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C. TH. J. ALKEMADE
Tj. HOLLANDER
P. J. KALFF

*Physics Laboratory of the State
University of Utrecht,
Bijlhouwerstraat 6,
Utrecht, Holland*

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Temperature Measurement in a Chemical Shock Tube Using Chromium Hexacarbonyl

THE use of chromium hexacarbonyl in a shock tube for the excitation of chromium lines, has been described by G. CHARATIS and T. D. WILKERSON¹. Later work by A. G. GAYDON

and I. R. HURLE² led to their describing measurement of temperature by reversal of the chromium resonance triplet at 4 254, 4 274 and 4 289 Å, against a background source using a double beam system. In the earlier work the excitation was at temperatures of 5 000° to 10 000°K behind the reflected shock, while in the later work measurements were made behind the incident shock in the temperature range 2 000° to 3 000°K.

The work reported below is of measurements made behind the reflected shock in a chemical shock tube in which mixtures of methane and argon were driven by hydrogen and nitrogen. Measurement was by the single beam method, but as previously stated³ the reproducibility of the performance of the shock tube had been improved sufficiently to allow matching with the background source, which was a tungsten ribbon lamp. Measurements were made in the temperature range 1 900° to 2 500°K.

In that chromium hexacarbonyl has a vapour pressure of about 0.25 mm of mercury at room temperature, the driven gas could be prepared containing this quantity of additive, and this was done in a 30 l. Pyrex vessel fitted with a stirrer. The driven section of the shock tube was then filled with this mixture. If a lower concentration of chromium was required, this mixture was diluted in the driven section with methane and argon mixture, from the main storage vessel. It was thus possible to measure temperature over a range of concentrations of chromium hexacarbonyl, and to observe the effect of the addition on the reactions occurring in the tube. The effect was judged from the results of experiments in which the shock tube was prepared similarly each time, and in which the following measurements were made: incident shock velocity, percentage methane decomposed, percentage methane converted to acetylene. Results of such experiments are shown in *Table 1*, where it will be observed that there is no detectable effect of the chromium hexacarbonyl on the reaction.

In previous work³ good agreement was obtained between temperatures measured in mixtures of shock-heated methane and argon by the sodium-line and C₂ (5 165 Å) reversal methods. The present measurements have been

Table 1. Effect of chromium hexacarbonyl on the decomposition of methane

Reaction conditions	%Cr (CO) ₆ added	Incident shock velocity (ft/sec)	% CH ₄ decomposed	% CH ₄ converted to C ₂ H ₂
25 lb/in ² abs. initial reaction partial pressure of CH ₄ . Measured temperature 2250°K. Reaction time 1 msec. Driving pressure 250 lb/in ² abs.	None	4 480	93	58
	0.01		93	58
	0.06	4 430	91	59
	0.065	4 480	95	60
	0.07	4 440	95	56
	0.075	4 440	94	57
	0.08	4 480	93	59
14 lb/in ² abs. initial reaction partial pressure of CH ₄ . Measured temperature 2250°K. Reaction time 1 msec. Driving pressure 130 lb/in ² abs.	None	4 550	96	63
	0.02	4 550	97	60

Driving gas: 95% H₂, 5% N₂. Driven gas: 90% Ar, 10% CH₄. Pressure ratio: 162.

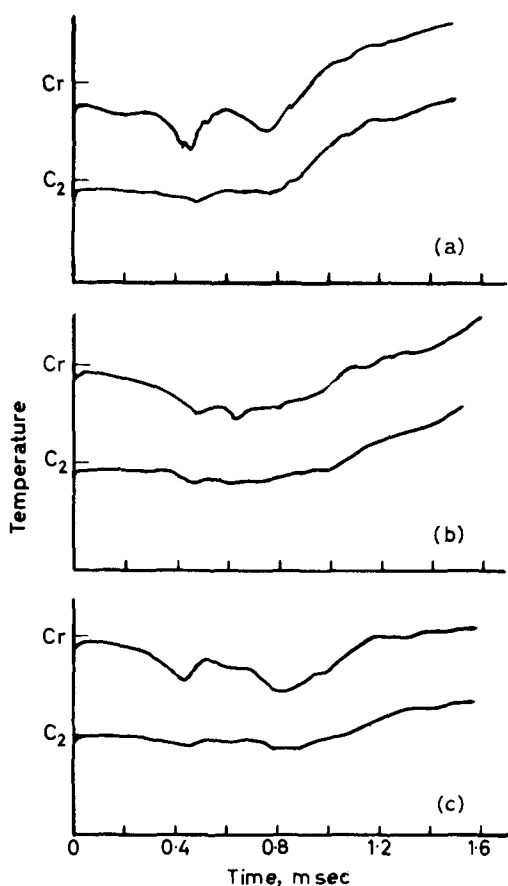


Figure 1. Oscilloscope records showing simultaneous C₂ and Cr temperature measurements. Pressure behind reflected shock 250 lb/in² abs. Backing lamp temperature: in Cr region, 2320°K, in C₂ region 2290°K. Chromium hexacarbonyl concentration: (a) 0.07, (b) 0.01, (c) 0.005 per cent

compared with those obtained by C₂ reversal by simultaneous observation of the C₂ and chromium reversal temperatures using photomultipliers of equal sensitivity that received radiation from the appropriate part of the spectrum. Typical oscilloscope records are shown in Figure 1 (a), (b) and (c). These and other experiments illustrate the fact that the values of temperature deduced are independent of the concentration of chromium hexacarbonyl. It is also seen that when temperature is measured by reversal of the chromium triplet, but at a setting for matching for C₂, the backing lamp temperature is slightly too low. This deviation is less than 50°, which is the normal accuracy of a single measurement. Because the emissivity of the tungsten filament varies with wavelength, there is a difference in temperature of 30° (as calculated from Wien's law) between that in the 5165Å region and that in the 4270Å region.

An alternative method of expressing the temperature difference was to compare the difference in time between the crossing by the two records of their respective matching lines. The time lag of the chromium record behind that of C₂ was consistent at 0.1 msec in the portion of the record representing the cooling period. This time lag arose from the temperature differential between the two records. The cooling rate is between 2 and 5 × 10⁵ °K/sec, thus representing a temperature difference between 20° and 50°. This variation results from whether the cooling is by the main rarefaction or by interaction at the interface. This difference is illustrated in Figure 1 (a) and (b). Thus a

comparison may be made by taking a specific example as follows:

Temperature during cooling measured by C_2 reversal: $2\,290^\circ\text{K}$

Temperature at the same instant by chromium triplet reversal: $2\,290^\circ + X + Y$

where X is 30° (as by Wien's law) and

Y is 20° to 50° (as described above).

From the foregoing it will be seen that the temperature of a reacting mixture of methane and argon, as measured by the reversal of the chromium triplet, is higher than that measured by C_2 reversal. The magnitude of this difference is between 30° and 80° , the temperature measured by the reversal of the chromium triplet being the greater. The existence of this temperature difference has been established in the investigations carried out, and it is independent of the experimental error which affects a single value by $\pm 50^\circ$. The main factors determining the magnitude of the experimental error were the calibration of the backing lamp, the precision of the ammeter³ readings, and the reflection and transmission effects at the windows and optics. All these were, however, common to both determinations.

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G. M. KIMBER*

D. H. NAPIER†

Vickers Research Ltd,

Sunninghill, Ascot, Berks.

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*Present address, B.C.U.R.A., Leatherhead, Surrey.

†Present address: Department of Chemical Engineering and Chemical Technology, Imperial College of Science and Technology, Prince Consort Road, London, S.W.7.

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Suggested Mechanism for Initiating Pressure Oscillations in Rocket Motors

RECENTLY, C. M. PLATTNER¹ and A. C. TOBEY² have noted the lack of sufficient information on the mechanism of reactions which

initiate harmful pressure oscillations in rocket motors. The problem is complex. Probably more than one initiating mechanism exists³. Once these oscillations are started, mechanisms are known whereby oscillations are amplified and maintained⁴. In view of Tobey's finding² that instability was not triggered when helium was injected into an experimental methane-oxygen rocket motor, we wish to call attention to related observations made at the Bureau of Mines⁵.

Studies of burning velocities of gases at elevated pressures were made in a spherical vessel. Pressure oscillations appeared when there were appreciable partial pressures of oxygen, nitrogen or carbon monoxide in the burnt gases; helium, hydrogen, carbon dioxide and water showed little if any tendency to induce pressure oscillations. Initial pressures were between 1 and 21 atm; fuels used were ethylene, hydrogen and carbon monoxide. The oscillation frequencies were usually between 800 and 2 500 c/s, which is in the range of 'high frequency' instability in rocket motors⁶. The amplitudes of the oscillations were usually within 30 per cent of the pressure at the end of combustion. Pressure oscillations were attributed to the delay in the partition of energy released by combustion into the molecular modes of vibration, particularly of certain diatomic molecules in the burnt gases⁵. Similar pressure oscillations were observed earlier at ordinary initial pressures and explained on the same basis⁷. We propose that pressure oscillations in rockets can be initiated by this delay.

J. GRUMER

Explosives Research Center,

Bureau of Mines,

4800 Forbes Avenue, Pittsburgh, Pa

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