

Eunice Foote's Experiments: an Analysis Based on Chemical Engineering

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This study presents an analysis of the results of the experiments made by Eunice Foote (EF), around the mid of 19th century, on the temperature increase of common gases (such as air and carbon dioxide) when heated by solar radiation. Eunice Foote (EF) is nowadays presented as a woman researcher whose contribution to scientific development in the 19th century has been largely ignored. EF was the author of an article titled "Circumstances affecting the Heat of the Sun's Rays" which contains some statements about a higher temperature increase of carbon dioxide with respect to air when heated by the sun's rays. This article is considered by some science historians as the first experimental proof of the greenhouse effect of carbon dioxide, a theme that is mentioned by the media every day. This analysis of EF experiments is carried out numerically using one chemical engineering process simulation software, with the aim of reproducing her results. Simulated results cannot reproduce EF experiments and are used to evidence some incongruencies in the experimental results. In the end, for the same absorbed energy, a simple heat balance on the gases considered shows that the temperature rise of carbon dioxide would be lower than that shown by air.

1. Introduction

The origin of this study is in a casually read article about Eunice Foote (EF) presented as a woman researcher whose contribution to scientific development in the 19th century has been largely ignored. Eunice Foote was the author of an article (Foote, 1856) titled "Circumstances affecting the Heat of the Sun's Rays" read before the American Association of Science and Arts on August 23, 1856. The article was comparing the temperatures of different gases (in particular air and carbon dioxide) obtained by exposing their containers to the sun's radiation. The EF article, which is less than two pages in length, was reviewed by Scientific American (1856) and presented as an example of the ability of a woman to investigate a subject with originality and precision. A recent article by Ortiz and Jackson (Ortiz and Jackson, 2020) discussed EF experiments in some detail reaffirming the importance of her findings in the history of science. The results of one experiment, solar heating of air and carbon dioxide, were summarized by EF as: "*The receiver containing the gas (carbon dioxide) became itself much heated very sensibly more so than the other—and on being removed, it was many times as long in cooling.*" The conclusion of the author is worded as: "*An atmosphere of that gas [carbon dioxide] would give to our earth a high temperature; and if as some suppose, at one period of its history the air had mixed with it a larger proportion than at present, an increased temperature from its own action as well as from increased weight must have necessarily resulted*" has some clear relations with the very actual and discussed climate-change topic. The following pages present an analysis of EF experiments from the point of view of chemical engineering and describe an attempt to reproduce her results.

2. Experimental equipment and reported results

The description of the experiments is presented as follows: "*The experiment makes use of two cylindrical receivers, of the same size, inside which a thermometer is placed. The cylinders are filled with one gas, exposed at solar radiation for few minutes, the temperatures reached by the gas are measured and compared.*" The gases mentioned are air, hydrogen, oxygen and carbonic acid (carbon dioxide). The dimensions of the two cylinders were specified as 4 inches in diameter and 30 inches in length. Table 1 presents these dimensions

and their conversion into SI units. There is no specification of the material of the containers that are assumed to be made of glass.

Table 1. Cylinder dimensions

Diameter		Length		Volume	
inch	4.0	inch	30.0	inch ³	376.9911
m	0.1016	m	0.762	m ³	0.006178

EF presented the results of her experiments (*"The observations taken once in two or three minutes, were as follows."*) in three tables discussing the following comparisons: 1) Exhausted air vs condensed air, 2) Dry air vs damp air, 3) Common air vs carbonic acid (carbon dioxide). In the following analysis, only the third experiment is considered: the results are reproduced in Table 2, where temperature values in Celsius degrees are added. The table reproduces the different air and carbon dioxide temperatures reached by solar radiation heating. It is impossible not to notice the inaccuracies in the description given by EF of her experiments, in particular: a) the unit of measure of the temperature is never defined, b) the pressure of the gas filling the cylinder is never measured. It must be noted that the review of the article by Scientific American adds the temperature unit reported as "Fah."

Table 2. Temperatures obtained after solar heating for Air and Carbon Dioxide

COMMON AIR				CARBONIC ACID GAS			
Shade		Sun		Shade		Sun	
°F	°C	°F	°C	°F	°C	°F	°C
80.0	26.7	90.0	32.22	80.0	26.7	90.0	32.2
81.0	27.2	94.0	34.44	84.0	28.9	100.0	37.8
80.0	26.7	99.0	37.22	84.0	28.9	110.0	43.3
81.0	27.2	100.0	37.78	85.0	29.4	120.0	48.9

3. Properties of gases and equipment

A summary of the properties of gases used in the experiments and of the equipment characteristics are presented and discussed. The air composition, defined as "US standard atmosphere" by the Handbook of Chemistry and Physics (Lide et al, 2007) is reproduced in Table 3. The mean molar mass results to be 28.964 g/mol and the density is 1225 g/m³ (1.225 g/l).

Table 3. Air composition at sea level (percent by volume)

No	Component	Volume fraction	No	Component	Volume fraction
1	N ₂	78.084	6	He	0.000524
2	O ₂	20.9476	7	Kr	0.000114
3	Ar	0.934	8	Xe	0.000087
4	CO ₂	0.0314	9	CH ₄	0.0002
5	Ne	0.001818	20	H ₂	0.00005

The properties of air and carbon dioxide, at atmospheric pressure, in the temperature range 0-100 °C are presented in Tables 4 and 5.

Table 4. Air properties at atmospheric pressure

Temperature	°C	0	20	40	60	80	100
Molar heat capacity	kJ/kmol °C	29.13	29.14	29.17	29.21	29.26	29.26
Weight heat capacity	kJ/kg °C	1.009	1.01	1.011	1.01	1.01	1.011
Conductivity	W/m °C	0.0239	0.0253	0.0267	0.0281	0.0295	0.0308
Density	kg/m ³	1.2703	1.1836	1.108	1.0415	0.9825	0.9825

Table 5. Carbon dioxide properties at atmospheric pressure.

Temperature	°C	0	20	40	60	80	100
Molar heat capacity	kJ/kmol °C	35.9	36.81	37.7	38.56	39.41	40.22
Weight heat capacity	kJ/kg °C	0.8157	0.8363	0.8566	0.8763	0.8954	0.9139
Conductivity	W/m °C	0.014933	0.016498	0.018087	0.019693	0.021311	0.022937
Density	kg/m ³	1.9379	1.8057	1.6904	1.5889	1.4989	1.4186

In the following numerical calculations, the air is considered a gas mixture formed by nitrogen (N₂), oxygen (O₂), argon (Ar), and carbon dioxide (CO₂) only. It is assumed that the experiments are performed at atmospheric pressure and by applying the ideal gas law, at equal temperature and pressure, the same volume of gas will contain the same number of moles. Being the molar heat capacity of carbon dioxide greater than the value of air, it follows that, when exposed to solar radiation, the expected temperature increase of carbon dioxide should be lower than that of air. Thus, the result would therefore be contrary to that stated by EF. Some attention should be devoted to the equipment used in the experiments. The first assumption to be introduced is that the cylinders are made of glass whose physical properties are assumed to be: heat capacity 0.840 kJ/kg K, density 2520 kg/m³, thermal conductivity 1.05 W/m K. The volume of the cylinder and its external area are shown in Table 6 and its weight, for thicknesses between 1 and 3 mm, is shown in Table 7.

Table 6 – Glass cylinder dimensions

Property	Unit	Value	Property	Unit	Value
Circumference	m	0.319186	Volume	m ³	0.006178
Cylinder area	m ²	0.24322	Head area	m ²	0.032429
Heads volume	m ³	0.000549	Total area	m ²	0.308078
Total volume	m ³	0.006727			

Table 7 – Glass cylinder weight by thickness

Thickness	Mm	1.0	2.0	3.0
Surface	m ²	2.76E-01	2.76E-01	2.76E-01
Volume	m ³	2.76E-04	5.51E-04	8.27E-04
Density	kg/m ³	2520	2520	2520
Weight	kg	6.15E-01	1.23E+00	1.84E+00

The mass of the fluid can be easily obtained from the molar volume of 22.414 m³/kmol at 0 °C and 1 atm. The number of mols may be a function of the pressure and considering a range between 1 and 3 atm, the mass of the fluid filling the cylinders is shown in Table 8.

Table 8. Fluid mass content by pressure.

Pressure	atm	1.0	2.0	3.0
Fluid moles	kmol	3.00E-04	6.00E-04	9.00E-04
Air weight	kg	0.008764	0.017527	0.026291
CO ₂ weight	kg	0.013235	0.026471	0.039706

It is easy to remark that the fluid weight used in the experiment is lower than 2% of the equipment weight and that the whole mechanism of heat transfer between the containing cylinder and the contained fluid is never mentioned nor considered by EF. The mass of the thermometer was probably greater than that of the gas.

4. Models for numerical simulation

The initial attempt of the interpretation of EF results was based on the numerical values of heat capacity and thermal conductivity of the fluids. Because the experiments involve fluid heating due to the sun radiation and cooling by the external ambient, heat capacity and thermal conductivity of the two fluids are obvious parameters. Since the heat capacity of carbon dioxide is higher than that of air so, for the same amount of energy flux, the temperature increase of carbon dioxide should be lower than that of air. A reverse temperature change, such as that described by EF, could be attributed only to the difference in thermal conductivity since the value of air conductivity is higher than that of carbon dioxide. Thus, the only qualitative explanation of the final higher carbon

dioxide temperature could be the result of lower heat flux from the contained fluid to the external ambient air through the cylinder wall. As shown afterward this hypothesis is not supported by numerical calculations of the phenomenon. To simulate the EF experiments the solution of the heat balance is required and a heat balance relation between the contained gas and the container can be written as:

$$m_g C_{p_g} dT_g + m_w C_{p_w} dT_w + dQ_{rad} + dQ_{ext} = 0 \quad (1)$$

Here the subscript **g** applies to the gas and **w** to the container wall, **m** is the mass, **C_p** is the heat capacity, and **T** the temperature. The first two terms take into account the heat exchanged between the contained fluid and the container, **Q_{rad}** is the sun radiation and **Q_{ext}** the heat exchanged between the container and the external ambient air. Since $m_g C_{p_g} \ll m_w C_{p_w}$, a heat flux from the inside fluid to the container implies a fluid temperature decrease of about 50 °C for 1 °C increase of the container temperature. The heat transfer calculation model implemented in the simulation considers the following effects and parameters: 1) Solar radiation at ground, the inclination at different hour of the day is considered, 2) External heat transfer coefficient between the glass wall and the surrounding air. The external heat-transfer coefficient is calculated taking into account the actual wind velocity, 3) Transient heat flux across the glass is considered and simulated on the basis of wall thickness, conductivity and heat capacity, 4) Internal heat transfer coefficient between the internal fluid and the inner glass surface. Owing to the large difference of mass between the containing apparatus and the contained fluid one can state that the final temperature of the fluid is a function of the experimental apparatus used. For the same external conditions and the same apparatus, the final fluid temperatures should be the same. The implementation of the sun radiation in the heat-transfer model was developed on the basis of the chapter on radiation of the book of White (1988).

5. Numerical simulation

The numerical calculations are performed using one simulation tool (XPSIM, 2023) developed for chemical engineering plant design and for the simulation of multi-phase fluid transport in chemical plants, pipelines, and pipe networks. It includes thermodynamic functions and equations of state for the calculation of vapor-liquid equilibrium and thermodynamic properties such as enthalpies and heat capacities as well as transport properties. Vapor-liquid equilibria calculations are not involved in this study, so pure component vapor pressures are used to verify that fluids are always in the vapor phase. Gas enthalpies and heat capacities are calculated using the GERG equation of state (Kunz and Wagner, 2012) and the transport properties by the Ely-Hanley model (1981,1983). At the earth's surface, the maximum solar irradiance can reach 885 W/m² and in the following calculations the solar irradiance is assumed to be 850 W/m² with a radiation heat factor equal to 0.5 is applied. This value is adjusted by considering the inclination of solar rays related to the geographical location and the time of day. The external wind velocity is assumed to be 2.0 m/s and some results of the effects of these factors will be presented. The thickness of the glass wall is assumed to be 3 mm. All dynamic simulations consider the same sequence of events as follows: 1) At the initial time the fluid is flowing across the cylinder at the selected pressure and temperature. 2) After 5 minutes the inlet and outlet valves are closed letting the fluid reach a thermal equilibrium with the surrounding air at the ambient temperature. 3). At time of 10 minutes the cylinder is exposed to solar radiation for 10 minutes letting the internal fluid absorb solar energy and reach a higher temperature eventually in equilibrium with external air. 4) At time of 20 minutes the cylinder is moved into the shade and the simulation is continued for up 30 minutes. The temperature of the fluid, its pressure, and other process parameters are sampled every second. The geographical site is assumed to be the New York City area (latitude 41 °, longitude -74 °) and the simulations are performed assuming the date of the summer solstice: 21 June 2022 at 12:00. The effects of glass transparency (transmitted and reflected radiation), that only half of the cylinder surface is directly irradiated and other effects are summed into a solar radiation heat factor set equal 0.5. A sharp dependence of the maximum gas temperature on the ambient conditions, defined by a) the hour of the day and b) the ambient wind velocity, has been found. Table 9 includes the temperature values calculated for air when the ambient air velocity is varied in the range 1-3 m/s for two different times of day.

Table 9. Maximum air and surface temperatures vs time and wind velocity

Time, hh:mm	Wind velocity, m/s	Air temp °C	Glass temp, °C
12:00	1.0	46.7	66.4
12:00	2.0	40.6	54.2
12:00	3.0	37.8	48.7
14:00	1.0	44.3	62.0
14:00	2.0	38.9	51.1
14:00	3.0	36.5	46.2

Of the four cases listed in Table 2, the calculated results for two cases are presented. The first case uses the same ambient air temperature for both fluids. The second case presents the maximum difference between the ambient temperatures for the two fluids. The pressure of the fluids used in the experiment is atmospheric. The carbon dioxide–air comparisons are presented in Figures 1a and 1b. The time interval required for carbon dioxide to reach the limiting temperature of the glass is higher than that of air due to the difference of heat capacity. The difference in thermal conductivity has an effect on the surface heat-transfer coefficients between the fluid and the internal glass surface but this difference has no significant effect on the maximum fluid temperature.

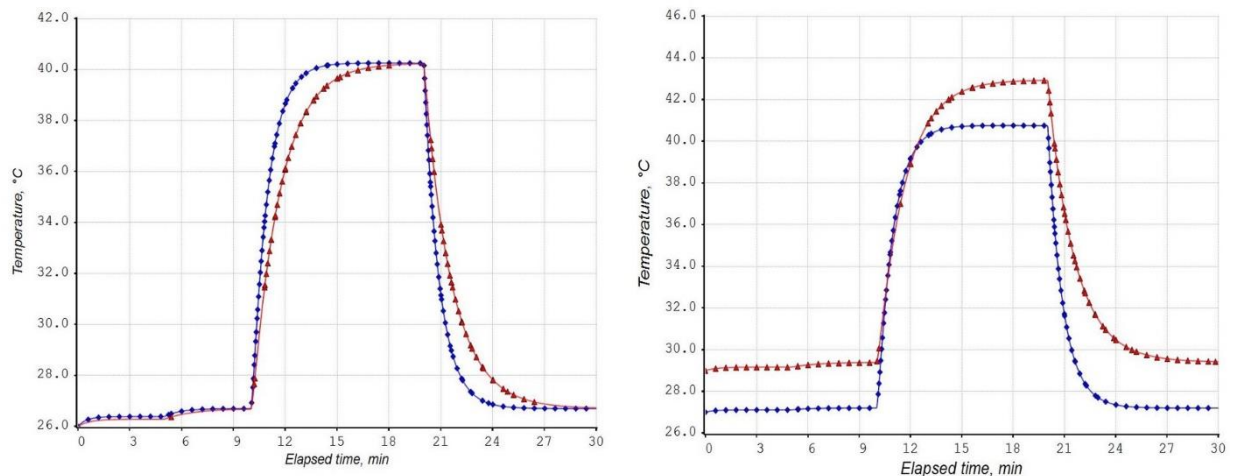


Figure 1 a, b: Experiment 3, Air (\diamond) and carbon dioxide (Δ) temperatures. Case 1 (a) and case 2 (b)

As mentioned by the EF article, the time required to cool down the carbon dioxide container is significantly higher than that of the air and this is clearly shown by the same figure. Figure 1a shows air and carbon dioxide temperature curves calculated with the same ambient temperature of 26.7 °C (80 °F) as defined by the first line of Table 2. Figure 1b presents the temperature curves for air and carbon dioxide for different ambient temperatures as given by the last line of the same Table 3: 27.2 °C (81 °F) for air and 29.4 °C (85 °F) for carbon dioxide. The summary of results from numerical simulations are shown by Table 10.

Table 10. Air and carbon dioxide temperatures

Case	Air		Carbon dioxide	
	Shade, °C	Sun, °C	Shade, °C	Sun, °C
1	26.7	40.3	26.7	40.2
2	27.2	40.8	29.4	42.9

6. Conclusions

The results of Eunice Foote's experiments could not be reproduced by chemical engineering simulations. Some considerations can be devoted to the more discussed experiment about the differences of temperature increase of air and carbon dioxide when subjected to solar radiation which is interpreted by many authors as an early result of the detection of carbon dioxide as a greenhouse gas. The simulations suggest that; being all ambient parameters the same, the contained fluids reach the same maximum temperature determined by the

container's thermal properties. The difference in the time necessary to reach the maximum temperature is defined by the mass of the fluid, heat capacity, and thermal conductivity. The results presented by EF can hardly be accepted as correct since are biased by a large number of effects and parameters not measured in the experiments. Out of four results (Table 2), it is remarkable that when air and carbon dioxide are heated starting from the same shade (external) temperature the two fluids reach the same final temperature. Besides the ambient (shade) temperatures of the CO₂ experiments are higher than those of the air so the maximum temperature reached is obviously higher. The highest carbon dioxide temperature in the sun is obtained when the ambient (shade) temperature is the highest. It is possible to conclude that EF results are the effect of different uncontrolled external conditions and her conclusions are not acceptable. The EF conclusion about the larger temperature increases of carbon dioxide with respect to the air is expressed as: *"The receiver containing the gas became itself much heated very sensibly more so than the other—and on being removed, it was many times as long in cooling"*, suggests that a higher container temperature is the effect of the higher temperature reached by the contained gas. This statement seems to ignore absolutely the mechanism of heat transfer between a contained gas and its container: it reverses the direction of heat flow attributing a function of heat pump to the internal fluid. By a straightforward application of the law of conservation of energy to an equal molar mass of air or carbon dioxide and by use of their physical properties, one can state that: for the same amount of incoming energy (solar radiation) exchanged between the ambient and the gas, the temperature increase of carbon dioxide is lower than that experienced by air.

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