On the influence of carbonic acid in the air upon the temperature of the ground

by Sylvain Cros PhD, École des Mines de Paris – ParisTech

SUMMARY

Svante Arrhenius hypothesised that glacial cycles on earth (since geological times) were the result of natural variations in the quantity of water vapour and carbon dioxide (CO₂) in the atmosphere. He established a quantitative relationship between the variation in the concentration of CO₂ and the variation in the average temperature of the earth's surface. From this he deduced that a doubling of the quantity of CO₂ in the air could lead to global warming of around 5° C. This result is surprisingly relevant today given that the scientists of the Intergovernmental Panel on Climate Change (IPCC) estimate this value to lie between 2.5 and 4.5° C.¹ Arrhenius's calculations are now known to be incorrect. Yet while the relative precision of his results was somewhat fortuitous, Arrhenius's research was a precursor to the quantitative models of the greenhouse effect which are used by climatologists today.



Figure 1: Svante Arrhenius (1857–1929). Image: Nobel Fondation.

^{1.} Fourth IPCC report, 2007, www.ipcc.ch.



BEFORE ARRHENIUS

Over the course of the 19th century, scientists began to better understand which factors governed the earth's surface temperature. A consensus gradually emerged that the sun was the only heat source influencing the lower layers of the atmosphere and that this played a significant role in the thermal equilibrium which determined the planet's temperature.

In 1824, Joseph Fourier (1768–1830) used his theory of heat to explain the origins of the earth's temperature.² He believed that the earth's temperature depended on the combination of three distinct heat sources: solar radiation, the temperature of space, and the earth's internal heat. He demonstrated that the latter was negligible but thought that the temperature of space was similar to that of the earth's polar regions (it is in fact much colder). He outlined a theory of the greenhouse effect produced by heat from the sun, affirming that the atmosphere is more transparent to solar radiation than to radiation reemitted by the earth (i.e. infrared radiation, which was not well understand at the time and known as "obscure heat"). This, he argued, maintains a surplus of heat close to the earth's surface:

The temperature is thus increased by the interposition of the atmosphere, because the heat, being in the state of light, meets with fewer obstacles before penetrating the air than when re-entering the air on being converted into obscure heat.³

There are a few things missing here, namely the fact that the absorption of the earth's infrared radiation by the atmosphere does not directly reduce energy losses towards space. Rather, the atmosphere emits infrared radiation as well as absorbing it – and it is the former that adds extra energy to the surface. It was not until 1861 that John Tyndall (1820–1893) would show how water vapour and carbonic gas are responsible for this greenhouse effect, as a result of their absorption bands in the infrared zone.

See James Lequeux's analysis of Fourier's article for <u>BibNum</u> ("Mémoire sur la température du globe terrestre et des espaces planétaire", *Mémoires de l'Académie royale des sciences de l'Institut de France*, Vol. 7 1827, 569–604).
Joseph Fourier, *op. cit.*



The greenhouse effect in the atmosphere's energy budget

The greenhouse effect as it is now understood is one component in the energy budget of the earth's atmosphere, as shown below.



Figure 2: Energy budget of the earth's atmosphere (grey layer above) [Diagram from A. Moatti, Les Indispensables astronomiques et astrophysiques pour tous, Odile Jacob, 2009]. The solar constant, which is equal to 1367 W/m^2 , measures the quantity of solar energy received by a surface area of $1m^2$ oriented perpendicular to the rays, at a distance of one astronomic unit (AU) (the distance from the sun to the earth). This heat is received by the side of the earth facing the sun (with a surface of πR^2) and is averaged for the whole external surface area of the earth (i.e. $4\pi R^2$). The mean incident solar radiation at the earth's surface is therefore 1367/4 = approx. 342 W/m (the value shown in the upper left-hand section of the diagram).

The earth's infrared radiation (obscure heat) is shown in the bottom right, at $390W/m^2$. It is absorbed by molecules in the atmosphere (water vapour, CO₂) at a height of $370W/m^2$ (and released into space at the height of the difference, i.e. $20W/m^2$). The same molecules emit radiation towards the earth's surface within the same wavelengths, at $330W/m^2$. This is the greenhouse effect.

In 1838, Claude Pouillet (1790–1868) had published a paper on "the radiative and absorbent powers of atmospheric air, and the temperature of space". This was a milestone work, as it was the first to measure and quantify radiative exchanges through the atmosphere. This paved the way to calculating energy and temperature exchanges at the earth's surface, both of which led on from Pouillet's work. Among his achievements, he measured the solar constant (the average radiative power at



the top of the atmosphere) to be 1228 W/m², in others words barely 10% lower than the current estimate value, which is 1367 W/m². He estimated the temperature of space, demonstrating that it is much lower than Fourier had assumed. He developed a simplified representation of the sun-earth-space system and a corresponding model that could be used to calculate surface temperature. As the laws of black-body radiation were not fully established at this time, he assigned a temperature of 1734 K to the sun. It was not until 1879 and the Stefan-Boltzmann radiation law that Joseph Stefan (1837–1893) would estimate a temperature which was very close to the one acknowledged today (5800 K).

At the close of the 19th century, there was no doubt that the radiation emitted by the earth and the atmosphere – which was still known as *obscure heat* – was infrared electromagnetic radiation. Samuel Pierpont Langley (1834–1906) was not only a pioneering aviator: he was also interested in the radiation of the sun and its influence on the earth's climate. His major contribution to this field was undoubtedly the refinement of the spectrobolometer (see panel), a complex and imposing piece of equipment that can be used to measure the radiation intensity of separate wavelengths.

Using this instrument, Langley was able to measure the emission spectrum of an object at room or relatively low temperature (between 0° C and 500° C).

We so habitually associate the idea of a spectrum with that of light, that there is a certain strangeness, at first in the idea even, of a "spectrum" formed by a cold body like, for instance, ice. Yet the ice surface must not only be capable of radiating heat to a still colder body, but according to our present conceptions of radiant energy, be capable of giving a spectrum, whether we can recognize it or not.⁴

Langley calculated the emission spectrum of an object at 100° C. He thereby obtained the first confirmation that, in the lower layers of the atmosphere, the spectra of solar radiation and radiation emitted by the earth's surface (of which the average temperature is 15° C) cover two disconnected spectral ranges. This empirically validated Fourier's hypothesis about the existence of an atmospheric greenhouse effect:

^{4.} Langley, S. P., 1886, "Observations on invisible heat-spectra and the recognition of hitherto unmeasured wavelengths, made at the Allegheny Observatory", *American Journal of Science*, 31(181), 1–12.



To the astronomer, because we find that the heat radiated from the soil is of an almost totally different quality from that which is received from the sun, so that the important processes by which the high surface temperature of the planet are maintained, can now be investigated with, we may hope, fruitful results in connection with the researches here described.⁵

A comparison of the spectra of solar and terrestrial radiation

The spectrum of solar radiation – at the top of the atmosphere – covers wavelengths of 0.2 to 3 μ m, with a maximum of around 0.5 μ m (in the visible region). Close to the surface, the upper reaches of this spectrum at 1 μ m are significantly reduced, having been absorbed by the lower layers of the atmosphere.



radiation after it has traversed the atmosphere (i.e. at sea level): its extent has been significantly reduced, notably beyond 1 000 N, through the absorption of the radiation by atmospheric water molecules. The left of the figure indicates the significant absorption of ultraviolet, in particular the most energetic UV radiation of between 100 and 300 nm.

⁵ Langley, op. cit.



The earth's emission spectrum, on the other hand, covers the infrared region between 1 and 50 μ m, with a maximum of around 13 μ m. The wavelength radiation found in both spectra (between and 3 μ m) is relatively weak in the lower layers. The solar and terrestrial spectra can thus be considered as separate.



In addition, Langley attempted to use his spectrobolometer to measure the temperature of the moon by analysing the infrared radiation it emitted. The fact that the moon has virtually no atmosphere made this task very difficult, because the temperature of the visible side of the moon varies markedly (between 100 and 280 K) depending on the lunar phase. Langley therefore could not use these data.





Figure 5: A bolometer used by Langley (Annals of the Astrophysical Observatory of the Smithsonian Institution, *Volume I, 1900).*

The bolometer (from the Greek *bolè*, radiation) contains a metal plate that absorbs radiation. The electrical resistance of this plate means its temperature can be estimated very precisely (from 10⁻⁵ à 10^{-6°} C). This is turn allows us to deduce the power of the incident radiation. When a rock-salt prism is added, the incident radiation splits in several directions. Each deviation angle corresponds to a specific wavelength. Using a manual rotary system, the bolometer's absorptive plate can be oriented towards the angle associated with the wavelength that one wishes to measure.

ARRHENIUS'S QUESTION

Svante Arrhenius opens his text by asking a highly relevant question about the influence of atmospheric absorption. Does this absorption entail that the earth's mean surface temperature reduces diurnal and seasonal variations, as Tyndall affirmed, or rather does it itself determine the mean temperature? He asks:

A great deal has been written on the influence of the absorption of the atmosphere upon the climate. Tyndall in particular has pointed out the enormous importance of this question. To him it was chiefly the diurnal and annual variations of the temperature that were lessened by this circumstance. Another side of the question, that has long attracted the attention of physicists, is this: Is the mean temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere?

The wording of this question gives a clear idea of the extent of knowledge in this area in 1896, when Arrhenius was writing. Yes, the atmosphere can absorb radiation. Yes, it plays a significant role in the thermal equilibrium between the earth, the sun and space. But does it moderate the variations? Or does it play a role in determining the mean temperature? After citing Tyndall, who argued for the first theory, Arrhenius invokes a bibliography reaching back to Fourier and his principle of the greenhouse effect. He does this to give weight to the second assertion, which is more fundamental in terms of its consequences.

Arrhenius explains that in order to answer this question, one needs to know the intensity of the telluric radiation (emitted by the earth) which is absorbed by the atmosphere. This can be done by calculating the latter's absorptive capacity. This



absorptive capacity was known to depend on the wavelength of the radiation. He therefore suggests calculating the spectrum absorption coefficients of water vapour and CO_{2} .

MEASURING THE ABSORPTION SPECTRUM OF THE EARTH'S ATMOSPHERE ... USING THE MOON'S RADIATION

Arrhenius would give new impetus to Langley's spectrobolometric observations. Because he thought that the temperature of the moon and the earth fall within the same order of magnitude, it followed that measuring the radiation of the moon through the atmosphere would equate to studying the radiation of a body such as the earth, with a temperature of 15° C.

Langley had measured the radiation of the moon at 21 different wavelengths distributed between 1 and 9.5 μ m. Each measurement was corrected in order to take into account the moon's phase and elevation angle, thereby making the measurements comparable. In addition, for each of his observations Langley had measured the relative humidity close to ground level.

Arrhenius would use these data to separately calculate the absorption spectrum of water vapour and CO_2 in the close infrared area. He therefore had to associate each of the observations (the radiative power of 21 wavelengths) with the concentration of water vapour vertically integrated in an atmospheric column (designated as W in his text and in this article) as well as the concentration of CO_2 (designated as K). He then put forward two hypotheses.

The first hypothesis is about water vapour. Arrhenius posits that W is proportional to air mass⁶ and the relative humidity measured close to ground level:

The quantity of aqueous vapour traversed is proportional partly to the "airmass", partly to the humidity, expressed in grammes of water per cubic metre. As unit for the aqueous vapour I have taken the quantity of aqueous vapour that is traversed by a vertical ray, if the air contains 10 grammes per cubic metre at the earth's surface.

^{6.} Air mass is a unitless physical quantity that corresponds to the optical path length through the atmosphere of a ray with a given wavelength. Air mass can be interpreted as the combined "absorption power" of the atmospheric components in a given wavelength.



Today, measurements taken using weather balloons (radiosondes) or satellites allow scientists to obtain very precise values for W, by taking into account the vertical distribution of the concentration of water vapour. However, estimating W on the basis of ground-level humidity and air mass was undoubtedly the most astute solution in 1896. Yet to obtain a good estimate of W using this method, the vertical profiles of the water vapour must be identical at all times and in all places, which, unsurprisingly, is rarely the case. Arrhenius himself mentions the limitations of this hypothesis when interpreting the initial results, which he judges unsatisfactory:

This effect is probably owing to the circumstance that the aqueous vapour in the atmosphere, which is assumed to have varied proportionally to the humidity at the earth's surface, has not always had the assumed ideal and uniform distribution with the height.

The second hypothesis concerns the simultaneous absorption of CO_2 and water vapour. Arrhenius posits that only these two gases can absorb infrared radiation. He also holds that the transmission of the atmosphere in the infrared range can be expressed as a product of the transmissivity due to the exclusive presence of either CO_2 or water vapour. This gives the following equation:

 $T(W,K,\theta) = 10^{Klogx(\theta)} \cdot 10^{Wlogy(\theta)}$

With *T* designating the total transmission of the atmosphere and θ designating the deviation angle of the bolometer prism (corresponding to a particular wavelength), Arrhenius designates *x* and *y* as the respective absorption coefficients for CO₂ and water vapour. Unfortunately, this essential equation is not included in the text. Yet it can be deduced from the results presented in Table II (p. 244). The description of *x* and *y* is inaccurate in that these coefficients are transmission – and not absorption – coefficients. Nevertheless, this second hypothesis is correct because the water vapour and CO₂ spectra are not statistically correlated. In other words, the wavelengths at which the water vapour absorbs the radiation hardly correspond at all with those at which CO₂ is absorbent. However, Arrhenius completely overlooks the significant absorption due to other greenhouse gases such a methane and ozone, whose effect was unknown at this time.⁷

^{7.} The scientific community as a whole has recognised methane and ozone as greenhouse gases since the early 1990s. Before the 1970s, techniques for measuring the atmospheric concentration of these gases were not



Arrhenius expects to see a decreasing function of radiation depending on the concentration of water vapour and CO_2 in the atmosphere. Assuming that the observations must be sorted into time periods in order to avoid variations in what he calls the "clearness of the sky", he divides the data into four periods.

This does not make the results more coherent. He therefore applies a correction to each of the four mean radiation values so that his results are more consistent with those he was expecting. Arrhenius justifies this correction on page 241, though he fails to offer any real explanation:

I have convinced myself that by this mode of working no systematic error is introduced into the following calculations.

He then calculates what he calls the spectrum absorption coefficients for water vapour and CO_2 (Table II, p. 244). He compares his results with those already published. He finds absorption bands of between 5 and 8 µm, which he attributes to the CO_2 , in accordance with the work of Friedrich Paschen (1865–1947) but contrary to that of Anders Jonas Angström (1814–1874). We now know that water vapour is much more absorbent in this spectral range than CO_2 . The latter has a 4.7 µm centred band, whose intensity cannot support the existence of a greenhouse effect. In addition, ozone and methane, which are also absorbent in this range, were not taken into account.

But the fundamental problem with this experiment is the absence of observations at 15 μ m. Though unknown at this time, this CO₂ absorption band is an essential component in this gas's role in the greenhouse effect (cf. Figure 4). In fact, the absorption of CO₂ detected by Arrhenius can be considered "a methodological artefact" [*un artefact de sa méthode*].⁸

^{8.} *Cf.* J. L. Dufresne, *L'effet de serre: sa découverte, son analyse par la méthode des puissances nettes échangées et les effets de ses variations récentes et futures sur le climat terrestre, dissertation submitted as part of the accreditation to supervise research, Pierre and Marie Curie University, January 2009.*



considered as valid. The contribution of these two gases to the total greenhouse effect – in terms of radiative forcing – is around 10%, while water vapour and CO_2 represent 60% and 26% respectively (National Oceanic and Atmospheric Administration, NOAA, http://www.ncdc.noaa.gov/oa/climate/gases.html).

THE SPECTRAL AND ANGULAR SUM: CALCULATING THE TOTAL MEAN ABSORPTION

Using his spectrum absorption coefficients, calculated by measuring lunar radiation, Arrhenius explains his method for calculating the total mean absorption of solar radiation by the earth's atmosphere.

But first he must perform a spectrum integration. Though he notes that the surface of the moon could reach temperatures of 100° C, he does not state how he has adapted his absorption spectrum to a body like the earth, with a temperature of 15° C. Yet the integrated absorption values he obtains are entirely correct when compared with what we know today, where W is equal to 1 (i.e. 10 grams of water vapour to a kilogram, as Arrhenius defines it) and K is equal to 1 (i.e. a CO_2 concentration of 300 ppmv, or 300 parts per million by volume in a given volume of air).⁹

As the absorption coefficients have been corrected to correspond to radiation traversing the atmosphere vertically, an angular integration must be performed in order to obtain the total absorption of the atmosphere in all directions. Arrhenius puts forward a new method called "diffuse approximation" (see panel below). This involves identifying an angle for which the transmissivity of the radiation is very similar to the sum of the transmissivities in all directions. This angle is designated by the inverse of its cosine and, as Arrhenius indicates, can be equated with an optical pathway. This shrewd method removed the need for long and fastidious integral calculus and is still used today in numerical modelling of atmospheric optics.

Diffuse approximation: The modern-day use of Arrhenius's method

The radiation diffused in the atmosphere can be considered as isotropic: its properties do not depend on its direction. The spatial integration of magnitudes such as transmissivity (τ) does not depend, therefore, on the thickness (*D*) of the layer traversed by the radiation. The total transmission is calculated integrally according to the angle of the pathway (θ):

^{9.} Arrhenius uses only relative values in his article: he does not provide an absolute value for the concentration of CO₂. His choice of 300 ppmv can be explained by the fact that this is the estimated value of the concentration of CO₂ in pre-industrial times. The current concentration of CO₂ is estimated to be 380 ppmv (IPCC 2007).



$$T(D) = 2\int_{0}^{\pi/2} \tau(\frac{D}{\cos\theta})\cos\theta\sin\theta d\theta$$

To calculate this integral, Arrhenius suggests finding the length that must be traversed by the total radiation in order for its absorbed fraction to be equal to the sum of the fractions absorbed by the elementary radiation in all directions. The integral can be approximated by determining a specific angle where the inverse of the cosine is α . The total transmission becomes

 $T(D) \approx \tau(\alpha D)$

in which Arrhenius empirically calculates α , termed the diffusion factor, by using variations of its absorption coefficients, depending on the optical pathway. He posits the value of 1.61. Most models of radiative transfer still use this approximation, though with a value of 1.66. This was a remarkable result on Arrhenius's part and still saves a significant amount of time when performing numeric calculations.

THE GREENHOUSE EFFECT MODEL: THE THERMAL EQUILIBRIUM BETWEEN THE EARTH, THE ATMOSPHERE AND SPACE

Arrhenius introduces this part of his paper by noting that Pouillet had already performed these calculations, but that they need to be updated. He is most probably referring to the Stefan-Boltzmann law on black-body radiation, which had not yet been developed in Pouillet's time. Arrhenius's model of thermal equilibrium is based on this law. The equations presented in his text correspond with current models of the greenhouse effect within a single layer (the physical quantities, including K, W and temperature, are considered to be vertically constant within the layer). He nevertheless posits two hypotheses that have since been invalidated by modern-day science:

- The emissivity and the absorptivity of the earth's surface do not vary across wavelengths (the hypothesis set out in equation 1, p. 255). This is incorrect if one considers the most reflective surfaces, such as snow and deserts.
- The atmospheric absorption of solar radiation reflected by the earth's surface is overlooked (equation 2, p. 256). Yet this is very significant, particularly above highly reflective surfaces such as deserts and surfaces covered by snow or ice.



Arrhenius then discusses taking into account snow and cloud cover – the most reflective surfaces in terms of solar radiation – yet his two previous (and incorrect) hypotheses render this consideration rather futile. He discusses the influence of vertical temperature profiles to introduce the notion of emission altitude and emission temperature. Here he places CO_2 at 15 km and water vapour at 233 m. Although a difference in altitude has indeed been observed, these data nonetheless seem rather extreme. Lastly, he concludes that all these phenomena compensate one another and that there is no need to modify his third equation (p. 256).

Calculating variations in surface temperature depending on the concentration of $\ensuremath{\text{CO}}_2$

Arrhenius uses the single-layer model he has just described to calculate the temperature of the earth and how it varies depending on K and W. For water vapour, he compiles a large set of meteorological data and from these he deduces, without any real justification, that the relative humidity at the earth's surface is more or less constant. This allows him to put water vapour to one side and obtain a relationship between the variation in temperature and the concentration of CO_2 .

Although he does not provide a precise formula, Arrhenius's measurements and calculations provide him with an important result, which is still relevant today:

Thus if the quantity of carbonic acid increased in geometric progression, the augmentation of the temperature will increase nearly in arithmetic progression.

That is to say, a doubling of the concentration of CO_2 leads to around a 5° C rise in the earth's mean temperature. This is very close to the range of between 2.5° and 4.5° C projected in the most recent IPCC report. However, it has been shown that the single-layer greenhouse effect model is not useful in calculating warming produced by a rise in CO_2 . In this respect, it would have been necessary to take account of the thickness of the atmosphere, as well as the vertical variation of radiative exchanges in the atmosphere (in other words, the vertical temperature profile).



THE GEOLOGICAL CONSEQUENCES

In the last section of his text, Arrhenius draws on the work of Gustaf Högbom (1857–1940), whose memoir he quotes at length.¹⁰ This memoir analyses past variations in the concentration of CO_2 in the atmosphere. Arrhenius explains that these coincide with significant variations in the mean temperature of the earth, which was the cause of periods of glaciation.

Though he sets aside astronomical factors (variations in the position of the earth vis-à-vis the sun) – which were later demonstrated by Milutin Milankovitch (1879–1958) – Arrhenius makes a rather visionary observation about the retroactive (feedback) effects of the climate system. Without going into complex calculations, he demonstrates that the earth's global temperature has a significant effect on snow cover, with these phenomena in turn acting upon the mean global temperature:

The geographical annual and diurnal ranges of temperature would be partly smoothed away, if the quantity of carbonic acid was augmented. The reverse would be the case (at least to a latitude of 50° from the equator), if the carbonic acid diminished in amount. But in both these cases I incline to think that the secondary action ... due to the regress or the progress of the snow-covering would play the most important role.

Feedback effects, particularly those linked with snow-covered surfaces and clouds, remain one of the root causes of uncertainty in long-term climate forecasting.

Arrhenius concludes by mentioning the geophysicist Luigi de Marchi (1857– 1936), who enumerated the possible reasons for past variations in global temperature but who, like Arrhenius, countenanced the transparency of the atmosphere as the only legitimate cause.¹¹ It comes as a surprise to observe that all the reasons for climactic variation set out by the Italian geophysicist are today accepted as relevant causes (astronomical factors, changes in vegetation, spatial distribution of continents and oceans, transparency of the atmosphere).

^{11.} Luigi de Marchi, Le cause dell'era glaciale, premiato dal R. Istituto Lombardo, Pavia, 1895.



^{10.} G. Högbom, Svensk kemisk Tidskrift, Bd vi, p. 169, 1894.

CONCLUSION

Arrhenius is known as the first scientist to have quantified variations in the earth's temperature as a result of variations in the atmospheric concentration of CO_2 . He was one of a number of important precursors to modern climatology, particularly because his research corresponds to the central question now examined in successive IPCC reports: what range of temperature increase is to be expected for a given variation in CO_2 ? However, the surprising exactitude of his results – compared to what we know today – is somewhat fortuitous. Despite the imperfections in his calculations concerning atmospheric absorption and an overly simplistic model of the greenhouse effect, Arrhenius's work, with its comprehensive view of natural climactic variations, continues to impress contemporary climatologists. Arrhenius emphasises the importance of taking into account climactic feedback effects and considers the carbon cycle as a key phenomenon in explaining variations in the earth's mean global temperature over time.

(April 2011)

(translated by Helen Tomlinson, published October 2015)

