

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

TEMPERATURE PROFILE OF GRAPHITE SURFACE BURNING IN A STREAM OF
OXYGEN

D. Kisch

(NASA-TM-75271) TEMPERATURE PROFILE OF
GRAPHITE SURFACE BURNING IN A STREAM OF
OXYGEN (National Aeronautics and Space
Administration) 12 p HC A02/MF A01 CSCL 21B

N78-21232

Unclas
G3/25 12349

Translation of "Über den Temperaturverlauf vor
im Sauerstoffstrom brennenden Graphitober-
flächen", Bunsengesellschaft fuer physikalische
chemie - berichte, Vol. 71, No. 1, 1967, pp. 60-64.



STANDARD TITLE PAGE

1. Report No. NASA TM-75271	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Temperature Profile of Graphite Surface Burning in a Stream of Oxygen		5. Report Date April 1978	
		6. Performing Organization Code	
7. Author(s) D. Kisch		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address SCITRAN Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASw-2791	
		13. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes Translation of "Über den Temperaturverlauf vor im Sauerstoffstrom brennenden Graphitoberflächen" Bunsengesellschaft fuer physikalische chemie - berichte, Vol. 71, No. 1, 1967, pp. 60-64.			
16. Abstract Using new methods for the objective measurement of the spectrum line reversal temperature in burning gases, the temperature pro- file at a graphite surface burning in a stream of oxygen has been measured. From the behavior of the reversal temperature, it follows that particles in longlived, high-energy states are present in the burning gas, and these bring about an over- excitation of the atomic species emitting the reversal line. Qualitative measurements show that a temperature maximum occurs at the expected distance of 1-2 mm from the graphite surface.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unclassified - Unlimited	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 12	22.

TEMPERATURE PROFILE OF GRAPHITE SURFACE BURNING IN A STREAM OF OXYGEN

D. Kisch*

INTRODUCTION

At temperatures above 1000°C, carbon reacts with oxygen so quickly /60** that at atmospheric pressure, the diffusion of oxygen to the surface of the carbon is the rate-determinative factor of the entire combustion reaction. Thus, the O₂-concentration decreases as we approach the carbon and the concentration of the product CO increases. In addition to the direct action of oxygen on the carbon, two secondary reactions occur: an additional combustion of the graphite by the Boudouard reaction ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$) and a homogeneous post-combustion of the CO originating from the above reaction and from the direct action of the oxygen. The effects of these reactions leads to a maximum CO₂-profile, as Wicke, Hugo, and Wurzbacher [1, 2] demonstrated on a theoretical and experimental basis (Figure 1).

As a result of the very exothermic CO-post combustion in the diffusion interface, there should be a temperature maximum in the vicinity of the CO₂-maximum. In order to check this, we attempted to measure the temperature field of such burning graphite surfaces.

I. APPARATUS

Due to the expected high temperatures (> 2000°C), thermoelements cannot be considered for quantitative measurements. Optic procedures of measurement which do not require any disturbing sondes to be inserted

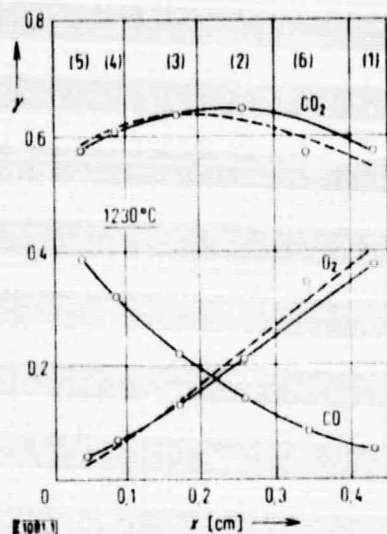
* Institute for Physical Chemistry of the University of Muenster.

**Numbers in margin indicate pagination in foreign text.

into the temperature field are needed. The measurement method selected was developed specifically for the present task of objective measurement of the spectrum-line reversal temperature in burning gases [4].

The optic and electronic arrangement of this procedure has already been detailed in a previous publication [3]. For our measurements, only the methane burner was replaced by a perpendicular reaction tube made of quartz-glass (6.5 cm diameter, 54 cm long). The oxygen is introduced into this tube from below and the graphite block with holder extends down from the top; see Figure 2. The holder consisted of a quartz-glass tube R of 10 mm diameter to which a cylindrical flowbody S was welded. A drilled ceramic block (steatite-magnesia) connected flush with the drilled graphite block (20 x 20 x 50 mm). By means of this arrangement and an appropriate starting run in the quartz tube (Distance of gas inlet to flow body is about 25 cm to contact of the turbulences occurring at the inlet) a laminar flow to the graphite block was achieved. A tungsten strip-helix was located inside the holding tube for heating the graphite block. This helix is surrounded by dry, O_2 -free nitrogen. This holder is hanged into the reaction tube by means of a water-cooled metal nose cap (see Figure 3). Two plane-parallel quartz-glass windows for the passage of the optic rays are located at the reaction tube. The graphite block was moved by means of an adjustment device at the metal nose cap so that one side grazes the optic axis. A third window located perpendicular to the optic axis (right part of Figure 3) makes it possible to measure the surface temperature of the graphite block at the opposite side pyrometrically and to control it automatically. (Because of the temperature gradients in the graphite block, thermoelements proved useless for this purpose).

A metal support frame holds the reaction tube on a cross-slide; in this manner the entire apparatus can be shifted horizontally or vertically. The horizontal motion was important to measurements using the intersection procedure [3, 4] in order to be able to shift the graphite block in proportion to the burnoff so that its side faces the optic ray passage. After determination of the linear rates of burn-off as a function of the surface temperature, this advance was automated by using a spindle and controllable electromotor and it was adjusted appropriately



ORIGINAL PAGE IN
OF POOR QUALITY

Figure 1: Concentration profile of a graphite surface burning in a stream of oxygen [1].

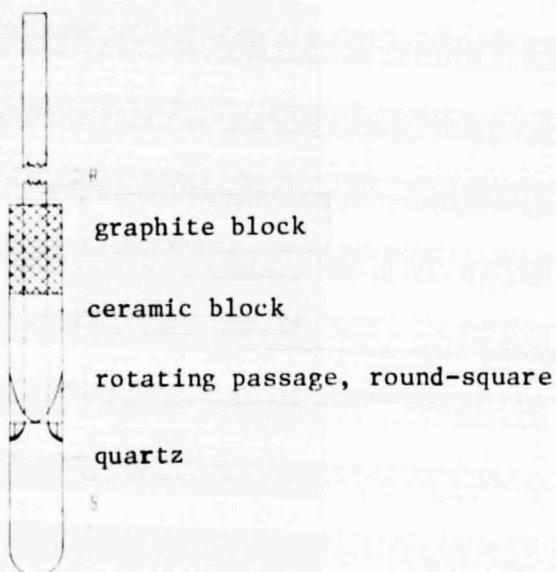


Figure 2: The holder for the graphite block.

at the beginning of each measurement. In measuring by the isotherm method, the horizontal adjustor was used to drive the selected region of the flame-zone across the optic ray path [3, 4].

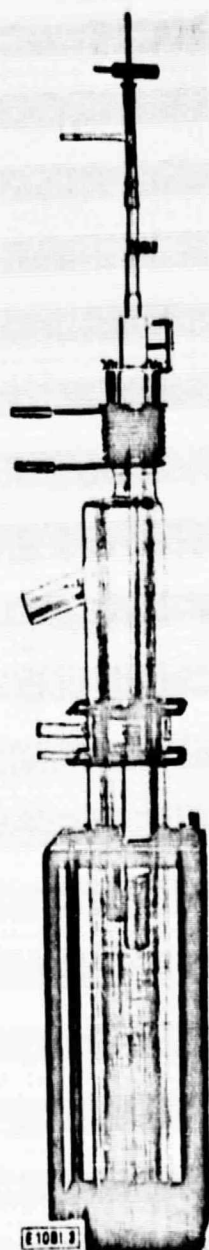
After triggering the reaction by means of the tungsten strip-helix heater, the temperature of the graphite block continues autothermically in the oxygen stream to about 1000°C . Since all measurements are taken at high temperatures, this temperature was held constant by a controlled

electric heater. The temperature indicator was a simple, self-made electric pyrometer with a Si-photo cell (solar cell) located in front of the third quartz-glass window which reacts to the entire radiation of the burning graphite surface. By means of a relay system, it controlled a partial circuit to the secondary electric heater. In addition, the basic load on the auxiliary heater was reduced during each measurement proportionally to the increasing graphite burn. This was accomplished by an electrically-controlled spindel resistor. This double control operated with such reliability that no time-fluctuations in graphite surface temperature were detected by an optic micropyrometer whose accuracy is cited at 1 degree at 1000°C.

To color a part of the flame-zone in front of the graphite surface,^{/62} we used a thin-wall, Pythagoras capillary tube (1 mm diameter) filled with a flame-coloring salt (usually NaCl). It was introduced into the reaction tube by a side support, visible to the left of Figure 3. Its mouth was always about 5 mm from the middle of the lower edge of the graphite block. The colored, emitting zone reached a diameter of about 10 mm when 10 mm above the mouth; this zone lay in the middle of the broad side of the graphite block*. The optic ray path was adjusted at this level to keep the reversal temperatures free from disturbances due to the lower edge and the side edges of the graphite. This adjustment also promoted the detection of a region of the colored zone where the gas temperature is constant along the ray path.

Since the CO-combustion is greatly catalyzed by traces of moisture, the procedure required extremely dry oxygen to maintain a spacially-pronounced flame zone of CO post-combustion before the surface of the graphite [1]. Therefore, the oxygen stream was passed in sequence through a trap filled with dry-ice/methanol, a tower with heated molecular sieve and a dessicator lined with P_2O_5 on glass-wool. The rate of flow was a constant $230 \text{ cm}^3 \text{ NTP/sec}$; the average linear flow rate in the reaction tube at the level of the graphite block was about 30 cm/sec.

*This type of coloring disturbs the shape of the flaming zone far less than the introduction of salt-mists with a gas flow from a sonde [4].



ORIGINAL PAGE IS
OF POOR QUALITY

Figure 3: Reaction tube with quartz windows, metal cap and hanging graphite-block holder. The white ceramic block is discernable below the windows.

II. PERFORMING THE MEASUREMENTS

Since only about 5 minutes are available for the measurements due to the rapid burn of the carbon, the so-called isothermal method was normally used. The method - detailed elsewhere [3] - consists in passing through the colored zone perpendicular to the optic-ray path

while keeping the temperature of the tungsten-strip lamp constant, and in doing this, the profile of the excess - or deficiency - intensity is recorded, that is, the emission or absorption of the colored zone is recorded. In one such procedure, all "zero-points" of the intensity (reversal points) were recorded along the traversed route in front of the graphite whereas the intersection method [3] permits measurement at one point only. Therefore, only a few measurements were taken with the intersection method for the sake of comparison.

After setting the desired strip-lamp current strength between 9 and 13 A (corresponding to reversal temperatures between about 1700 and 2200 °K), the graphite block was heated by the tungsten strip helix - in already-flowing oxygen - and its temperature control was switched on. The coloring tube was put into position, and the monochromator was set to the maximum of the resonance line after shielding off the strip-lamp (maximum deflection of the measurement instrument at the phase-sensitive amplifier*).

Then, the flame zone to be studied is passed through at great distances from the graphite (emission of the pure strip-lamp radiation) horizontally through the ray-path until the image of the tungsten strip of the lamp is shaded out by the graphite block. The recorded curve of a Na-D reversal measurement before the burning graphite surface is illustrated in Figure 4; the evaluation of this type of curve has been reported elsewhere ([3], see also [4, 6]).

Because of the rectangular shape of the blocks, measurements could only be taken to within 0.5 mm of the broad side of the block because of the aperture geometry.

The surface temperature of the graphite was always determined pyrometrically; the emission capacity assumed to be equal to 1 is a good approximation [4].

*Adjustment of the monochromator to the resonance line by means of spectral lamps did not prove beneficial [4].

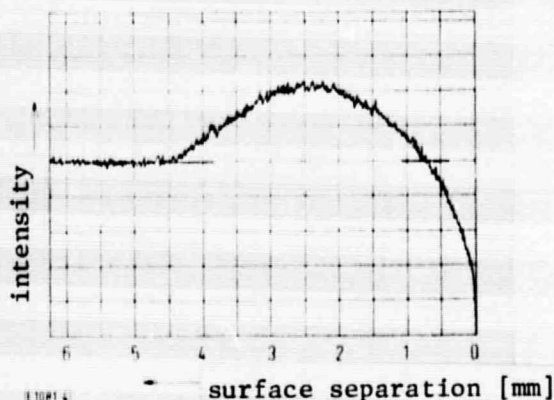


Figure 4: Recorded curve of a Na-D reversal measurement by the isothermal method. Surface temperature of the graphite block, 1400 °K; tungsten lamp current: 10.0 A ($S_{\lambda} = 1875$ °K).

III. MEASURED RESULTS

From the curve shown in Figure 4, we see that at a distance to the surface of 0.75 ± 0.1 mm, the temperature of the flame zone is equal to the set black-temperature of the tungsten-strip lamp (reversal temperature 1875 °K). With increasing distance from the surface, the flame temperature increases beyond this (excess emission); at a distance of about 3 mm, it should again equal the strip-lamp temperature, and from there as far as the edge of the colored zone at about 4.5 mm, the intensity curve should run below the horizontal isotherm of the simple lamp radiation. One such intensity minimum, caused by the absorption in the colder peripheral zones of the colored region, did not occur in Figure 4, although it was always observed for measurements on Bunsen-burner flames (see [3], Figure 7). It could not be found in any of the numerous curves taken under different conditions. The reversal temperatures obtained, increase uniformly with increasing distance from the surface of the graphite. This is shown in Figure 5 for a /63 measurement series with constant surface temperature. The measured points of the isotherm method were obtained at different settings of the tungsten strip lamp (Fig. 4); measurements with the intersection method, also shown in Fig. 5, had the same profile. Even at higher surface temperatures (up to 1550 °K) and with the K-resonance line used instead of the Na-D line, profiles of the reversal temperature were always obtained which rose uniformly up to the extreme edge of the colored zone.

In order to at least determine the existence of a temperature maximum

qualitatively, the flame-zone was traversed horizontally by PtRh 10PtRh (EL 18) - thermoelements (wire gauge 0.1 and 0.05 mm, blank splice). A profile obtained in this manner at 1400 °K is also entered in Figure 5. According to this it is certain that a maximum of the (reversal) temperature occurs at about 1900 °K at 1-2 mm distance in front of the burning graphite surface.

The contrasting, very anomalous profile of the line reversal temperatures is indicative of significant deviations of energy distribution from thermal equilibrium in the flame-zone. It has long been known that for "dry" CO-oxidation, highly active CO_2 molecules are formed first

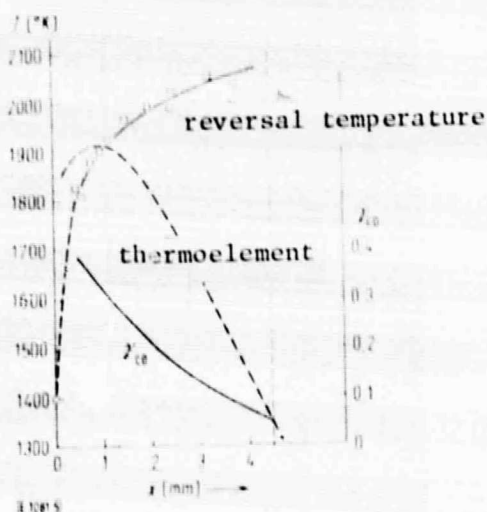


Figure 5: Temperature profile of the graphite surface burning in a dry stream of oxygen at 1400 °K.

- - point measured by the isotherm method
- - point measured by the intersection method
- γ_{CO} - mole fraction of carbon monoxide, schematic from [1].

(designated below as CO_2^*) which store the important amounts of liberated chemical energy in the form of oscillation energy [7]. The lifespan of these over-excited oscillation states is very long in pure CO_2 or in CO_2/O_2 mixtures, but it can also be greatly reduced by the addition of suitable catalysts [10]. According to Metter [8, 10], carbon monoxide and especially hydrogen and steam are excellent catalysts for ensuring equilibrium of energy distribution of the CO_2^* molecules.

Since the free alkali atoms are much easier to excite electronically by the transfer of oscillation energy than by translation energy [9], the results of line-reversal measurements for deviations from thermal equilibrium correspond more to the oscillation temperature of the highly excited CO_2^* molecules than to the translation temperature.

The CO-concentration rises uniformly out to the surface of the graphite, as shown in Figure 5. As a result of the effect of the CO-molecules (catalytic effect), the reversal temperatures measured there come closer and closer to the equilibrium values.

By addition of a suitable catalyst - like H_2 or H_2O molecules - one should be able to attain temperature equilibrium in the entire post-combustion zone. But since even the CO-oxidation is greatly accelerated by such catalysts, an addition of 2-3% steam - which would be needed here [7] - would initiate CO - after burning in the pores of the graphite block and no flame zone would form in front of its surface. Additions of smaller quantities of steam (up to about 500 ppm) and various other gases had no notable influence on the profile of reversal temperature. Without an equilibrium distribution of energy to the degree of freedom of all gas molecules, a temperature in the thermodynamic sense is not defined. But nevertheless, in order to arrive at temperature data, the electron populations of the individual degrees of freedom of all gas molecules would have to be determined by IR-methods, for example, and the appropriate equilibrium temperatures would then be calculated from the total energy obtained.

The line reversal and the thermo-element measurements did point up, however, that a maximum of translation temperature is present at the expected distance of 1-2 mm in front of the graphite surface. At a temperature of the graphite surface of 1400 °K, the maximum is at about 1900 °K.

Thanks are due Dr. E. Wicke for his valuable suggestions regarding this work and for his support and participation.

These studies were promoted within the framework of the project

"Basic Research in the area of chemistry and physics on soft coal and coke" under the participation of the Essen Soft Coal Mining Union of the Main Office of the European Community on Coal and Steel.

REFERENCES

1. Wicke, E., and Wurzbacher, G.: Int. J. Heat Mass Transfer 5, 277 (1962).
2. Hugo, P., Wicke, E., and Wurzbacher, G.: Int. J. Heat Mass Transfer 5, 929 (1962).
3. Kisch, D., Mahnig, M.: Bunsuenges. physik. Chem. 71, 54 (1967)
4. Kisch, D.: Dissertation, Muenster, 1966 /64
5. Kisch, D.: Graduate work, Muenster, 1963.
6. Mahnig, M.: Graduate Work, Muenster, 1966
7. David, W. T. and Pugh, B.: Nature [London], 140, 1098, (1937).
8. Metter, I. M.: Phys. Z. Sowj., 12, 232, (1937).
9. Gaydon, A. G.: Nat. Bur. Standards Circ. 523, p. 1
10. Gaydon, A. G.: Spectroscopy and Combustion Theory, London, 1948.