

Barium Exhaust Spectrum during the Expansion of Combustion Products through a Nozzle into Vacuum

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(Z. Naturforsch. 26 a, 1147—1155 [1971]; received 1 April 1971)

The emission spectrum from a two-phase nozzle jet, consisting of combustion products of Ba and CuO, revealed that non-equilibrium amounts of excited and ionized Ba atoms occur only during the nozzle starting transient.

Traces of BaO- and Cu₂-molecules could be identified in the cold outer parts of the jet.

The particle temperature near the nozzle, derived from novel measurements of apparent color and brightness temperature, confirms LTE calculations if the vaporization of excess Ba is taken to be a fast process.

Introduction

A more detailed investigation of the optical emission from combustion products of Ba and CuO, effusing through a nozzle into vacuum, was motivated by several reasons:

1. Because of the relevance of this process in the production of Ba-vapor clouds in space experiments¹, a thorough understanding and control of this type of hitherto little investigated two-phase expansion was to be achieved. Some unusual gas dynamic features in the later stages of the expansion required better definition of the initial flow conditions for full description².

2. In upper atmosphere releases³ chemi-excited and chemi-ionized Ba atoms had been observed, which had challenged explanation of the mechanism and significance of this phenomenon.

3. Attempts⁴ have been made to estimate the vaporization efficiency of such processes on the basis of emission measurements on excited Ba, the results being clearly at conflict with methodologically well founded absorption measurements⁵.

4. Finally, a two-phase jet effusing into vacuum, represents (especially during the nozzle starting transient) a realm for various non-equilibrium phenomena which deserve attention by themselves.

The emission spectrum with absorption lines from the outer layers of the exhaust plume, and time resolved measurements of the apparent brightness temperature of the finely dispersed particulate matter⁶ were to reveal some of the particularities of this type of flow.

Experimental

a) Gasdynamic Characterization of the Jet

About 100 g of compressed Ba—CuO mixtures^{7, 8} of various compositions with small additions of NaN₃ have been ignited in 50 cm³ combustion vessels equipped with a convergent tungsten nozzle of 0.2 cm² critical orifice area.

The reaction products (liquid Ba, BaO, Cu and gaseous Ba with N₂) were ejected into a 20 m³ vacuum chamber, initially at 10⁻⁵ Torr (Fig. 1). The burning rate of the solid reactants was so fast, and the aperture of the orifice so small, that chemical conversion inside the plenum chamber could be considered complete during effusion of the majority of the products.

Only the nozzle starting transient during the first 10 msec after ignition is affected by the ignition and combustion process. Thereafter, the effusion of the fragmentation liquid can be described in terms of a steady-state with the mass-flow rate decaying almost linearly within a period of 150 msec, which is roughly in accordance with computations based on the assumption of inviscid equilibrium flow between plenum and nozzle throat⁹. Due to an ablative coating, heat losses to the reaction vessel are negligible and, apart from

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¹ G. HAERENDEL, R. LÜST, and E. RIEGER, *Space Res.* VII, 77 [1967].

² W. SMILGA, *Z. Naturforsch.* 23 a, 417 [1968].

³ G. T. BEST and N. W. ROSENBERG, *Spectroscopic Studies of Barium Releases*, IAGA, Symposium on Aeronomic Ionization Processes, Madrid, Sept. 1969.

⁴ C. S. STOKES, E. W. SMITH, and W. J. MURPHY, NASA CR-1415, Aug. 1969.

⁵ W. BRUNNER, H. FÖPPL, and K. W. MICHEL, *Astronautica Acta* 15, 613 [1970].

⁶ C. BATALLI-COSMOVICI, *Z. Naturforsch.* 24 a, 677 [1969].

⁷ W. BRUNNER, C. BATALLI-COSMOVICI, and K. W. MICHEL, *Physica* 41, 218 [1969].

⁸ W. BRUNNER, *MPI-PAE/Extraterr.* 16/1968.

⁹ R. D. AUER, *MPI-PAE/Extraterr.* 8/1968.



radiation, the flow can be considered adiabatic. Most of the vaporization of excess Ba takes place in the plume outside of the nozzle⁹, where a degree of vaporization up to 20% has been measured^{7, 8}.

Vaporization and cooling rate depend on the droplet sizes, which have been measured to lie between 0.1 and $40\ \mu$ ¹⁰. The discrete radiation and absorption of vapor phase species did not affect the continuous background emitted by these particles and used for the derivation of particle temperature.

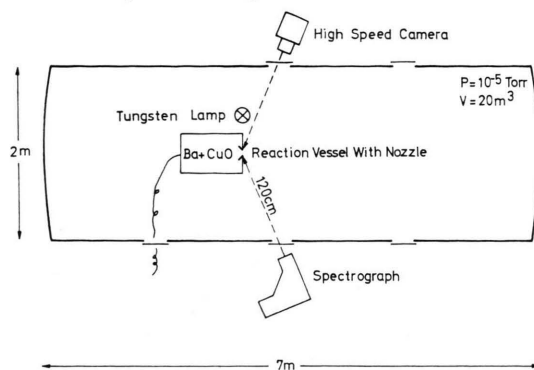


Fig. 1. Vacuum chamber with experimental set-up.

b) Exhaust Spectrum

A Zeiss three prism spectrograph was set up, as shown in Fig. 1, in order to study the exhaust spectrum and to determine the color temperature (camera: $f=27\text{ cm}$; aperture ratio 1 : 5.5; spectral range 3600 to 10 000 Å; dispersion at 5000 Å: 47 Å/mm; line resolution at 5000 Å: 1 Å). The nozzle-to-slit distance was about 120 cm. Because of the rapid cooling of particles, appreciable emission occurred only close to the nozzle exit. The spectrograph was focused onto the center of the nozzle with the aid of a He-Ne laser ($\lambda=6328\text{ Å}$).

The absorption and emission spectra in the range 3990–7500 Å were calibrated by comparison with spectra of the iron arc and various hollow cathode lamps.

The recorded absorption lines and bands are summarized in Table 1 and Fig. 2* and represent a "Fraunhofer spectrum" (the background being the bright plume) of partly molecular origin. The appearance of bands of BaF, BaCl, CuCl and CuF is due to impurities in the mixture. Only in the hottest mixture (Ba : CuO = 1 : 1) did two BaO bands appear ($\lambda=5492.7$ and 5349 Å) as BaO has a very low vapor pressure¹⁴.

Cu₂-bands could be observed only in absorption in the green system (A → X) and in the blue system (B → X). In the latter system the (0, 2), (0, 1), (0, 0) and (1, 0) vibrational transitions appear of comparable intensity (Fig. 2) as in absorption studies¹⁵ on equilibrium gas mixtures in a King furnace of about 2000 °C.

The emission spectrum for Ba is shown in Table 2 and Fig. 2; many lines of Fe, Ca, Cu, Sr and Cr were observed but are not tabulated.

The time correlation of this emission spectrum with the nozzle starting transient was verified by means of high-speed photography using an interference filter¹⁶. The high-speed camera (Hitachi – 2000 pictures/sec) was mounted as shown in Fig. 1. The filter has its transmission maximum at the wavelength of the Ba-II resonance line ($\lambda=4554\text{ Å}$) which is always the strongest line in the emission spectrum.

The radiative species distribute themselves like a rose bud around the orifice lip (Fig. 3). This phenomenon lasts no longer than about 3 msec before the maximum pressure is reached (80 atm inside the combustion vessel, about 50 atm at the nozzle) (Fig. 4a).

Probably these excited and ionized species are non-equilibrium combustion products¹⁷ which are carried out by a fast gaseous precursor, preceding the slower

Table 1. Absorption spectrum. Molar mixture ratios Ba : CuO = 1 : 1 and 1.5 : 1. Exact wavelengths in Ångstrom based on Refs. ^{11–13}.

Lines:	Ba I	5535,48*	6527,31	6595,33	6675,27	6865,69	Ref. ¹³
	Na	5889,96	5895,93				Ref. ¹²
	Sr I	4607,33*					Ref. ¹²
Bands:	BaCl	5136,0	5139,2	5167,0	5240,5	5320,8	
	BaF	4950,8	5000,6				
	BaO	5349,7	5492,7				Ref. ¹¹
	CuCl	4846,9	4881,5				
	CuF	4932,0	5061,1				
	Cu ₂	4856,3 (1,0)	4901,5 (0,0)				Green System, A→X
		4497,7 (2,0)	4546,4 (1,0)	4596,9 (0,0)	4653,4 (0,1)		Blue System, B→X

* Figs. 2, 3 and Fig. 7 a, b see page 1148 a und 1152 a.

¹⁰ C. BATALLI-COSMOVICI and K. W. MICHEL, AIAA Journal **8**, 983 (May) [1970].

¹¹ R. W. B. PEARSE and A. G. GAYDON, The Identification of Molecular Spectra, Chapman, London 1963.

¹² M. I. T. Wavelength Tables, The Technology Press, Wiley & Sons, Inc., New York 1960.

¹³ B. M. MILES and W. L. WIESE, Atomic Data **1** (No. 1), 1 [1969].

¹⁴ R. S. NEWBURY, G. W. BARTON, and A. W. SEARCY, J. of Chem. Phys. **48**, 793 [1968].

¹⁵ N. ÅSLUND, R. F. BARROW, W. G. RICHARDS, and D. N. TRAVIS, Ark. Fys. **30**, 171 [1965].

¹⁶ C. BATALLI-COSMOVICI, MPI-PAE-Extraterr. 12/1968.

¹⁷ G. H. MARKSTEIN, Heterogeneous Reaction Processes in Metal Combustion, XI. Symposium (International) on Combustion, Pittsburgh 1967, p. 219.

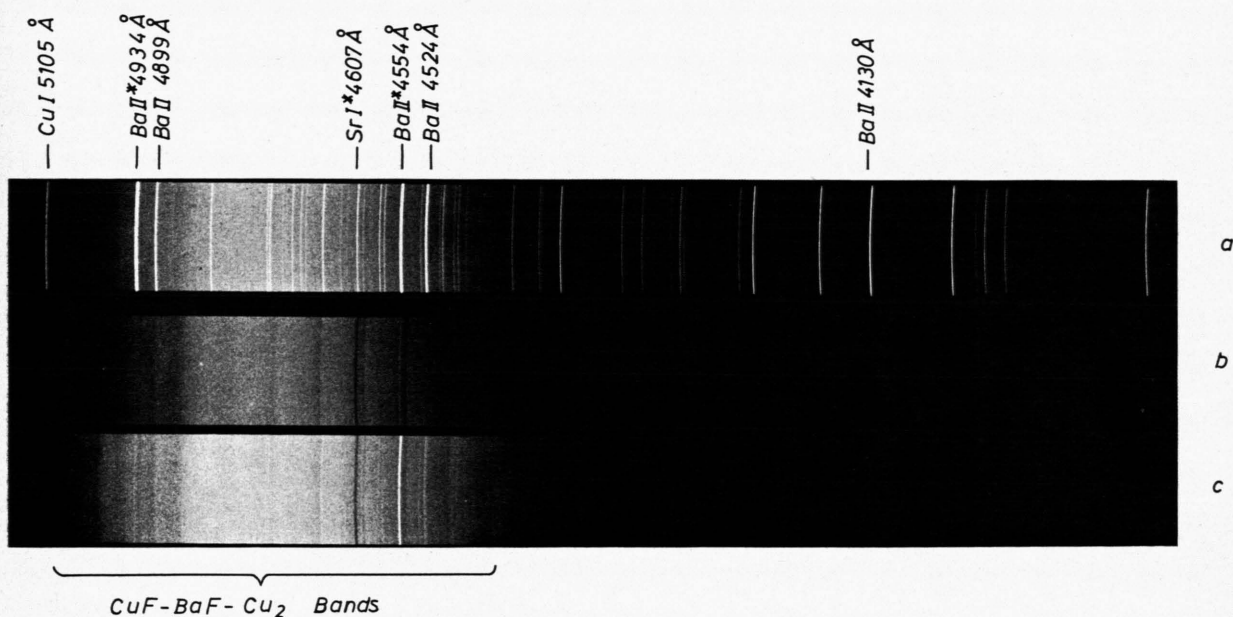


Fig. 2. Exhaust spectrum between $\lambda=3990$ and $\lambda=5105$ Å. Molar mixture ratios Ba : CuO = a) 3 : 1; b) 2.5 : 1; c) 2 : 1, without addition of NaN_3 . Emission=white lines; Absorption=black lines and bands.

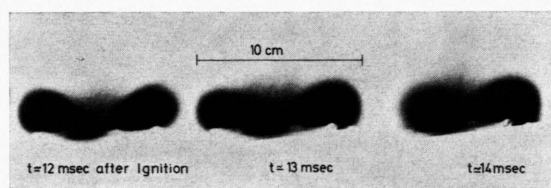


Fig. 3. Ion-distribution around the nozzle ($\phi=5$ mm) during nozzle starting transient. High-speed camera with filter at $\lambda=4556$ Å, $\Delta\lambda=44$ Å.

Table 2. Emission spectrum of Ba. Molar mixture ratios Ba : CuO = 2 : 1 - 2.5 : 1 - 3 : 1 - 3.5 : 1 - 4 : 1. Exact wavelengths in Ångström based on Ref. ^{12, 13}.

Ba I	3993,40	3995,66	4132,43	4166,00	4239,56	4242,61	4264,42	4283,10
	4323,00	4332,91	4402,54	4406,85	4431,89	4488,98	4493,64	4505,92
	4523,17	4579,64	4591,82	4619,92	4628,33	4673,62	4691,62	4700,43
	4726,44	4902,90	5424,62	5535,48*	5777,62	5800,23	5805,69	5826,30
	5971,70	5997,09	6019,47	6063,12	6110,78	6341,68	6450,85	6482,91
	6498,76	6527,31	6595,33	6675,27	6693,84	6865,69	7095,94	7120,33
	7195,24	7280,30	7488,08					
Ba II	4130,65	4267,95	4297,60	4325,73	4405,23	4509,60	4524,93	4554,03*
	4899,93	4934,09*	5981,25					
Ba ?	4291,16	4359,55	5853,68	6141,72	6867,87			

* = Resonance line, I = neutral atom, II = Ionized atom, ? = Unclassified.

two-phase flow. If one assumes that this gaseous precursor consists of N₂, some Ba atoms and negligible amounts of particulate matter, one calculates a critical velocity of 900 m/sec at the nozzle throat.

From the radius of the ring which radiates at 4554 Å and the gasdynamic maximum velocity of the gases ($v_{\max} = 2300$ m/sec) follows a radiation decay time of some $0.5 \cdot 10^{-4}$ sec in the rarefied Prandtl-Meyer-fan of the plume. The brightness temperature of the ions is about 100 °K higher than the equilibrium temperature (2500 °K) (see p. 1150).

The absence of any luminiscence of Ba ions in the core of the jet may be explained by the higher gas densities and quenching of excited species on the centerline. As long as the combustion is not completed (for times less than 10 msec), i. e. as long as the maximum pressure has not been reached, these excited particles evidently can be transported through the nozzle by the fast gaseous precursor before the relaxation. Later, during the stable flow, the combustion is complete and the flow is so slow (100 m/sec) ^{7, 8} that the electronically excited particles have relaxed before passing through the nozzle.

The emission and absorption spectroscopy with the radiating nozzle beam as optical background shows clearly that apart from the very short induction period, ions and electronically excited atoms do not pass from the combustion chamber into the vacuum in appreciable concentration.

c) Brightness and Color Temperature at Nozzle Exit

In the case of incandescent particles neither brightness nor color temperature correspond to the real temperature. Generally, the color temperature is higher, the brightness temperature lower to an extent which is given by the light scattering properties of the particles (absorptivity, emissivity) and optical density ^{18, 19}.

Thus, the two temperatures had to be measured, enabling interpolation of the true temperature with reasonable confidence limits.

Timewise and locally resolved pictures could be obtained of the outer jet layers for determining the apparent brightness temperature, whereas the color temperature was yielded as a time integrated quantity by the spectroscopic technique.

The brightness temperature T_s can be derived from Wien's law:

$$E(\lambda, T) = c_1 \lambda^{-5} e^{-c_2/\lambda T} \quad (1)$$

with: $c_1 = 2 h c_2$ and $c_2 = c h/k$ (c = velocity of light, h = Boltzmann's constant, k = Planck's constant).

Equation (1) applies only as long as $\lambda T < 3000$ cm °K. Comparing the intensities E_1 and E_2 from two black bodies at the temperatures T_{s1} and T_{s2} , we can deduce from Eq. (1) the equation of the "isochromatics" ¹⁹:

$$\ln E_1/E_2 = c_2/\lambda (1/T_{s2} - 1/T_{s1}). \quad (2)$$

In our case we call the known brightness temperature at the wavelength λ (transmitted by the filter) and intensity of a calibrated tungsten lamp (which can be considered as a black body) ²⁰ T_{s1} and E_1 . The unknown brightness temperature and intensity of the nozzle beam is called T_{s2} and E_2 .

The color temperature T_f is characterized by the intensities ratio at different wave-lengths of the radiation.

From Eq. (1) we obtain by differentiation with respect to λ :

$$\frac{d \ln E}{d \lambda} = \frac{1}{\lambda} \left(\frac{1.437}{T \lambda} - 5 \right) = \chi.$$

¹⁸ F. RÖSSLER, *Optica Acta* **11**, 21 [1964].

¹⁹ G. A. W. RUTGERS, *Temperature Radiation of Solids*, Handbuch der Physik, S. FLÜGGE (Herausgeber) **26**, 129 [1958].

²⁰ G. A. W. RUTGERS and J. C. DE VOS, *Physica* **20**, 714 [1954].

For two different color temperatures T_{f1} and T_{f2} follows:

$$1/T_{f2} = (1/T_{f1} - 3.48 \lambda) \chi_2/\chi_1 + 3.48 \lambda. \quad (3)$$

1. Determination of the Brightness Temperature T_s

A tungsten lamp (Osram Wi 14), calibrated with a pyrometer ($\lambda = 6560 \text{ \AA}$), was mounted in the vacuum chamber at a distance of 10 cm sideways from the nozzle and the high speed camera equipped with an interference filter was focussed to the nozzle as shown in Fig. 1.

Different quantities of light for the construction of the density curve were not obtained by variation of the light source, as is the usual procedure. It was done instead by means of controlled variation of exposure time with constant temperature of the W-lamp. This variation followed automatically from the slow speeding up of the film, but required control of the Schwarzschild effect²¹. The latter was found to be negligible within the accuracy of these measurements. The film velocity was measured by means of a stroboflash (Dawe Type 1209 A) at 25 flashes per second.

For determining E_1/E_2 in Eq. (2) densitometer traces were taken of the axial brightness variation of individual pictures of the jet and of the W-lamp.

So both local and time resolution (typical exposure time 0.57 msec) of the jet were obtained. In Fig. 4 the curves for the radiation of the jet and for the W-lamp are shown which is essentially a straight line apart from small variations due to dust deposits on the windows. The luminosity of the ions ($\lambda = 4554 \text{ \AA}$, Fig. 4 a) shows an effective temperature maximum of 2450°K , i. e. about 100°K higher than the temperature maximum of the beam ($\lambda = 6328 \text{ \AA}$, Fig. 4 b).

Measurements on identical mixtures gave maximum brightness temperatures which differed by as much as 250°K .

Also color temperatures reflect such variations.

For mixtures with molar ratios Ba : CuO = 2.5 : 1 we obtain a mean maximum brightness temperature of $T_s = 2360 \pm 50^\circ\text{K}$ right at the nozzle exit and about 10 msec after commence of the effusion. The highest temperature was obtained with:

Ba : Cu = 1 : 1 and 1.2 : 1 with $T_s = 2460 \pm 50^\circ\text{K}$. These values are to be compared with computed thermodynamic equilibrium temperatures of 2550 and 3400°K for the 2.5 : 1 and the 1 : 1 mixture respectively⁸.

2. Determination of the Color Temperature T_f

The spectra of the jet near the nozzle were taken by means of the Zeiss-spectrograph.

For exact alignment to the nozzle lips and as a precise reference point for the wave lengths, laser light ($\lambda = 6328 \text{ \AA}$) reflected from the nozzle was recorded on the same plate.

After the experiment the W-lamp, mounted at the point of the nozzle, was recorded through a step filter on the same plate. With the W-lamp exposure times of the order of a second were required to obtain the same density as from the jet (effective duration of emission 3 – 100 msec). Therefore, Schwarzschild corrections had to be applied in the order of about 5% (Kodak plate type 103 a – D)²¹.

The emission intensity, thus derived from the densitometer tracings, are plotted in Fig. 5 versus wavelength.

From the aperture of the spectrograph, the brightness of the jet in dependence on time (Fig. 4 b) and on distance from the nozzle (Fig. 6) follows that the apparent color temperature is governed by the hottest jet region of about 5 cm^2 near the nozzle in the time interval 5 – 10 msec after the beginning of the effusion. The contribution of the continuous emission from the other parts of the jet and at later periods of time altogether is less than 10%. So it could be accounted for by a perturbation analysis. The color temperature T_f of the radiating nozzle beam can be calculated from the gradient of these curves following Eq. (3) where we set:

$$\frac{\chi_2}{\chi_1} = \frac{E_2(\lambda_2) - E_1(\lambda_1)}{E_1(\lambda_2) - E_1(\lambda_1)} \cdot \frac{E_1(\lambda)}{E_2(\lambda)};$$

T_{f2} = Unknown color temperature of the beam, T_{f1} = Temperature of the W-lamp (pyrometric value), and E_2 and E_1 the corresponding densitometer values.

We choose from the linear region of the curve two values of λ that differ by about 50 \AA . From the corresponding curves one finds at λ_1 and λ_2 values of E_1 for the W-lamp and of E_2 for the nozzle beam.

The value of λ can be chosen as mean value be-

²¹ G. BOLDT and K. H. STEPHAN, MPI-PAE/Extraterr. 19/1963 also KODAK Scientific and Technical Data, P-9 [1962].

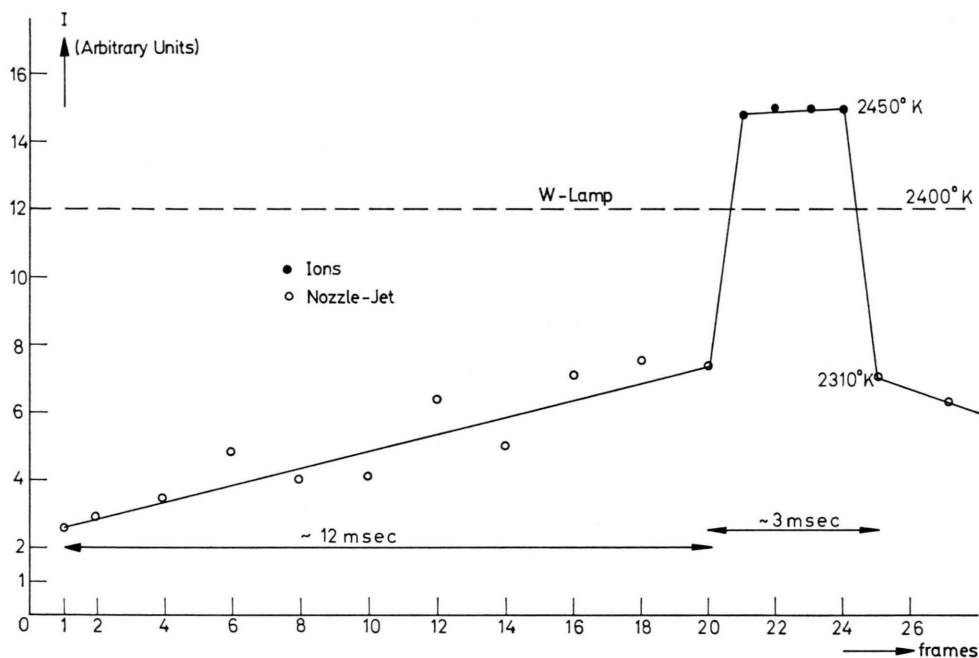


Fig. 4 a. Brightness temperature at the nozzle.
Filter at $\lambda = 4556 \text{ \AA}$, $\Delta\lambda = 44 \text{ \AA}$.
Molar mixture ratio Ba : CuO = 2.5 : 1, without NaN_3 .

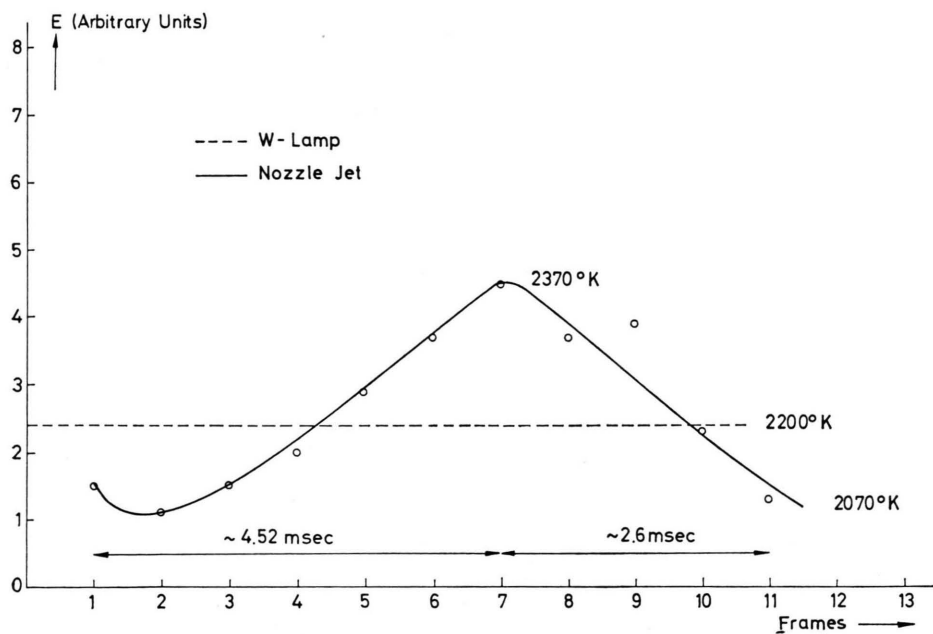


Fig. 4 b. Brightness temperature at the nozzle.
Filter at $\lambda = 6328 \text{ \AA}$, $\Delta\lambda = 20 \text{ \AA}$.
Molar mixture ratio Ba : CuO = 2.5 : 1, with addition of NaN_3 .

tween λ_1 and λ_2 . Color temperatures for tungsten were adopted from Refs. ²⁰ and ²².

The measured color temperature is about 400 °K higher than the brightness temperature, without correction due to radiation contributions from other

parts of the jet and other times than for maximum brightness region specified above.

Graphic integration of contributions of radiation from colder zones to phases of expansion with lower maximum temperature shows that the true maxi-

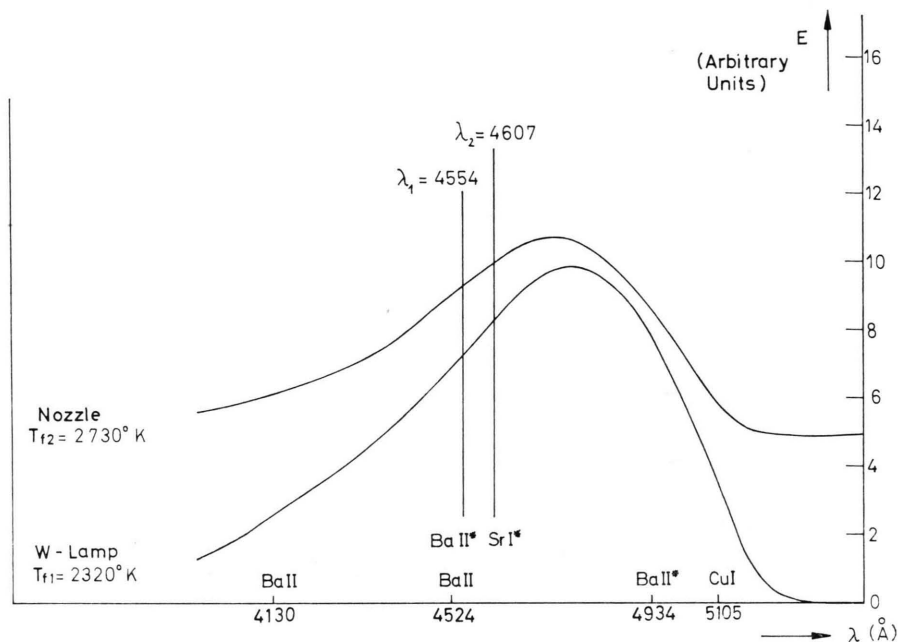


Fig. 5. Time averaged color temperature at the nozzle.

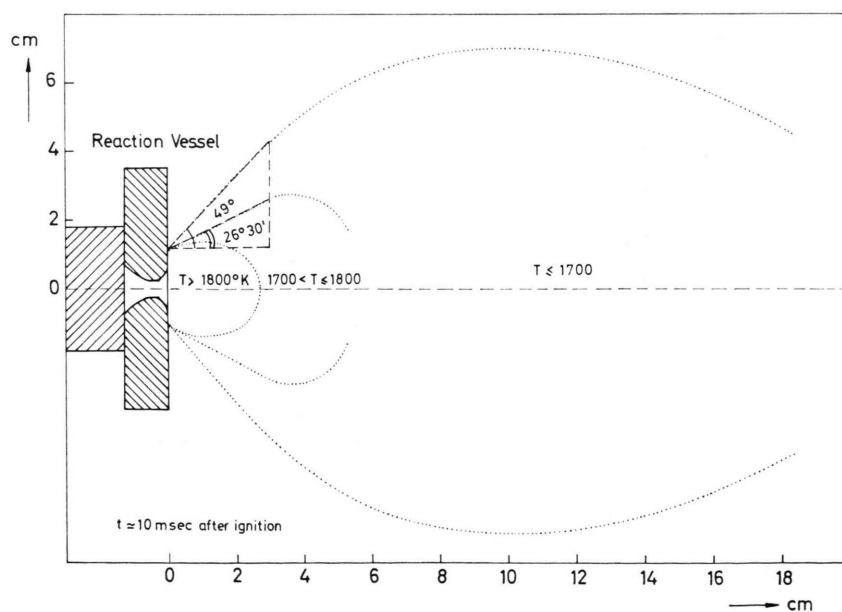
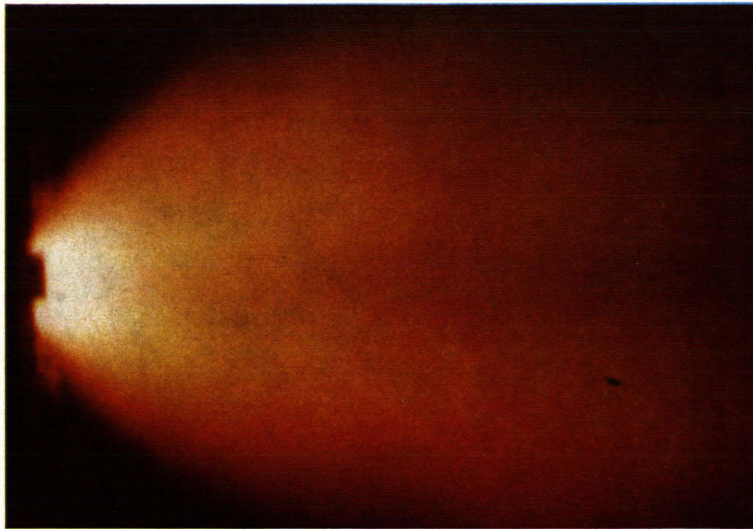
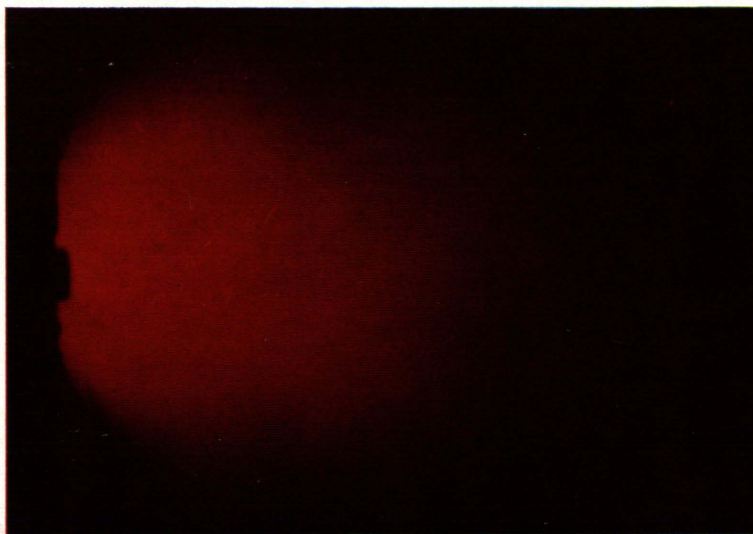


Fig. 6. Apparent temperature of the nozzle plume derived from densitometer tracing of color film corresponding to Fig. 7 a.

²² A. G. WORTHING, J. Appl. Phys. **11**, 421 [1940].



a



b

Fig. 7. Thermal radiation of particulate matter from exhaust plume of Ba—CuO combustion into a vacuum. Pictures taken with a high-speed camera (1750 pps).

imum color temperature in the most luminous phase can only exceed the measured values by about 100 °K.

Thus the difference between color and brightness temperature at the time of maximum emissions is around 500 °K.

Discussion

It has been shown that it is possible to obtain adequate measurements of the apparent maximum brightness and color temperature of the outer layers of a two-phase jet by means of simple techniques. Even though the results demand by no means high accuracy, they set limits to the initial conditions of the effusing products and allow comparison with thermodynamic equilibrium calculations⁹.

The results on temperature measurements can be summarized as follows:

Shortly after ignition of the reaction mixture Ba/CuO products of comparatively high temperature effuse through the nozzle. This non-steady effusion period of a few msec, during which the so-called nozzle starting transient appears, is followed by a period which covers most of the effusion time of some 200 msec with products at appreciably lower temperature. The nozzle-starting transient is associated with escape velocities into vacuum around 800 m/sec, whereas the average velocity during the main phase is 140 m/sec^{8, 16}.

For the nozzle starting transient, apparent values for both the maximum brightness and maximum color temperatures near the orifice could be derived. In the case of the most efficient mixture for the production of Ba-vapour clouds in space (molar ratio Ba/CuO = 2.5) these values are 2360 °K and 2730 °K, respectively. Similar differences between color and brightness temperature are observed for other disperse systems, e. g. flames containing hot dielectric particles²³, and they were shown to be in accord with a true temperature which lies between the apparent values of brightness and color temperature. Thus, the true maximum temperature of the incandescent particles in the outer layers of the jet (the jet is optically thick at all times in the neighborhood of the nozzle) during the nozzle starting transient will be 2500 – 2600 °K. Thereafter, bright-

ness temperature drops rapidly to below 1800 °K which corresponds to true temperatures of less than 1900 °K.

The temperature during the nozzle starting transient corresponds closely to the thermodynamic equilibrium temperature of 2550 °K inside the reaction vessel. Radiation cooling of particles with radii $r = 0.34 \mu$, which represent the area average over the measured particle size distribution¹⁰, would, indeed, scarcely lower the initial temperature during a flight time of about 20 μ sec to a distance of 2 cm from the nozzle rim (Fig. 8). (The average emissivity of the hot droplets was taken as 0.2¹⁶.) Cooling by vaporization, however, is expected to lower the temperature of droplets with $r < 1 \mu$ to less than 2000 °K within 10 μ sec, if dif-

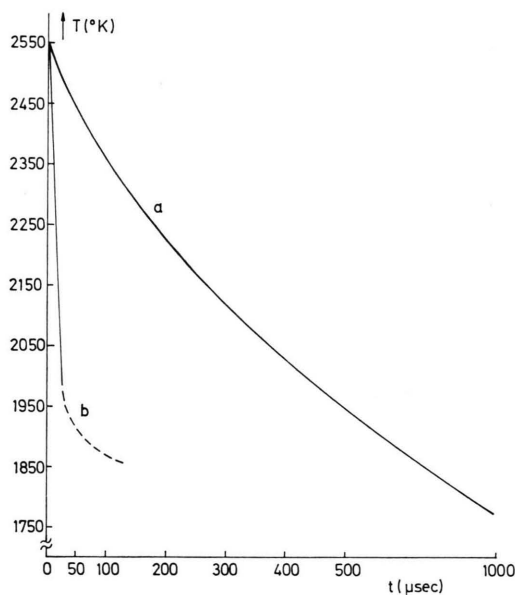


Fig. 8. Temperature decrease of particles ($r = 0.34 \mu$) due to radiation and vaporization cooling.

a) Radiation Cooling

$$\frac{1}{T^3} = 4.9 \cdot 10^{-12} \frac{t}{r} + \frac{1}{T_{\max}^3} \quad (\text{Ref. }^{16})$$

with $T_{\max} = 2550 \text{ °K}$.

b) Vaporization Cooling

$$1 - \varphi = \frac{6}{\pi^2} \sum_{\nu=1}^{\infty} \frac{1}{\nu^2} \exp \left[\frac{-\nu^2 \pi^2 D(T) t}{r^2} \right] \quad (\text{Ref. }^8)$$

φ = Degree of Vaporization, D = Diffusion Coefficient
($= 0.3 \cdot 10^{-5} \text{ cm}^2/\text{sec}$ for $T > 1900 \text{ °K}$);

$$\frac{d\varphi}{dT} = \frac{\varphi}{T} - \frac{C}{L_v} < 0 \quad (\text{Ref. }^9)$$

with C = Specific Heat (total), L_v = Heat of Vaporization).

²³ H. G. WOLFARD and W. G. PARKER, Proc. Roy. Soc. London **62**, 523 [1949].

fusion of excess barium to the droplets' surface is taken as the dominant vaporization mechanism which has been shown to be in agreement with the measured terminal vapour yield⁵. Hence, the observed temperatures around 2500 °K during the nozzle starting transient can only be understood, if the relevant particles do not contain any evaporable excess Ba.

Initial deviation of the effusing products from uniform average composition can be rationalized if the metal combustion is considered to proceed, crudely speaking, in two steps, as inferred also from analysis of the burning rate (see Ref. 5, Fig. 2):

1. In the reaction zone CuO and smaller Ba grains are heated by convective heat transfer and react stoichiometrically to form liquid Cu and BaO at an initial temperature of about 3000 °K, leaving excess Ba almost cold.

2. Thermal equilibrium including excess Ba in the form of larger grains occurs more slowly (time constant typically 5 msec, depending on inert gas pressure) ** and establishes the thermodynamic equilibrium temperature of 2550 °K⁹. The latter corresponds to the observed temperature of about 1900 °K during the main phase of the effusion if rapid vaporization beyond the nozzle throat is accounted for. At temperatures below 1900 °K diffusion of liquid Ba to the droplets surface becomes so slow that vaporization cooling is not competitive any more with radiation losses. This lower limit is important in designing reaction mixtures giving optimum vapour yields. The particle temperature of 1750 °K after 1 msec suggested by the radiation cooling mechanism (Fig. 8), agrees with measurements at a nozzle distance of 10 cm and at a flow velocity of about 100 m/sec.

The intermediate products of the first reaction step can only be observed if entrained by the fast gaseous precursor during the nozzle starting transient which follows ignition for about 10 msec. The intermediate reaction products of this first step do not contain any excess Ba. Thus vaporization cooling is not possible in this case and the high initial temperatures of 2500–2600 °K are due to the inefficiency of radiation cooling (Fig. 8). The high

initial non-equilibrium temperature (such temperature spikes are also observed in stationary pure gas flames²⁴) also accounts for the large amount of excited and ionized Ba atoms during the first 10 msec of effusion. The fact that intensity of the Ba emission lines appears to be the same for rich and lean mixtures (Fig. 2), confirms again the assumption that the first reaction step, yielding reaction products at an intermediate temperature of about 3000 °K is to a first approximation independent of the amount of excess Ba, even though the latter determines the final heat balance.

Details of ion production and population mechanisms of excited levels in this heterogeneous flow system can, of course, not be derived from measurements of this type. Even though the spectrum resembles the one from a flow discharge through Ba/O₂/N₂²⁵, the presence of particle surfaces will require additional considerations in explaining excitation of Ba atoms.

The present conclusions from the study of ionized and excited Ba produced in the chemical reaction are:

- Ba ions are only a minor primary component in the two-phase jet. Practically all Ba is in the ground state and ions observed in rocket releases are the result of photoionization²⁶.
- Chemi-ionized Ba, also reported from rocket releases³, is associated with a nozzle starting transient of short duration and characterized by entrained intermediate products of the combustion process. These intermediate products have much higher than equilibrium temperature. The concomitant ions are deflected after passing through the nozzle (Fig. 3) which might be associated with perturbations recorded occasionally by the electrical system of rockets during barium releases.
- The emission lines of Ba cannot be taken as a measure for the vapour yield in laboratory studies, because they appear in conjunction with an initiation step of the combustion and are not correlated with the state of the vapour jet during the main phase of the effusion.

** All chemical and thermal relaxation processes inside the reaction vessel proceed much faster at pressures around 250 atm, such as occur in the reaction $\text{Ba}(\text{NO}_3)_2 + 12 \text{Ba}$.

²⁴ A. G. GAYDON, *The Spectroscopy of Flames*, Chapman and Hall Ltd., London 1957.

²⁵ R. J. OLDMAN and H. P. BROIDA, *J. Chem. Phys.* **51**, 2764 [1969].

²⁶ L. HASER, in: *Aurora and Airglow*, p. 391, B. M. McCormac Edit., Reinhold Publishing Corporation, New York 1967.

Together with the detection of chemi-ionized species under controlled laboratory conditions, the spectroscopic technique allowed also to allocate trace components of Cu_2 and BaO to the short initiation period of the effusion process. Later on, the particle temperature is too low to vaporize these species.

Even though many problems in the mechanism of metal combustion remain to be solved, a number

of puzzling phenomena observed during upper atmosphere releases seem to have been rationalized, so as to make Ba vapour clouds a well defined tool of space research.

Acknowledgements

We wish to thank Prof. Dr. REIMAR LÜST for supporting this work. We are also indebted to Mr. J. ROEB for the experimental assistance.

Zur „Abbildung“ komplexer Bildfunktionen in der Elektronenmikroskopie

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(Z. Naturforsch. 26 a, 1155—1168 [1971]; eingegangen am 15. April 1971)

New developments in the image reconstruction procedures for electron microscopy proposed by us are reported here. Reconstruction procedures with visible light for complex functions are described. In one variant of the procedure bright field micrographs for various tilting of the primary beam are combined. It is shown that in this case a further increase in resolution by a factor of 2 and simultaneous improvement in depth of focus are attainable. The depth of focus is at least equivalent to that of a normal instrument working with a wavelength of $\lambda/4$. It is shown that zone correction plates can be used in the microscope according to the same principle. The higher resolution improves the discrimination between heavy and light atoms with the aid of anomalous scattering. The discrimination by anomalous scattering is compared with that attainable by elastic—inelastic scattering (in Crewe's Scanning Microscope) at various resolutions. Some preliminary experiments have been done.

Vor einiger Zeit haben wir neue Verfahren zur rechnerischen Rekonstruktion von Bildfunktionen mit Korrektur der Bildfehler (Erhöhung der Auflösung) für die Elektronenmikroskopie beschrieben¹⁻⁴, von denen eines (Hellfeldaufnahmen des Objektes mit Aperturblenden, welche als komplementäre Halbebenen ausgebildet sind) mit einer von LOHMANN⁵ und von BRYNGDAHL und LOHMANN⁶ für Registrierung und Entzifferung von Hologrammen angegebenen lichtoptischen Methode („Einseitenbandholographie“) verwandt ist. Wir hatten auf

die Bestimmung der vollständigen komplexen Bildfunktion (getrennte Registrierung von Real- und Imaginärteil) besonderen Wert gelegt. Das ist für die Elektronenmikroskopie von Interesse, da Schweratome Elektronen mit beträchtlicher Phasenverschiebung (im Gegensatz zu Röntgen-Strahlen!) streuen. Wie wir ausgeführt hatten, lassen sich dann durch gewichtete Differenzbildung Schweratome gegen Leichtatome diskriminieren. Kürzlich hat HANSZEN^{7,8} unseren elektronenmikroskopischen Halbebenenbildrekonstruktionsprozeß — allerdings nur für den

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² W. HOPPE, Acta Cryst. A 26, 414 [1970].

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⁶ O. BRYNGDAHL u. A. LOHMANN, J. Opt. Soc. Amer. 58, 620 [1968].

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⁸ K. J. HANSZEN, Vortrag Intern. Kongr. Elektronenmikroskopie, Grenoble, Vol. I, 21 [1970].