *near IR* ( $\lambda = 0.8 - 3 \mu\text{m}$ ), being emitted at high temperatures ( $> 1000 \text{ K}$ ), and *medium IR* ( $\lambda = 3 - 50 \mu\text{m}$ ) occurring at lower temperatures as true heat radiation.

While the relevant literature is rich in theory, it is poor in basic empirical investigations and experiments, at least concerning thermal and thus other than spectroscopic measurements. So it is astonishing that the commonly alleged light-adsorption law of Bouguer, Lambert and Beer traces back to work being published in the years 1729, 1760 and 1852 – hence at times where electric light was not available, and artificial light had to be delivered by candles or by oil lamps. Photometers being used at that time – like those of Rumford or of Ritchie – utilized the fact that the intensities of two comparing light sources being casted abreast on a white surface decrease reciprocally to the square of the difference in distance. A lot of materials, being readily available nowadays, were then not known, particularly synthetic materials. Moreover, the early work, being written in French, Latin (Lambert, 1760), German or English, was usually quite extensive, laboured and hardly comprehensible. E.g. the “Photometria” of Lambert, published in 1760, comprises 547 pages, 1243 paragraphs, 40 experiments, 52 theorems and 107 figures (see e.g. table I in fig. 1).

Hence, for better understanding the historical progress concerning the states of the knowledge and the relevant measurement methods, first of all the milestones will be listed up which have been reached from Newton until Planck, not only considering the results and methods being applied but also the materials and instruments being available at that time, due to the technical progress. Thereby, besides spectroscopic investigations concerning light absorption, also light emission phenomena will be taken into account, as well as the thermal conduction measurements in gases. Subsequently, some prominent items will be described more detailed, likewise discussing their deficiencies from the present point of view. Finally, the recent work will be reviewed insofar it exhibits novel experimental approaches.

T. Allmendinger, Historical Review: Measurement methods concerning the thermal behaviour of gases under the influence of IR-radiation, especially focussing the greenhouse assumption. <http://allphyscon.ch> (Sept. 2016)

- Isaac Newton, 1672: “New Theory about Light and Colors”: The light-spectrum
- Christiaan Huygens, 1678: “Traité de la Lumière”: The wavy character of light
- Pierre Bouguer, 1729: “Essai d’optique sur la graduation de la lumière”
- Jean-Henri Lambert, 1760: “Photometria”: Contribution to the absorbance law for light
- William Herschel, 1800: Discovery of the infrared radiation
- Wilhelm Ritter, 1801: Discovery of the ultraviolet radiation
- Thomas Young, ca. 1802: Determination of wave-lengths, three-colour-theory
- John Dalton, 1808: Colour blindness, law of multiple proportions, atom hypothesis
- Joseph Fraunhofer, 1814: Discovery of single lines in the spectrum of sunlight
- P.L. Dulong/A.T Petit, 1817: Besides the formulation of the law about the heat capacity of the solid elements, measurements about the heat transfer of gases and in the vacuum were made, too (Fig. 2; see comment below)
- August Beer, 1852: Measurement of the red-light absorbance in coloured fluids
- Kirchhoff/Bunsen, 1858: Development of the spectral analysis
- John Tyndall, 1861: “On the Absorption and Radiation of Heat by Gases and Vapours, and on the Physical Connexion of Radiation, Absorption, and Conduction.” (Fig. 3; see the comment below)
- Thomas A. Edison, 1879: Invention of the electric light bulb based on a carbon filament
- M. J. Stefan, 1879: The formulation of the temperature-dependence-law for the energetic radiative intensity including the assumption of a back-radiation, based on the empirical data of Dulong/Petit
- Ludwig Boltzmann, 1884: Delivered the theoretical foundation of Stefan’s law on the basis of the electromagnetic light theory
- S.P. Langley, 1884: Spectroscopic investigations of the light absorption by the Earth’s atmosphere
- A. Schleiermacher, 1888: Development of a basic method for measuring the heat conductivity of gases and the heat transfer in the vacuum (see below)
- Wilhelm Wien, 1896: Law for the spectral shift of the black-body radiation
- Lummer/Pringsheim, 1899: Instrumental perfection of the radiation measuring (Fig. 4)
- Max Planck, 1900: Quantum theory about the energy dispersion in the black-body radiation spectrum.

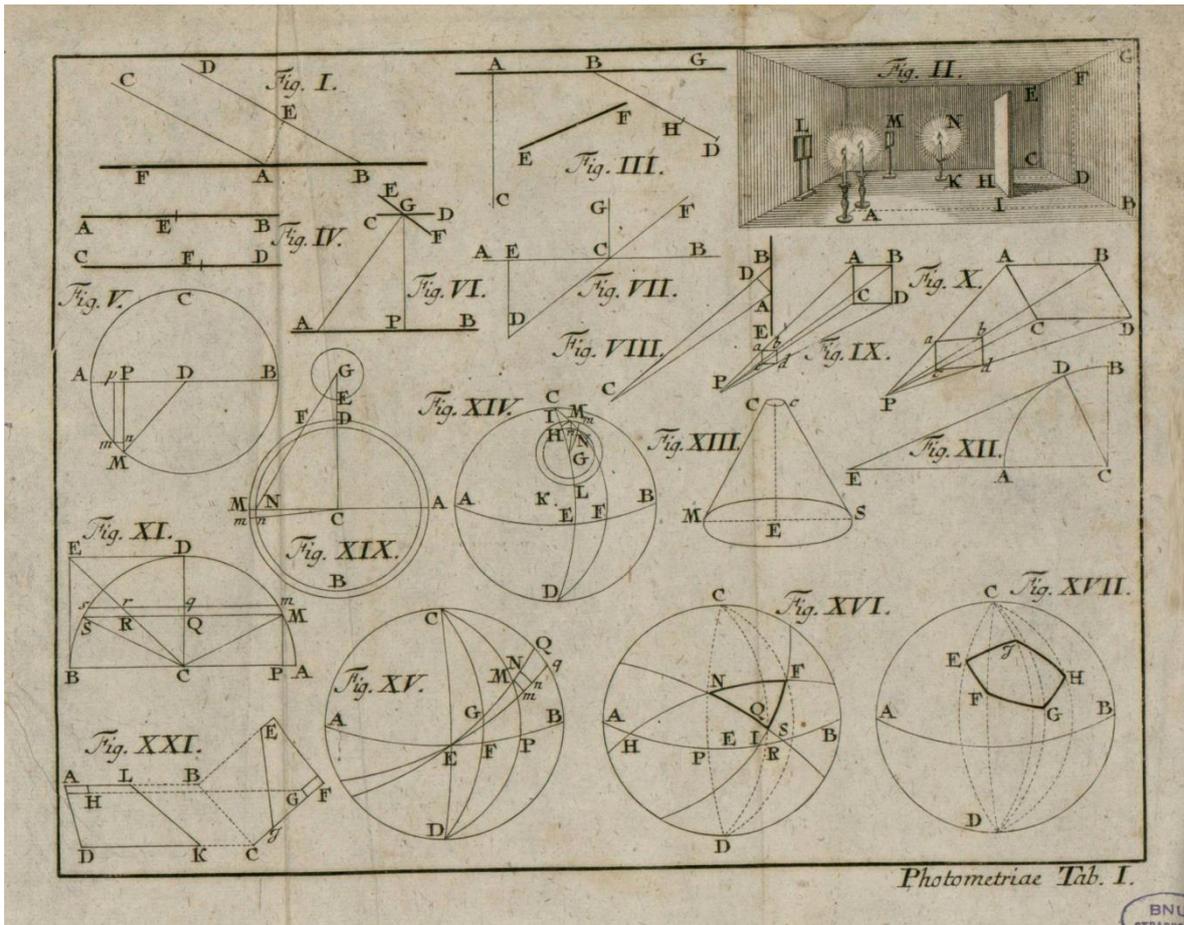


Fig. 1: Table I in Lambert's "Photometria" (1760)

Pl. 3 Tome VII. Annales de Chimie et de Physique.

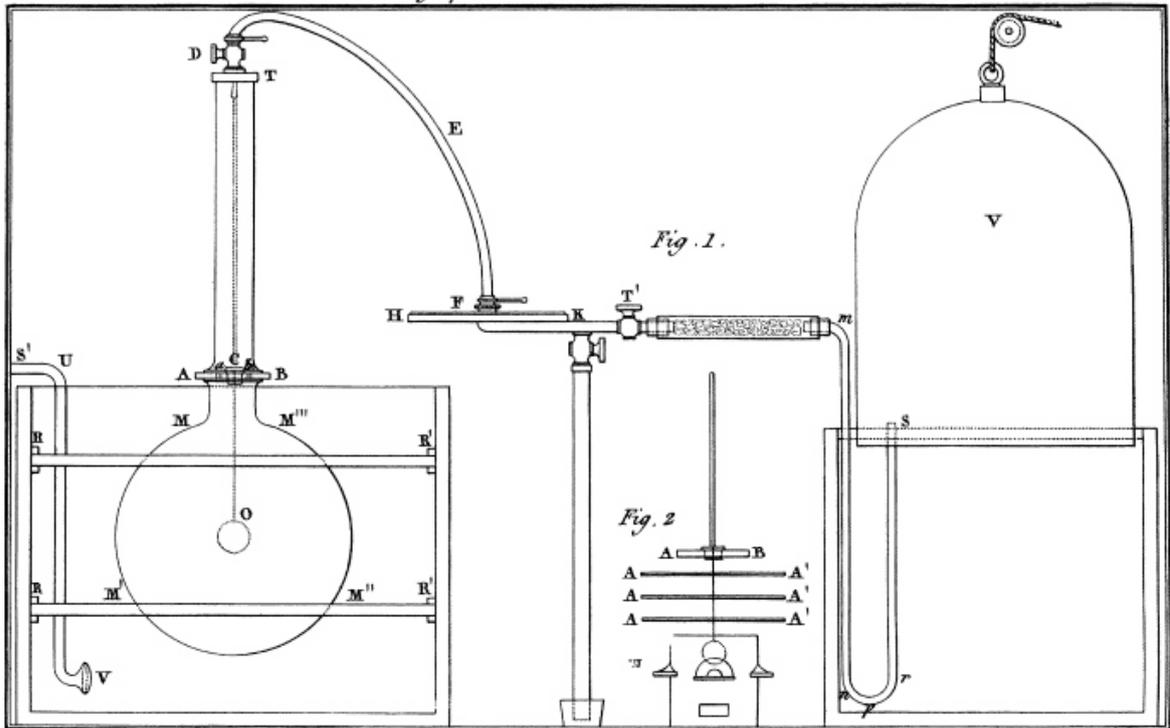


Fig. 2: Equipment of Dulong/Petit (1817)

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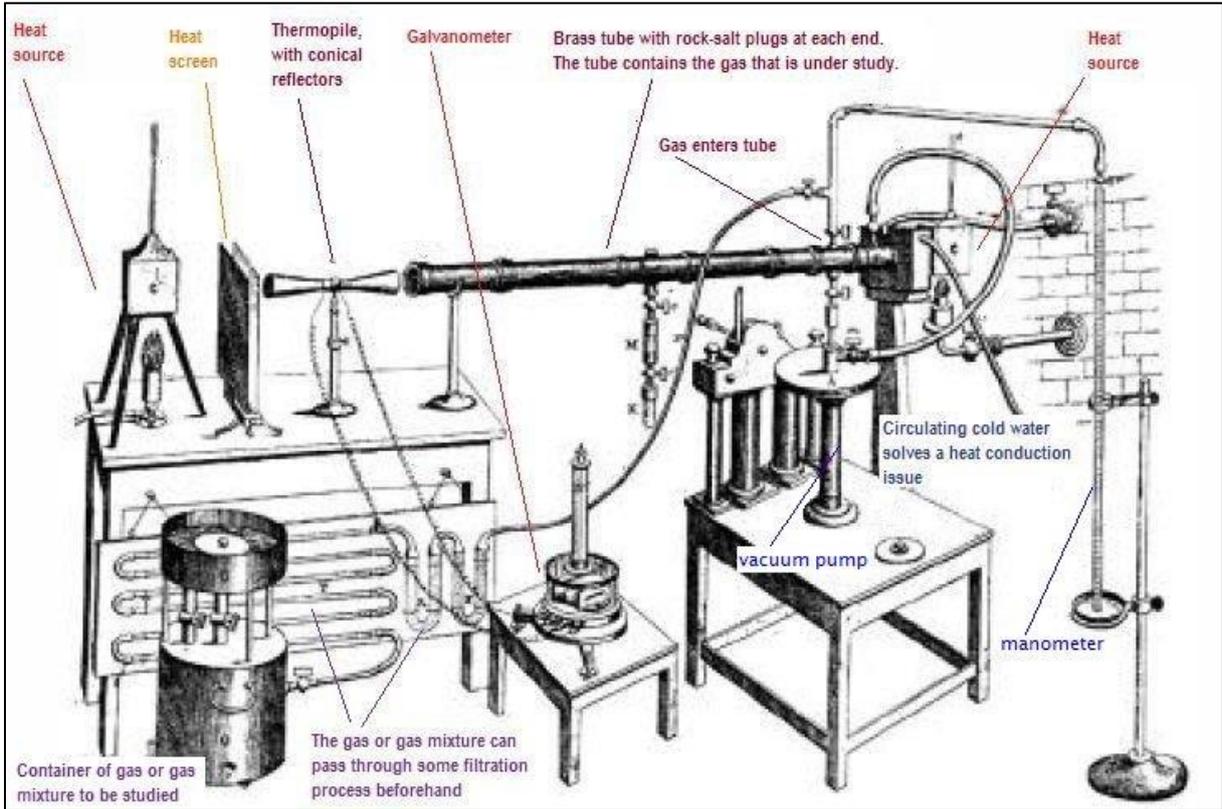


Fig. 3: The preferred apparatus of Tyndall (1861), with annotations being inserted afterwards

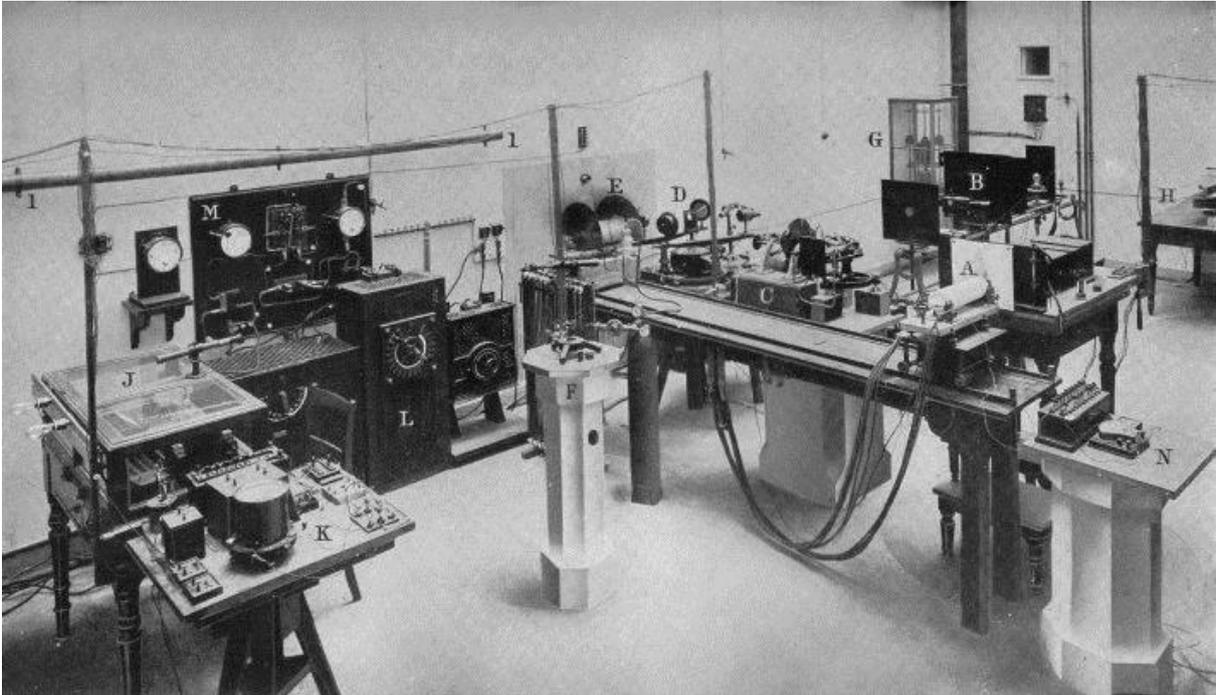


Fig. 4: Equipment of Lummer and Pringsheim (1899)

## 2. Original Measuring Methods

Nearly all of the hitherto known measuring methods being carried out with gases and/or in the vacuum trace back to ancient work made in the 19<sup>th</sup> century. They shall be critically discussed although solely *medium infrared radiation* is involved, i.e. thermal radiation occurring at comparatively low temperatures ( $\lambda > 3 \mu\text{m}$ , cf. Planck's distribution, fig. 14):

[1] The method of **Dulong and Petit (1817)** allows the measurement of heat spreading in the presence of gases as well as in the vacuum. As drafted in fig. 2, in the centre of a spherical vessel MM'M''M''' a ball O is positioned which is previously warmed-up to an elevated temperature while the spherical vessel is surrounded by a further vessel being filled with ice-water and thus keeping the wall of the spherical vessel constantly at 0°C. After the start of the experiment, the central ball gradually cools down with a decreasing rate. As a central ball, the bottom of an Hg-thermometer was used, in some cases being coated with silver. The spherical vessel was made from copper, allowing an evacuation and thus determining heat spreading in the vacuum. The starting temperature ranged up to 260°C allowing the study of quite large temperature gaps. The eminent advantage of this method is the absence of any lateral walls along the radiation or heat conduction path which may disturb the energetic conditions.

Thereby, the author's interpretation of the results is less important than that one given by **M. J. Stefan (1879)** delivering the well-known Stefan's law, later being theoretically founded by **L. Boltzmann (1884)**. It is given by the generally-known formula for the *radiant flux*  $P$

$$P = A \cdot \sigma(T_1^4 - T_2^4) \quad \text{with } \sigma = \text{Stefan-Boltzmann constant} = 5.67 \cdot 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}, \text{ and } A = \text{area}$$

However, in Stefan's paper the relation is not given in this form but also exhibiting some ambiguities with respect to units impeding the feasibility to compare the values. Moreover, his analysis is not consistently comprehensible: Certainly, there is no reason to query the fourth power of the absolute temperature  $T$ . But it is not intelligible that the role of the spherical vessel (being from copper) should be neglected owing to the argument that the heat conductivity of air is much larger than that one of copper, disregarding that the perpendicular diffusion distance inside the copper envelope is much smaller than the distance between this envelope and the surface of the central thermometer-ball. As a consequence, this distance – or more generally: the distance between two interacting solid bodies – is non-existent in that formula. Besides, it is not sufficiently regarded that this law may solely be valid for black bodies, and not for metallic mirrors or glassy surfaces such as the here applied ones.

[2] The method of **A. Schleiermacher (1888)** for determining the heat conductivity of gases is in a certain way related with the method of Dulong and Petit since it operates with a heated central body and an encircling form, too. However, the central body is not a ball but a rod or a wire, and the encircling form is not a hollow sphere but a (glass) tube, implying a cylindrical and not a spherical topology. Moreover, the coaxial wire – being from platinum – is not cooling down during the process but holed at a constant temperature by applying an electric current leading to a steady state. The encircling tube is held at a certain temperature, too, due to an outer vessel filled with ice-water or with boiling water, while the temperature of the central wire is calculated as a result of the current strength and the electrical resistance.

In spite of its old age, the work of Schleiermacher is of special interest since several parameters have been varied allowing to study the respective basic impacts: besides the gas kind in the tube and the gas pressure (including the vacuum case), also the reference temperature in the outer vessel (0°C and approx. 100°C) and the radius of the tube have been altered (apparatus I: 12.1 mm; apparatus II: 7.8 mm). The published results, being given in tabular form and not in diagrams, are only scarcely interpreted by the author himself but enable an own evaluation by drafting diagrams considering relative but not absolute values. Similarly to the apparatus of Dulong and Petit, within this apparatus a linear dependency of the intensity cannot be assumed for the spreading of heat or energy - i.e. Fick's first diffusion law is not valid here because of the two dimensional character of the process -, thus a more complex mathematic model would be necessary. But it would exceed the scope of the present work focussing such a detailed model, besides an empirical evaluation, since it is not relevant for the own apparatus design. Moreover, statements about the influence of the materials are not possible based on Schleiermacher's data since these have not been varied, i.e. in any case the encircling tube was from glass whereas the central wire was from platinum hence being not at all black bodies. Later publications, such as those of Weber (1917, I & II) or of Guildner (1962), the latter one delivering an intricate theory but using another cell design, shall not be discussed here. A comprehensive topical description is given by Wiegleb (1987).

Regarding **fig. 5**, the *pressure-independency* of the thermal conductivity gets obvious. However, the two apparatus – exhibiting different radii of the glass tubes – yielded different results, whereby those being received using the tube with the wider radius were significantly lower, that which certainly be the implication of the above mentioned radius effect. As revealed in **fig. 6**, this difference may be well compensated by multiplying the results of apparatus II by the quotient (correction factor) of the two radii, namely by  $12.1/7.8 = 1.55$ .

In **fig. 7**, relative plots according to Stefan's law have been made, varying the lower temperature as well as the apparatus (i.e. the diameter of the glass tube). The fact that the curves are not linear and not horizontal reveals that Stefan's law is *not* fulfilled in this case, while **fig. 8** reveals fairly a similar radius-dependency as in the above case. Presumably, the deviance of Stefan's law is due to the special character of the utilized materials being not black bodies. Anyway, these results cannot prove the Stefan law.

**Fig. 9** displays the temperature dependence of thermal conductivity in the case of air, comparing cases with different lower temperatures (i.e. the reference temperatures in the outer vessel). Thereby, it is not surprising that the conductivity is higher at the elevated temperature. However, the value of the empirical correction factor 1.245 being applied in **fig. 10** doesn't correspond to the theoretical value being expected according to the kinetic gas theory which was later developed by Meyer, Maxwell and Boltzmann. Therein, a temperature dependence on the radical of the absolute temperature is postulated, delivering in this case the factor 1.167 (= radical of the quotient of the two absolute temperatures). Thus the empirical factor is larger than the theoretical one (the empirical one is  $(T_2/T_1)^{0.71} = 1.245$ ), meaning that the theory or the measurement is either not correct, or not sufficient. The detected additional heat transfer may be explained by a heat radiation within the gas, probably partly by the heat radiation in the vacuum, and partly by a heat radiation mediated by the gas molecules.

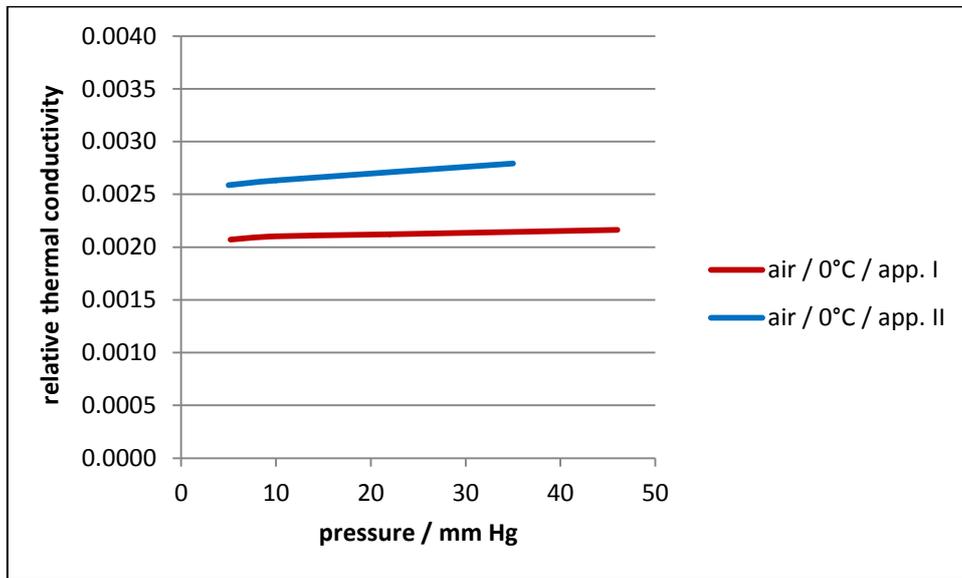


Fig. 5: Pressure-dependence of the thermal conductivity of air, based on the measurements with the lower temperature (of 0°C), using the two different tubes (app. I, with  $r = 12.1$  mm, and app. II with  $r = 7.8$  mm); according to Schleiermacher (1888)

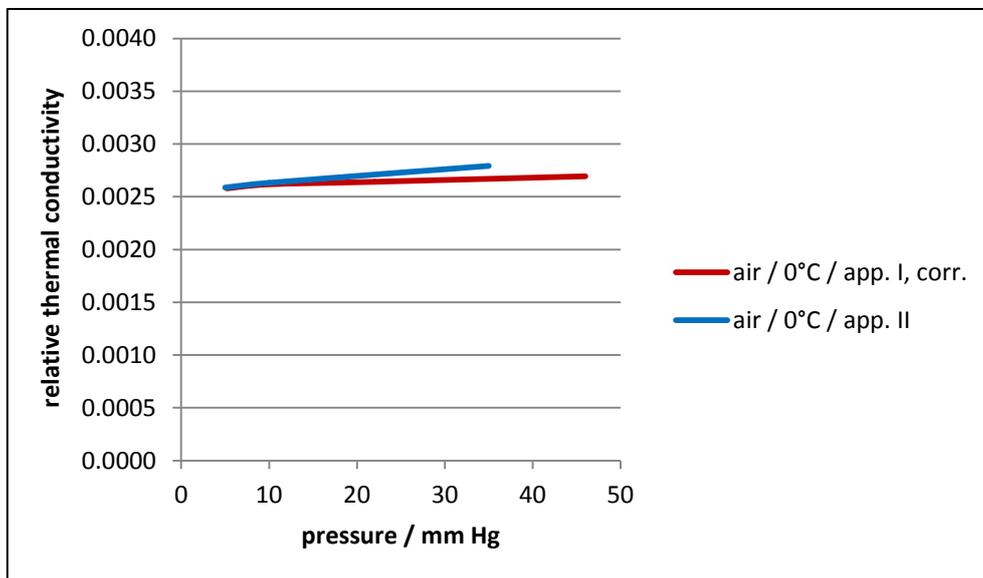


Fig. 6: Pressure-dependence of the thermal conductivity of air, based on the same data being used in Fig. 5, but those concerning apparatus I ( $r = 12.1$  mm) being corrected by multiplication with the factor  $12.1/7.8 = 1.55$

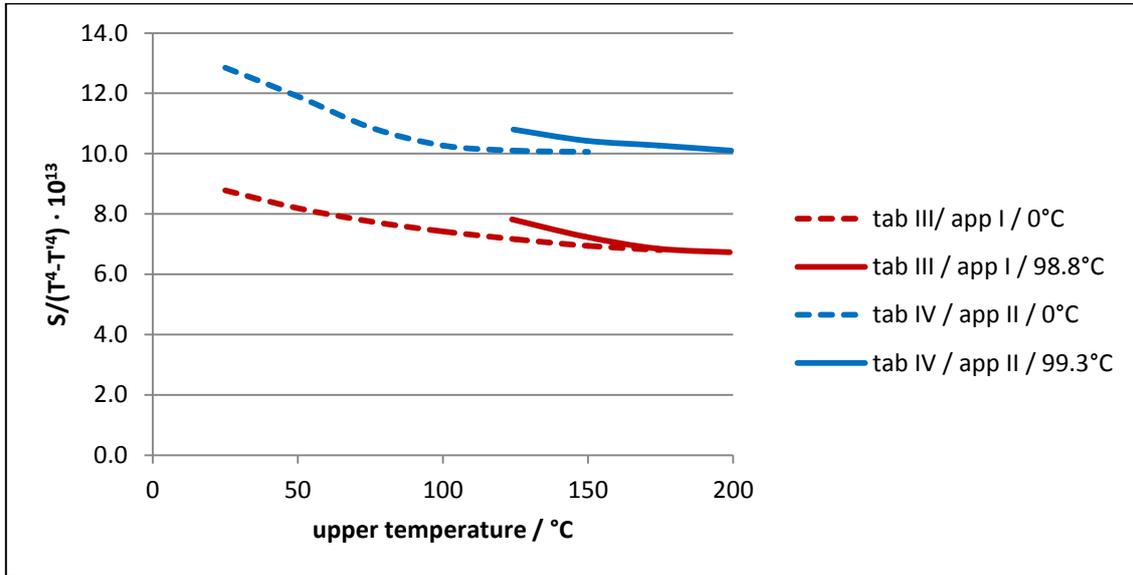


Fig. 7: Stefan-plots for two different lower temperatures (0°C and approx. 100°C) with air, using the two different tubes (app. I with  $r = 12.1$  mm, and app. II with  $r = 7.8$  mm); according to Schleiermacher (1888)

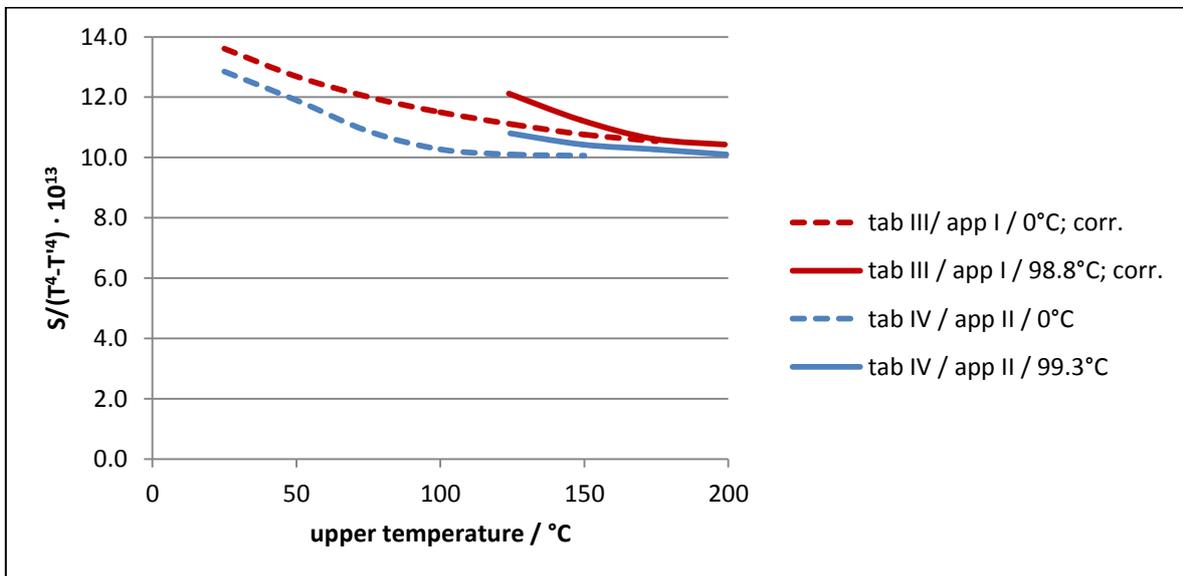


Fig. 8: Stefan-plots based on the same data being used in Fig. 7, but those concerning apparatus I ( $r = 12.1$  mm) being corrected by multiplication with the factor  $12.1/7.8 = 1.55$

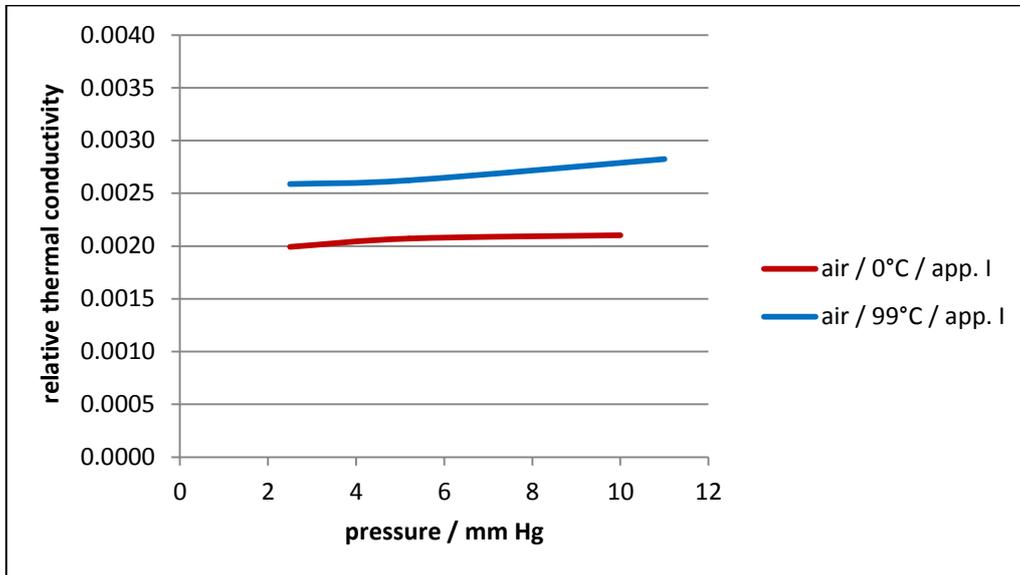


Fig. 9: Temperature-dependence of the thermal conductivity of air, based on the measurements using apparatus I at two different lower temperatures (0°C and 99°C); according to Schleiermacher (1888)

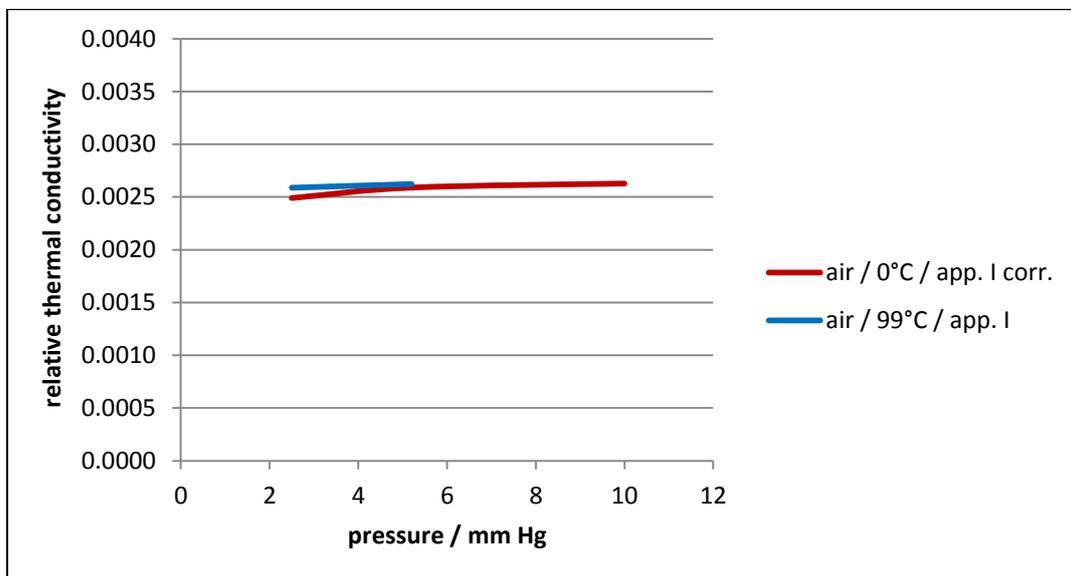


Fig. 10: Temperature-dependence of the thermal conductivity of air, based on the same dates being used in Fig. 9, but those concerning the lower temperature being corrected by multiplication with the empirical factor 1.245

[3a] The Irish physicist **John Tyndall** was the first one who delivered empirical data for underpinning the hypothesis that carbon dioxide would be the cause for an atmospheric warming-up inducing that what we call now a »greenhouse effect« (Tyndall 1861, 1863, 1872). His preferred apparatus, first published in 1861 and drafted in fig. 3, consisted of a long tube from brass (polished inside, length 4 feet = 122 cm, diameter 2.4 inches = 6 cm) which he filled with various gases at different pressures but which also could be evacuated admitting measurements in the vacuum. The ends of the tube were capped with slabs of rock salt crystal (sodium chloride), a substance known to be highly transparent to heat radiation. A standard Leslie cube from copper, coated with lamp-lack and filled with boiling water, emitted radiation that – after passing an intermediate chamber preventing heat conduction - traversed the tube and interacted with the gas before entering one cone of a differential thermopile. Radiation from a second, opposite Leslie cube passed through a screen and entered another cone. The common apex of the two cones, containing a differential thermopile junction, was connected to a galvanometer which measured small voltage differences. The intensity of the two sources of radiation (i.e. of the two Leslie cubes) entering the two cones could be compared by measuring the deflection of the galvanometer which is proportional to the temperature difference across the thermopile. Different gases in the tube, as well as different gas pressures, caused varying amounts of deflection of the galvanometer needle.

Hence, by this – quite expensive – apparatus another measuring principle was realized than it had been applied using the two hitherto mentioned ones: Now the radiation spread occurs not spherically – as in the case of Dulong and Petit -, or cylindrically – as in the case of Schleiermacher – but *linearly*, across a long tube. Therefore, interaction of the examined medium and the tube-wall may occur, being not easily estimated, above all in hindsight. A further handicap of this apparatus is the impossibility of determining the radiation power of the Leslie cubes, thus solely allowing relative measurements.

But in particular, the kind of the radiation sources – namely of Leslie cubes – implies, due to the comparatively low temperature of the heat source, solely the emission of *medium-wave IR* ( $\lambda = 3 - 50 \mu\text{m}$ ) which isn't relevant to the climate question, instead of *near-IR* ( $\lambda = 0.8 - 3 \mu\text{m}$ ), meanwhile being clear as the relevant factor becoming obvious from the latest determination method for the solar reflection coefficient on surfaces (cf. *ASTM Standard E1918-06*). Tyndall couldn't know that, since then Wien's distribution law, and even less Planck's radiation law, was not known. But it is at least interesting that Tyndall didn't detect any adsorption by pure air (unlike in the case of carbon dioxide or of other strongly absorbing gases, particularly of an »olefiant« gas) when he worked at lower temperatures, while at higher temperatures he found a weak absorbance by air. This would mean that air doesn't absorb medium-wave IR-radiation while it becomes absorbing at lower IR-radiation waves – which will be the subject of this paper.

Besides of these systematic faults, Tyndall's consideration exhibits some theoretical faults which may be excused by the fact that he had made pioneer work, and that then the knowledge about radiation was quite poor. But it is amazing that he speaks of »water atoms«, and that he obviously didn't know the absorption law of Bouguer-Lambert-Beer implying an absorption coefficient. Instead of this, he calculated on the base of – inversely proportional –

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absorption units leading to completely false results with respect to the atmosphere. Nevertheless, the values given in table I are useful when plotted in a diagram (fig. 11), revealing that the absorption isn't altogether proportional to the pressure but decreases at low pressures.

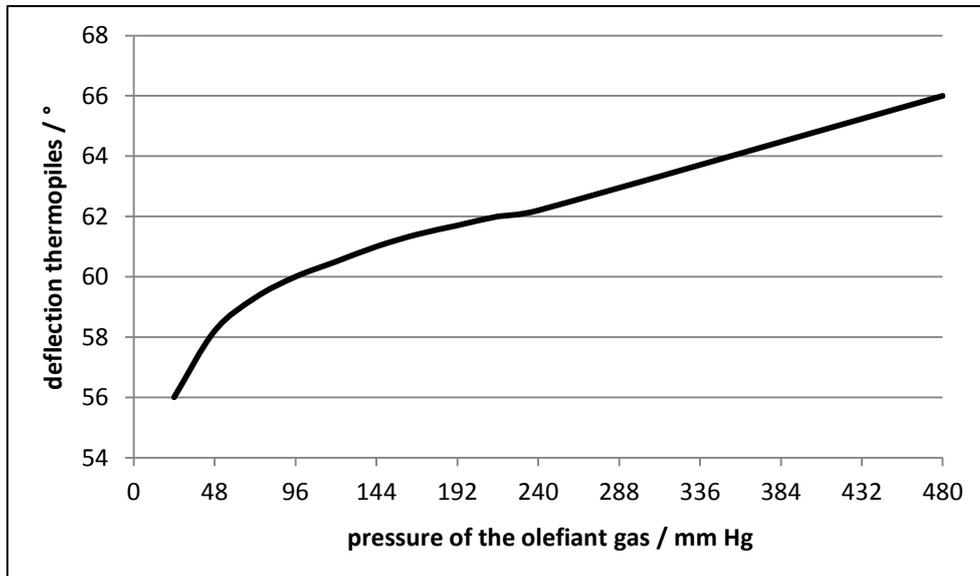


Fig. 11: Thermopile deflection delivering the relative absorption degree of an olefiant gas at variable pressures; according to Tyndall (1861, table I, page 180)

[3b] Forty years later, a similar apparatus was used by **Arrhenius**, focussing the carbon-dioxide adsorption of infrared radiation and using a 50 cm long iron tube but two different IR-sources, namely - besides a Leslie-cube at 100°C – a hollow body from smutted copper being chilled down to -80°C by a mixture of dry ice and ether. He varied the pressure but within such a high range that no significant deviation from linearity appeared (fig. 12).

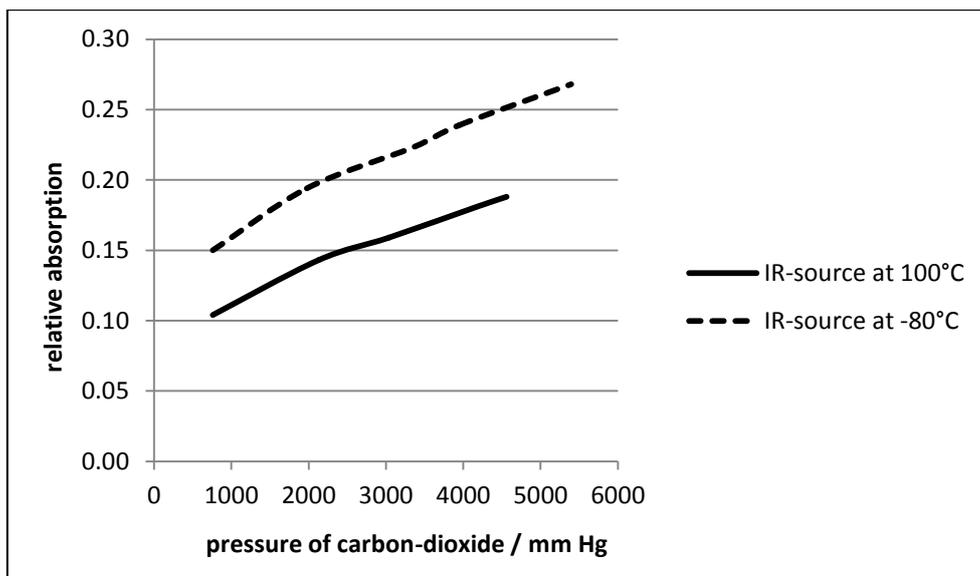


Fig. 12: Relative absorbance of carbon-dioxide with two different IR-sources, according to Arrhenius (1901), p. 692

[3c] At the same time (1901), **Knut Ångström** made IR-absorption measurements with carbon-dioxide using a two-chamber tube and varying the tube length as well as the carbon-

dioxide concentration by adding air to distinct amounts. But since he used three different radiation sources delivering varying badly defined kinds of radiation – namely an Argand-lamp, a Bunsen-burner and a blackened platinum-spiral being heated up to 300°C -, his results are difficult to interpret, and thus of limited interest.

In a manner, Tyndall's apparatus is similar to an *infrared-spectroscope*. However, there is a principal difference insofar as spectroscopy is based on *monochromatic* radiation, i.e. solely a narrow range of the electromagnetic spectrum is used. Moreover, preferably *visible light* and *liquids* are affected, as it is notably apparent from the work of **Beer (1882)** who studied the absorption of red light in coloured liquids using an oil-lamp as the light source and a dark-red coloured glass plate as a filter. Beer studied the intensity-loss as a function of the sample-thickness, varying the thickness between 1 and 2 dm. His empirical result may be written as

$$I/I_0 = \mu^{-d} \quad \text{where } \mu = \text{Beer's absorption coefficient, and } d = \text{thickness (normalized)}$$

However, this formula doesn't match the formula which is given in modern textbooks, namely

$$I/I_0 = e^{-\varepsilon \cdot c \cdot d} \quad \text{where } \varepsilon = \text{absorption coefficient, } c = \text{concentration.}$$

The latter one, being known as the Bouguer-Lambert-Beer law, is derived theoretically by integration, assuming that the differential intensity-loss is proportional to the present intensity which decreases insofar as the intensity decreases.

Anyway, that law is not generally valid but linked to certain boundary conditions:

- It presumes that the absorption is enough strong influencing the intensity of the light; but with a low adsorption coefficient the adsorption will probably occur linearly to the thickness of the sample, and not exponentially.
- When an artificial light source is used, its intensity principally decreases inversely proportionally to the square of the distance, even in the absence of an absorbing sample. This may be relevant when the absorbance-distance is wide (as e.g. at Tyndall's apparatus).
- When IR-radiation is used, instead of visible or UV-light, the situation becomes much more complicated. As lab-experience has shown - and as also the results of Tyndall being displayed in fig. 11 let suppose -, quantitative IR-measurements are generally not feasible.

Nevertheless, the hitherto alleged results admit the conclusion that, in contrast to air, carbon-dioxide adsorbs heat radiation to a considerable extent. However, this absorption solely occurs in the medium-IR wave length range (fig. 13), corresponding to the emission range of low temperature black-body radiators according to Planck's law (fig. 14). Moreover, the determination of the real absorption coefficient – exhibiting the dimension  $\text{bar}^{-1}\text{m}^{-1}$  - was not possible since the local radiation power was really not known, apart from the fact that a pressure-independent absorption coefficient does not exist, as mentioned above. And finally, it has to be regarded that spectroscopic methods solely enable statements about the loss of radiation energy when a beam passes through a sample, but not about the question what happens with the lost energy, especially in the case where infrared radiation and gases interact. So it is not stringent that absorbed radiative energy should completely be converted into heat which is, in the case of gases, the result of kinetic translation of the atoms or

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molecules. Rather it is conceivable, as Max Planck has postulated in 1900, that these atoms or molecules behave as *oscillators* exhibiting excited energy states. Since these states are metastable, the absorbed energy may be emitted back – but in any direction - without ever having been transformed in heat motion, while such a transformation of oscillation energy into kinetic energy may only partly occur. But in contrast to Planck's theory concerning the radiation of black bodies, there exists no empirically verified theory about the radiation of gases. Rather, for atmospheric radiation modelling the black-body theory is adducted, but that appears unlikely.

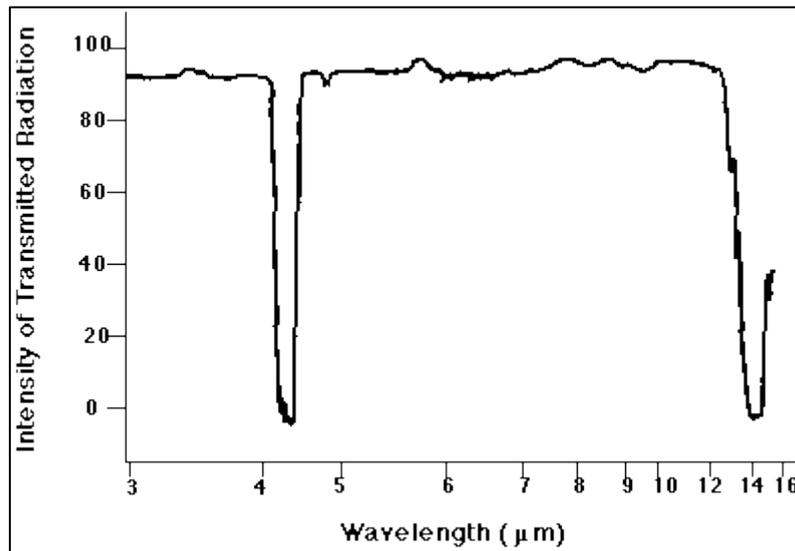


Fig. 13: IR-spectrum of carbon-dioxide [http://wag.caltech.edu/home/jang/genchem/ir\\_img7.gif](http://wag.caltech.edu/home/jang/genchem/ir_img7.gif)

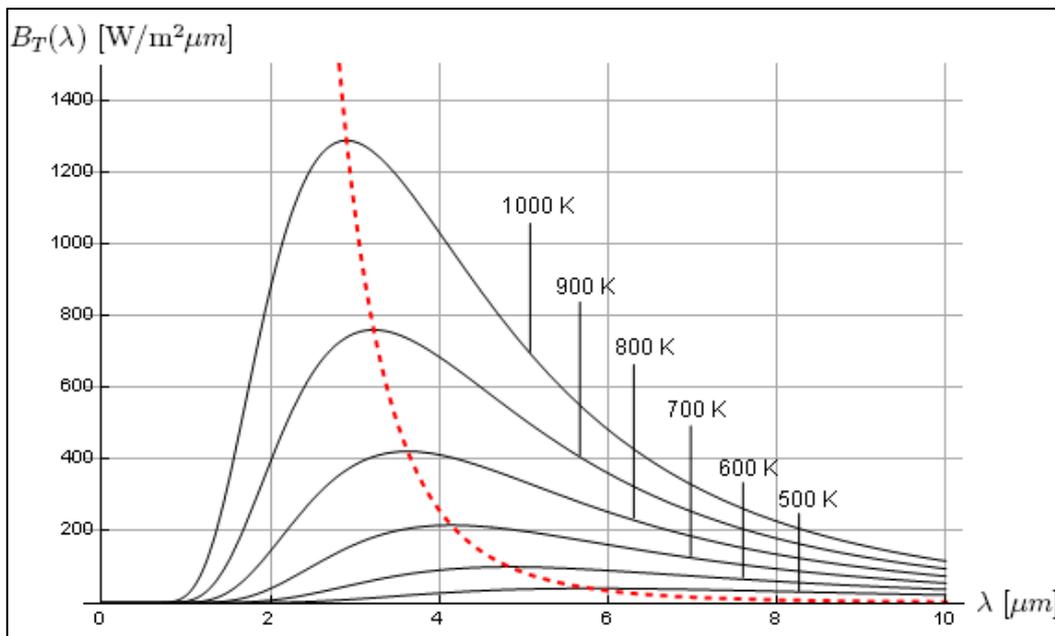


Fig. 14: Specific spectral radiation  $B_T(\lambda)$  of a black body at different temperatures, the red dotted line describing the respective intensity maxima (according to Planck's law)

Normally, molecule-spectra of gases are calculated by quantum-mechanical methods. Those have been mainly focussed in the context of the greenhouse gases. The relating theory, being outlined e.g. in the textbook of Boeker and van Grondelle (2011), is quite complex and shall not be discussed in detail here, except one item: the statement that any IR-activity of molecules or atoms requires a shift of the electric dipole moment, so that two-atomic homonuclear molecules are ever IR-inactive, must be regarded as a theorem and not as principal natural law, since numerous examples of nonpolar substances are known where an interaction with electromagnetic radiation occurs, e.g. at halogens where even coloured – and thus visible - light is absorbed.

With respect to practical measurements, the general interest was more and more geared to spectroscopic methods for analytical applications, using artificial light sources and photo-detectors, the light usually being resolved by a prism in combination with a frame. However, in astronomy as well as in meteorology the direct analysis of natural light, in particular of solar light, plays still a certain part (Zerlaut/Bird, 1989), whereby the measuring of the absolute intensities is needed here much more. But while the over-all intensity (given in  $\text{Wm}^{-2}$ ) may be easily determined by temperature measurements at a blackened cavity - or by electronic instruments (bolometers) being gauged by such blackened cavities -, wave-specific measurements are much more delicate, particularly when infrared radiation is affected, since the medium for splitting the radiation may absorb parts of it leading to systematic measuring errors. E.g. for the “spectro-bolometer” being used by Langley (1884, p. 130), an interference due to the glass-prism may occur since glass absorbs IR-light. Even grating infrared spectrometers, e.g. that one described by Thompson et al. (1994), may exhibit some intrinsic deficiencies since glassy materials such as glass-lenses and glass-prisms are necessary for focussing the beam, not least these of the telescope, and the complicated equipment of Lummer and Pringsheim, being relevant for determining black-body radiation and showed in fig. 4, presages the difficulties which may attend such measurements. When gases are concerned, the circumstances are even more intricate, especially when they absorb only slightly, and when the absorption bandwidth is wide so that an absorption effect may be overlooked.

But beyond these difficulties, an essential aspect had been omitted in the above quoted literature, namely the fact that solely *medium-IR* had been regarded – and not *near-IR* as it occurs in direct and in reflected solar light. With respect to that, no investigation had been made – except one being reported in a previous paper of Knut Ångström (1900). Therein, he describes an apparatus consisting of two 40 cm long glass-tubes being arranged side by side within a wider tube from wood, the latter one serving to the visual and thermal isolation, and exhibiting plates from fluorspar, on one end, and thermocouples on the opposite end. When one tube was filled with air, and the other with pure carbon-dioxide, and when the tubes were oriented perpendicularly to the sun beam, practically no temperature difference could be ascertained. That means: both gases either didn't absorb any sunlight – or they absorbed it to the same extent. Since this result didn't come to his expectations (and to the current opinion of that time), Ångström changed his focus subsequently regarding medium-IR, leading to his already alleged publication in 1901. Apart from that, solely the intensity-loss of the incident light has been measured, but not directly the warming-up of the embedded gas by measuring its temperature. That's a fatal deficiency because the intensity loss might be undetectable.

Since then, apparently no thermal measurements have been made with gases in the presence of IR-radiation, in particular of sunlight, too. In default of further published results, a diploma thesis will be alleged, originally being written for didactic objectives but containing some interesting aspects (Sirtl, 2010). Similarly to Tyndall's experiments, on one side of a horizontal tube, being filled with a gas and laterally sealed by transparent foils, an IR-radiator was provided while on its opposite side a thermopile was positioned. Additionally, in the centre of the tube a temperature sensor was attached (fig. 15). Moreover, a tube from plexiglass was used - instead of a metallic one -, and the variously applied radiators exhibited much higher temperatures than the Leslie cubes of Tyndall. In any case, obviously a limiting temperature was reached. But as exemplarily revealed in fig. 16, no significant differences appeared when different gases such as carbon-dioxide or surrounding air were used. When a 150 W infrared lamp was inserted, absolutely no effect could be detected. Certainly, this apparatus exhibits several deficiencies, such as the high IR-radiative absorbency of the plexiglass-tube and its high thermal capacity. Hence these results are only of limited interest.

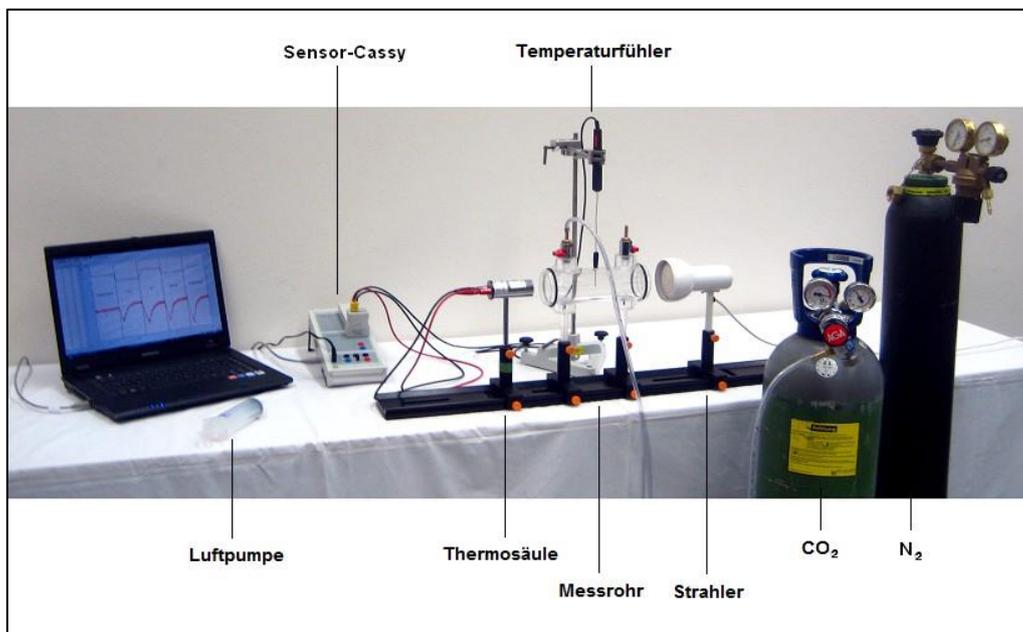


Fig. 15: Preferred equipment of Sirtl (2010)

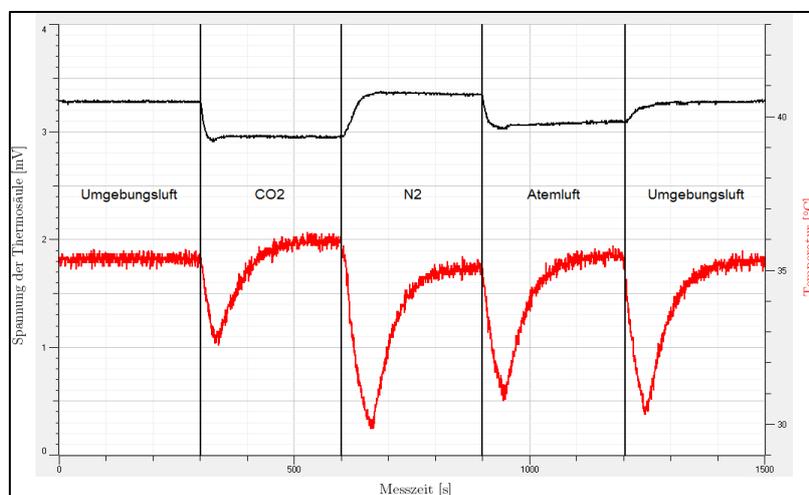


Fig. 16: Temporal course at different media using a 60 W ceramic radiator (Sirtl)

### 3. Summary and Conclusions

The hitherto known basic measuring methods being carried out with gases and/or in the vacuum, particularly that one of Tyndall being widely – but often not correctly - quoted with respect to the greenhouse theory, trace back to ancient work made in the 19<sup>th</sup> century being relied on materials which were then available. Besides simple heat conduction, they solely concerned medium infrared radiation, i.e. thermal radiation occurring at comparatively low temperatures ( $\lambda = 3 - 50 \mu\text{m}$ ), instead of near IR ( $\lambda = 0.8 - 3 \mu\text{m}$ ) being relevant in this context. Moreover, they ever involved the spectroscopic principle where the intensity loss of a radiation beam is measured, but not the temperature increase of the involved gas. Hence, no empirical data are yet available whether, and to which extent, a gas is warmed-up under the influence of near IR-radiation. Furthermore, very weak absorbance cannot be detected since the intensity loss is too low. Such measurements would afford an apparatus exhibiting a very low heat capacity and a perfect thermic isolation which are not given at the equipment being usually employed for demonstration and education purposes at schools.

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