

12525 Saratoga Creek Drive
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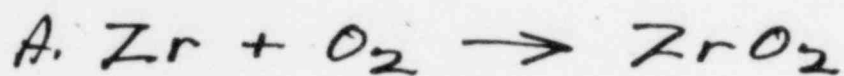
Dr. J. Hendrie
USNRC
Washington, D.C. 20555

Dear Commissioner Hendrie,

I believe the attached curve on peak temperature from SECY-80-107 (Figure 4) is erroneous even though this has little bearing on hydrogen production and implications. However, the umbrella of conservatism should not be an umbrella for acceptance of fundamental errors. Specifically, the curve implies a peak temperature that is limited by the amount of Zircaloy reacting; and that a solid Zircaloy rod would reach a substantially higher temperature. Of course, the thermodynamics of the process has been ignored in this analysis. (over)

I would highly appreciate having your expert staff report the following calculations to me at their convenience.

What is the maximum flame temperature for the following reactions assuming no excess reactants?



and

~~2Zr +~~



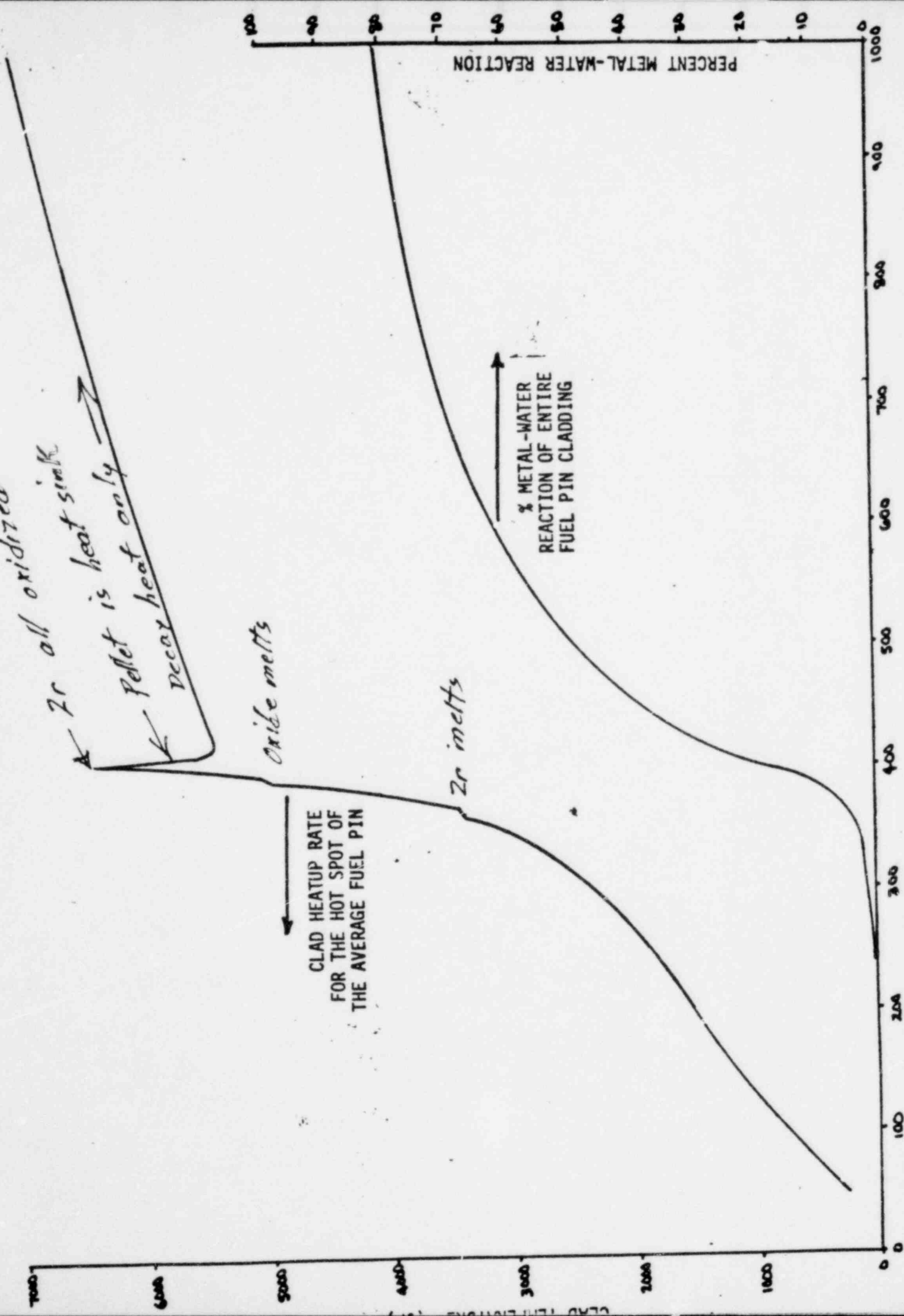
I think case A is independent of pressure, but case B may be pressure dependent. I'd like to see results for 1, 10, 100, and 150 atm. but I'm not particular.

I'm surrounded by code crazy Kineticists who ignore thermodynamics, but the whole world should not be so.

Very truly yours,

Robert H. Lyse

FIGURE 4 FUEL CLAD TEMPERATURE RESPONSE



See p. 50

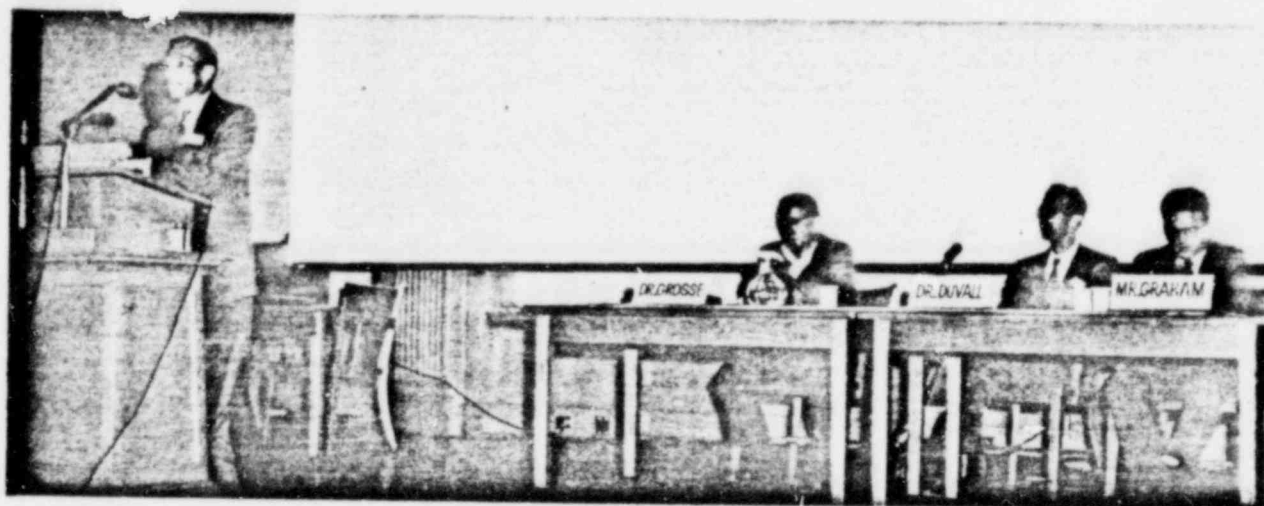
- *Proceedings of the Symposium on*

**"HIGH TEMPERATURE-
A TOOL FOR THE FUTURE"**

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CHEMICAL PROCESSES AS METHODS OF ACHIEVING HIGH TEMPERATURES

DAVID ALTMAN

Chief, Physics Section, Jet Propulsion Laboratory

THE LAST SEVERAL DECADES have witnessed an era in which it was fashionable to break down various barriers that had hitherto been more or less considered immovable. One was the sound barrier, which has been pierced by modern jet planes. Another was the atomic nucleus, which was dismembered by high-energy radiation, and, in some cases, by low-energy neutrons. The availability of almost unlimited energy from nuclear reactions implies that ultra-high temperatures can be obtained. Indeed, the thermonuclear bomb is reported to develop a temperature of the order of 100 million degrees C. Controlled nuclear reactions, however, are run at much lower temperatures. One limitation at present appears to be the chemical stability of the structural materials.

In employing chemical energy as a source of heat for generating temperature, a real barrier exists that can be called the "chemical barrier." Under a given set of conditions, this barrier represents a temperature range where dissociation of molecular species is occurring thereby destroying the very energy source responsible for the chemical heat release. It is obvious therefore, that if no other energy source but chemical

is initially provided, it is impossible to transcend the dissociation region for the products of the reaction.

Internal Energy States

Before discussing the characteristics of the chemical barrier and how it may be varied by operating conditions, it would be desirable to review the various forms of energy in molecules. The percentage distribution of energy as translation, rotation, vibration, dissociation and ionization for hydrogen at one atmosphere and various temperatures are shown in the block diagram, Fig. 1. The only energy mode that contains an appreciable amount of energy over the entire temperature range is translation. Since this mode is rapidly excited by collisions, it is frequently taken as the measure of "temperature" in systems where one or more of the other modes are not in equilibrium. A graphical representation of the same data is given in Fig. 2. The chemical barrier is represented by the region between 3000 and 5000 degrees K where the rotational and vibrational energies decrease eventually to negligible quantities due to dissociation. Indeed, the reaction between two H atoms initially at 298 degrees K yields a

temperature of 4080 degrees K at one atmosphere. Due to equilibrium, the reaction is only about 35 percent complete.

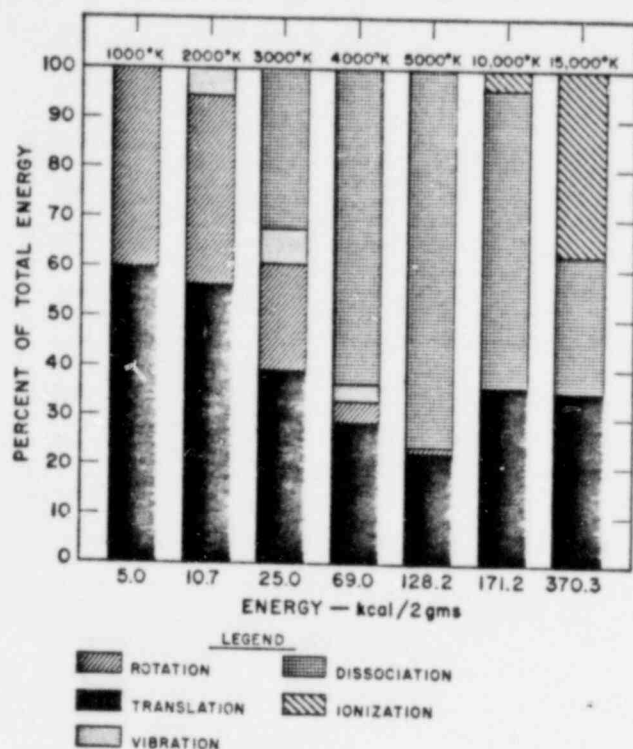


FIGURE 1. Energy distribution in H₂ at one atmosphere.

Chemical Heat Source

The energy change of any chemical reaction originates fundamentally from the valence forces in chemical bonds. Consequently, the heat released in any constant volume process is given by the difference in

TABLE I—BOND ENERGIES AND MAXIMUM TEMPERATURES

Bond	D_0 (kcal)	ΔS_{298}^* (cal/°)	T^{**} (°K)
HF	135	23.8	5000
AlO	138	(26.4)	4600
LiF	139	22.2	5400
PO	143	24.3	5100
NO	150	24.8	5300
BO	161	27.9	5100
CN	175	26.0	5800
SiO	184	29.3	5500
NN	225	27.4	7100
CO	256	29.0	7600

* ΔS_{298} for diatomic molecule to gaseous elements.
**Calculated from:

energies of the bonds newly formed and those just broken. Thus, at constant volume, the heat release in chemical change for a gaseous reaction is:

$$Q = \sum_P n_i(BE)_i - \sum_R n_j(BE)_j$$

where P and R refer to the products and reactants and BE is the bond energy. In a constant-pressure process, the heat effect is altered slightly by the work done on or by the system due to the change in the pV product.

In Table I are listed the bond energies of some typically strong bonds. It is clear that the triply-bonded nitrogen and the occurrence of resonance between doubly- and triply-bonded carbon monoxide can cause these two species to have the most energetic bonds known. Also listed in the table are characteristic "bond temperatures" defined as that temperature where the standard free-energy change to atoms is zero. Approximately, it indicates the temperature for a hypothetical constant-pressure reaction employing the gaseous atoms

$$\Delta F = D_0 + 2T - T \left(\Delta S_{298} + 2 \ln \frac{T}{298} \right) = 0$$

$$\therefore T \approx \frac{10^3 D_0}{\Delta S_{298} + 2 \left(\ln \frac{D_0}{9} - 1 \right)}$$

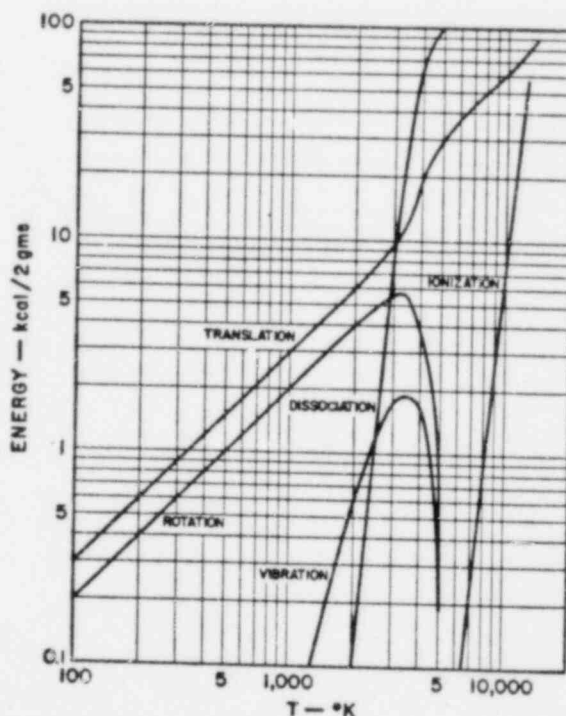


FIGURE 2. Distribution of energy in hydrogen at one atmosphere.

at 298 degrees K as reactants. These "temperatures" are calculated approximately and are intended to be

indicative rather than true values. Here again both CO and N₂ stand out as two almost unique species. Their thermal barriers occur at the highest temperatures of any species known. Herein lies the clue for selection of chemical reactions to yield maximum flame

TABLE II—FLAME TEMPERATURES AT ONE ATMOSPHERE

Reaction	Temperature (°K)
1. H ₂ + ½ O ₂ = H ₂ O	3120
2. C ₂ H ₂ + 3/2 O ₂ = 2CO + H ₂ O	3500
3. H ₂ + F ₂ = 2HF	3950
4. 2H = H ₂	4180
5. C ₂ N ₂ + O ₂ = 2CO + N ₂	4850
6. C ₄ N ₂ + 2O ₂ = 4CO + N ₂	5260
7. C ₄ N ₂ + 4/3 O ₂ = 4CO + N ₂	5515
8. C + (½ O ₂ + 2N ₂) = CO + 2N ₂	1470
8a. C + (O ₂ + 4N ₂) = CO ₂ + 4N ₂	2370
9. C + ½ O ₂ = CO	3500
9a. C + O ₂ = CO ₂	3150

temperatures; namely, the choice of unstable reactants involving only the elements, C, O, and N at a 1:1 atom ratio of C to O.

reactions 8 and 9a. When carbon burns in air, a higher temperature results when CO₂ is formed as compared to CO. This is an expected result. When carbon burns in pure oxygen, however, the stoichiometric balance to CO₂ yields a lower temperature than a balance to CO. The answer to this apparent discrepancy is obtained from a consideration of the high-temperature dissociation of CO₂. At the temperature of 3500 degrees K and one atmosphere, it is found that CO₂ is 75 percent dissociated into CO and O₂. As a consequence, the addition of oxygen at 298 degrees K to CO at 3500 degrees K causes more cooling by dilution than heat release by reaction. In other words, CO becomes a very poor combustible at temperatures exceeding 3000 degrees K.

It is clear, therefore, that one can locate a range of maximum flame temperatures obtainable by chemical means based on which species are present as products. A plot of enthalpy of the various species H₂O, HF, CO, and N₂ relative to 298 degrees K at one atmosphere is shown in Fig. 3. Once again it is clear that a given enthalpy per two atoms results in a much higher temperature for CO and N₂ than for the other species. Various isobaric flame temperatures are indicated for various reactions. One may consider as "limit temper-

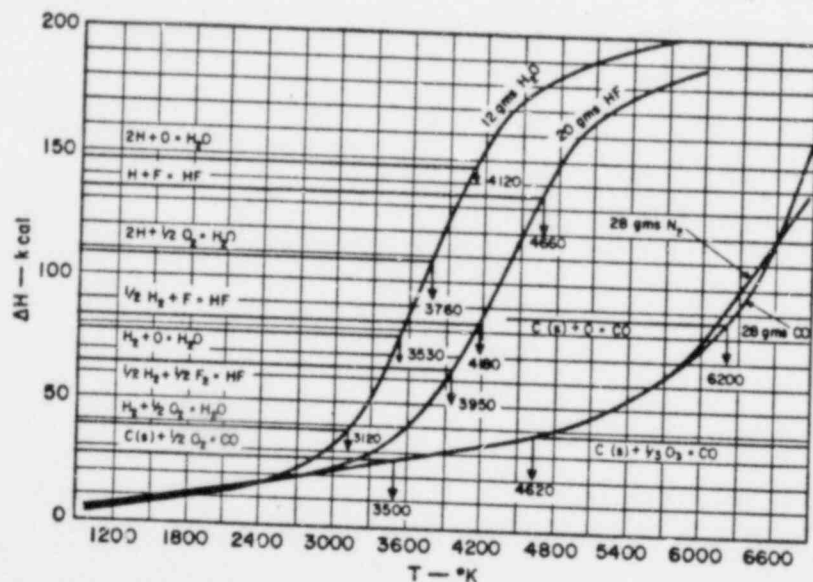


FIGURE 3. Heat content—temperature diagram for H₂O, HF, CO, and N₂ relative to 300 degrees K (1 atm).

A list of typical energetic reactions is shown in Table II. It is clear that the reactions of C₂N₂ and C₄N₂ to give CO and N₂ yield the highest flame temperatures reported,[1] thereby corroborating the conclusion drawn from bond energies. An interesting result is shown in

atures" those obtained from the hypothetical reaction employing the atoms at 298 degrees K.

A further process that can add to the temperature barrier is ionization. This process is important in the range of the chemical barrier if the degree of ioniza-

tion at say 50 percent dissociation is significant. Table III contains a listing of the percent ionization occurring when some of the stronger bonds containing metal atoms with reasonably low ionization potentials are 50 percent dissociated. For all except the LiF molecule ionization contributes little to the characteristics of the chemical barrier. LiF can be considered a special case since it is an energetic bond involving an easily ionizable alkali atom. Thus, at the relatively high temperature required for bond dissociation, appreciable ionization results.

TABLE III—PERCENT IONIZATION AT THE 50 PERCENT DISSOCIATION POINT

Species	D_0 (kcal)	T_{50} (°K)	I^* (e.v.)	Ionization** (%)
AlO	138	4300	5.96	1.5
LiF	139	4900	5.36	9.2
BO	161	4700	8.26	0.2
SiO	184	5200	8.12	0.7
CO	256	7100	11.22	1.0

*For the metal atom; **Total pressure is 1 atm.

Effect of State Variables on Temperature

For an adiabatic reaction, variation of pressure or volume during reaction must be specified for the determination of temperature, as well as the absolute value for final pressure or volume. With regard to variation of state parameters, it is common to characterize reactions as being either at constant pressure or at constant volume. Combustion reaction in a gun barrel, however, is one illustration of a system in which neither pressure nor volume is held constant. The variation in the pV term during reaction determines the quantity of reaction heat converted to mechanical work and this effect is noted at all temperatures. The influence of the level of final pressure, however, is noted for perfect gases only at high temperatures where it affects the extent of dissociation.

Constancy of Pressure or Volume

The heat-balance equations for determining the isobaric and isochoric flame temperatures can be written:

$$\Delta H_R(T_0) = \Delta H(diss) + \int_{T_0}^{T_p} C_p dT = \bar{C}_p(T_p - T_0)$$

$$\Delta E_R(T_0) = \Delta E(diss) + \int_{T_0}^{T_v} C_v dT = \bar{C}_v(T_v - T_0)$$

where $\Delta H_R(T_0)$ is the enthalpy change of reaction

going to stable products at T_0 , $\Delta H(diss)$ is the enthalpy required to dissociate the products at T_0 to the extent characteristic of equilibrium at T_p , and C_p is the isobaric heat capacity of the product mixture at a composition characteristic of equilibrium at the temperature T_p . The quantities \bar{C}_p and \bar{C}_v represent average quantities containing the heat effects due to dissociation. Since $\Delta H_R \cong \Delta E_R$ for energetic reactions, it follows that

$$\frac{T_v - T_0}{T_p - T_0} \approx \frac{\bar{C}_p}{\bar{C}_v}$$

For temperatures below dissociation, $\bar{C}_p/\bar{C}_v = \gamma \approx 1.2$ or 1.3 indicating a 20 to 30 percent increase in flame temperature for an isochoric reaction as compared to one which is isobaric. At higher temperatures where the flame gas is dissociated, however, both heat capacities are increased by the appropriate term $Q(diss)/(T - T_0)$. The effect is to reduce γ in some cases to a value as low as 1.02. As a consequence, for energetic reactions where the product gases are extensively dissociated, isochoric flame temperatures tend to approach isobaric values.

To illustrate, consider the following reactions terminating at one atmosphere pressure. The isobaric flame temperature of C burning in O_2 to yield CO is 3500 degrees K, whereas the isochoric flame temperature is about 4350 degrees K, an increase of approximately 850 degrees K. On the other hand, when H_2 reacts with O_2 to form H_2O , the isobaric flame temperature is 3120 degrees K, whereas the isochoric flame temperature is only about 3220 degrees K, an increase of approximately 100 degrees K. In the case of CO, the effective value of γ is 1.265, while in the case of H_2O , it is only 1.035. The answer lies in the fact that at 4350 degrees K, CO is less than 0.2 percent dissociated, while at 3220 degrees K, H_2O is over 35 percent dissociated, all values at one atmosphere. Thus the expedient of operating a reaction at constant volume to obtain a gain in temperature is effective only if the system is below the dissociation region.

Level of Pressure

A general characteristic of all high-temperature dissociation reactions is that there is a mole increase with reaction. Consequently, the reaction can be repressed by increasing the pressure. Since the temperature of hot flames is limited by the degree of dissociation, it follows that an increase in pressure results in an increase in temperature. Table IV contains a derivation of an approximate equation expressing the temperature increase of a simple dissociation reaction in an

adiabatic system as a function of pressure. The final equation accurately predicts the fact that temperature is independent of pressure both below and above the dissociation points (i.e., $\alpha = 0$ or 1). The maximum effect appears to be near the 60 percent dissociation point from an examination of the partial derivative of T with respect to α . The logarithmic dependence on

TABLE IV—EFFECT OF PRESSURE ON TEMPERATURE AT CONSTANT ENTHALPY

$$MX = M + X \quad Q = \Delta H(298)$$

$$1 - \alpha \quad \alpha \quad \alpha$$

$$\alpha^2 = \frac{1}{1 + \frac{p}{K}}; \quad 1 - \alpha^2 = \frac{1}{1 + \frac{K}{p}} \quad \dots (1)$$

$$2d \ln \alpha = \frac{d \ln K - d \ln p}{1 + \frac{K}{p}} \quad \dots (2)$$

Constant enthalpy:

$$dH = Qd\alpha + (9 + \alpha) dT = 0 \quad \dots (3)$$

$$\therefore 2d \ln \alpha = - \frac{2(9 + \alpha) dT}{Q\alpha} \quad \dots (3')$$

Combining Eqs (2) and (3'):

$$d \ln K + \frac{2(9 + \alpha) \left(1 + \frac{K}{p}\right)}{Q\alpha} dT = d \ln p \quad \dots (4)$$

$$\left[\frac{Q}{RT^2} + \frac{2(9 + \alpha)}{Q\alpha(1 - \alpha^2)} \right] dT = d \ln p \quad \dots (5)$$

Integrating and letting \bar{d} and \bar{T} be suitable average values between T_1, p_1 and T_2, p_2 :

$$\Delta T = T_2 - T_1 \cong \frac{\left(\frac{Q}{R}\right) \ln \frac{p_2}{p_1}}{\left(\frac{Q}{RT}\right)^2 + \frac{2(9 + \alpha)}{R\alpha(1 - \alpha^2)}} \quad (6)$$

Also:

$$\left(\frac{\partial T}{\partial p}\right)_H = \mu C_p = \frac{\frac{Q}{Rp}}{\left(\frac{Q}{RT}\right)^2 + \frac{2(9 + \alpha)}{R\alpha(1 - \alpha^2)}} \quad (7)$$

Chemical Processes

pressure indicates a rapidly diminishing effect at very high pressures. Table V contains some calculations on the temperature increases with pressure for CO and

TABLE V—EFFECT OF PRESSURE ON TEMPERATURE AT CONSTANT ENTHALPY

T_1 ($^{\circ}$ K) (1 atm)	CO				N ₂			
	α (T_1) (1 atm)	$p \Delta T_2$			α (T_1) (1 atm)	$p \Delta T_2$		
		10 atm	100 atm	1000 atm		10 atm	100 atm	1000 atm
4000	0.0004	12	25	37	0.0009	16	35	50
5000	0.0108	165	330	500	0.0172	210	415	620
6000	0.0988	510	1000	1540	0.121	540	1090	1630
7000	0.428	830	1650	2500	0.421	920	1840	2760

N₂ at one atmosphere initial pressure and various arbitrary temperatures. The table shows the small effect at low values of degree of dissociation. Because of the high bond energies of these species, the effect at only 1 percent dissociation is surprisingly large.

Some flame temperatures at 1 and 20 atmospheres are given in Table VI. The large effect for H₂O at the relatively low temperature of 3120 degrees K is again evident from the large degree of dissociation. The flames yielding only CO and N₂ show corresponding effects at the much higher temperatures.

TABLE VI—FLAME TEMPERATURES OF SELECTED REACTIONS

Reaction Temp ($^{\circ}$ K)	H ₂ + $\frac{1}{2}$ O ₂ H ₂ O	C ₂ N ₂ + O ₂ 2CO + N ₂	C ₄ N ₂ + 2O ₂ 4CO + N ₂	C ₄ N ₂ + $\frac{1}{2}$ O ₂ 4CO + N ₂
T (1 atm)	3120	4850	5260	5520
T (20 atm)	3500	4980	5660	6020
ΔT	380	130	400	500

Effect of Kinetics on Temperature

All arguments presented so far are based on the fact that sufficient time is provided in the combustion reaction to maintain complete equilibrium. One can consider kinetic effects as pertaining both to chemical change and to internal energy-state transitions. With regard to the latter, vibrational transitions have received the most attention since they are the slowest to excite. When temperature is generated only by combustion, however, then since the breaking of bonds generally involves a sequence of many vibrational transitions, it is reasonable to suppose that if chemical equilibrium is obtained vibrational equilibrium is prob-

ably closely maintained also. Obviously this argument does not necessarily hold in the region of active combustion where reaction is still occurring, nor does it apply to activated intermediates. In the latter case, however, their mole fractions are generally small so that the equilibrium over-all energy balance is not much disturbed. The effect of including activated species is a lowering of temperature.

With regard to non-equilibrium persistence of major products of combustion in the final flame gases, several species are of major concern. They are NH_3 , NO , and to a lesser extent CH_4 , C_2H_4 and C_2H_2 . These species are usually out of equilibrium in the sense that their concentrations are in excess. Equilibrium in those cases would require further decomposition to the elements which kinetically is relatively slow except at high temperatures. The fixation of nitrogen in which NO is formed is a practical case where use is made of the slow rate of decomposition of NO below 2000 degrees K.

When one of the above mentioned species is in excess, the flame temperature will be high if the molecule has a positive heat of formation (NH_3 and CH_4) and low if it has a negative heat of formation (NO , C_2H_4 and C_2H_2). However, decomposition kinetics have fairly high activation energies and therefore at temperatures exceeding 2000 degrees K, such non-equilibrium effects are not likely to occur. They have been observed for low energy flames but it can be concluded that for energetic flames exceeding 2500 degrees K, chemical non-equilibrium in normal combustion is not an important phenomenon.

Ultra-High Temperatures

In conclusion, mention can be made of other processes that have recently been used to develop high temperatures. Arcs and discharges can develop temperatures over 5000 degrees K. The flaming electric discharge [2] can produce temperatures approaching 10,000 degrees K to boil the most refractory substances known. The reports at this Symposium indicate that temperatures to 30,000 degrees K have been reached. The shock tube employing rare gases has been used to obtain temperatures reportedly up to 20,000 degrees K or higher. By the nature of the process, however, these temperatures cannot be localized for any appreciable time, say exceeding a second. Recently, intense electric discharges employing the "pinch effect" have yielded temperatures in the range of several hundred thousand degrees. Temperatures in the nuclear fission bomb are in the vicinity of 10^8 degrees K, while those in the nuclear fusion bomb are about 10^8 degrees K. On the other hand, temperatures which can be obtained in controlled nuclear reactors are presently limited by materials of construction (~ 3000 degrees K). A fertile field for future research lies in exploring the possibilities of utilizing nuclear reactions between the limits of present day reactors and bombs.

REFERENCES

1. KIRSHENBAUM and GROSSE, *Jl. Amer. Chem. Society*, 78, 2020 (1956).
2. F. DANIELS, "High Temperatures—Chemistry," *Scientific American*, 197:3, Sept., 1954, p. 116.

THE PRODUCTION OF HIGH TEMPERATURES BY CHEMICAL MEANS AND PARTICULARLY BY THE COMBUSTION OF METALS

A. V. GROSSE

President, Research Institute of Temple University

HIGH-TEMPERATURE research was started at Temple in the fall of 1948. The objectives of the program were [1] to devise and develop chemical methods for the production of high temperatures in the range of 3000-6000 degrees K, and [2] to study physical and chemical phenomena at these high temperatures. After its inception this research program was supported by the Office of Naval Research, the Office of Ordnance Research, and at the present time is sponsored by the Air Force Office of Scientific Research.

A set of photographs illustrating the various methods developed and results obtained is presented here along with explanations of them.

The following summary is taken essentially from the Final Report on the Office of Naval Research project [13], with additions bringing it up to date.

All of the work during the first five years can be classified in two general phases: The combustion of metals and the combustion of gases. Under each of these general phases of combustion several specific topics were investigated and a complete listing of all this work is given below.

The Combustion of Metals

Ignition Temperatures of Metals

Very little work has been done dealing with the ignition temperatures of metals. For this reason such a study was initiated in this laboratory. The ignition temperatures of about 20 metals were measured in a specially designed furnace. Metals were then classified into two groups based upon whether they ignite above or below their melting point. It was not found possible to correlate ignition temperatures with any properties of the metal although it was noted that a general decrease in the ignition temperature occurred in the first two groups of the periodic table as the atomic weight increased. A complete discussion is found in the ninth progress report.*

*The nine Progress Reports and four Technical Reports mentioned are identified in the References.

Burning Characteristics of Metals

A discussion of the theory of metal combustion is given in our third technical report. In this discussion the reasons are given why some metals will not burn. The discussion also covers the methods for predicting which metals will burn to produce high temperatures.

Metals burn in different ways. Aluminum, for instance, ignites after it melts and as a result a burning pool of molten metal is observed during the combustion. In this case the pool of metal takes on a brilliance that makes it impossible to observe this phenomenon with the naked eye. The combustion product is molten aluminum oxide. Molten aluminum metal, being lighter, floats about on the liquid oxide during combustion. Because of these conditions it has been termed the "skating-sun phenomenon." This phenomenon is described in our first progress report and in our second technical report.

Observations made during the combustion of other metals are described in our second progress report and in our ninth progress report. In the latter an explanation is given as to why some metals form "suns" during combustion and some do not.

Centrifugal Reactors

The first descriptions of centrifugal reactor furnaces are given in the third progress report and are continued in the fourth progress report.

In view of the skating-sun phenomenon observed during the combustion of aluminum a cylindrical furnace was designed that could be rotated at 300 rpm. The sun is thereby spread (by centrifugal force) over the entire inside area of the furnace and the generated heat is concentrated in the free volume of the reactor. When these reactors were operated for a short period the oxygen feed was discontinued. The combustion, of course, was terminated but the intense heat within the furnace boiled out some of the remaining aluminum and a jet of aluminum vapor was obtained at the furnace exit. This stream ignited as soon as it hit the air to form an extremely luminous flame. Photographs of

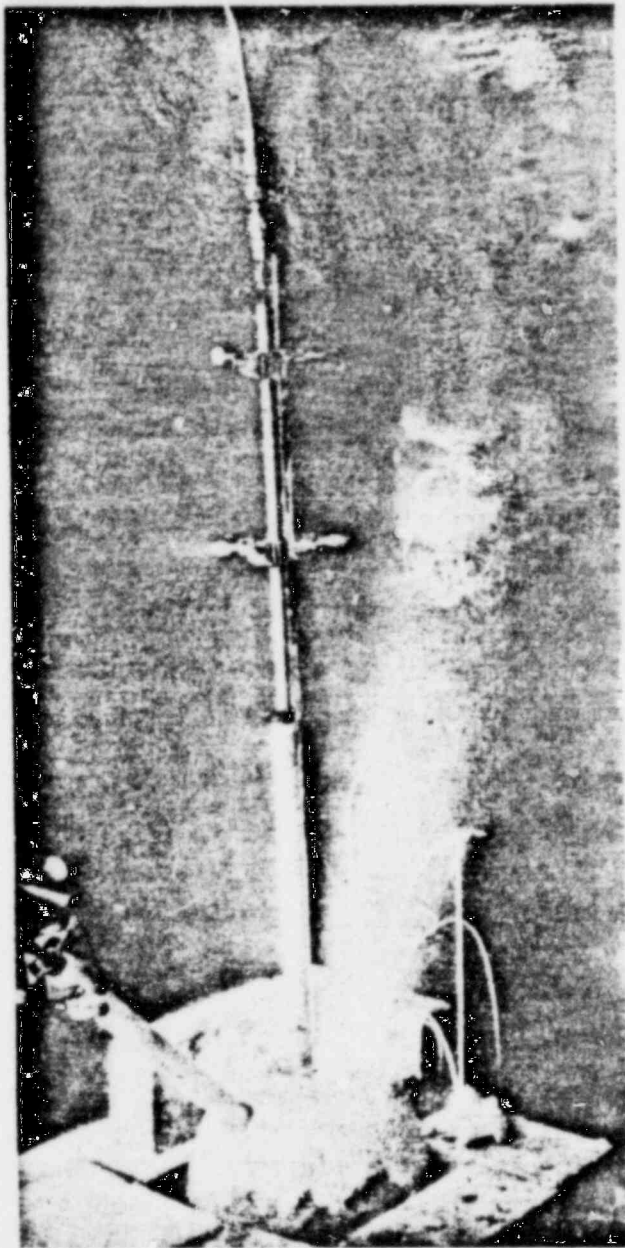


FIGURE 1. Aluminum is burned in oxygen in a spherical pot furnace made out of aluminum oxide (inside diameter of hollow sphere, 7 inches). Oxygen is fed through alumina tube from the top; aluminum rod is fed through a stuffing box in the tube at the side. Inside temperature about 3800 degrees K. Note intense radiation coming from the port hole, with some particles of burning aluminum shooting out of the port.

the centrifugal reactor and of the burning vapor are presented in the third progress report.

Combustion at High Pressures

The aluminum "skating sun" was observed even during the combustion at 150 psia. These experiments

were made to study high-pressure combustion techniques and to observe combustion behavior at elevated pressures.

High-pressure combustion leads to increased combustion temperatures. The theoretical combustion temperature for aluminum in oxygen is 3800 degrees K at one atmosphere and 4400 degrees K at ten atmospheres. These experiments are described in our second and third progress reports. Combustion of magnesium at these pressures is also described.

Combustion at Low Pressures

It was found possible to maintain the combustion of aluminum in oxygen at pressures as low as 4 mm Hg. Under these conditions the "sun" phenomenon was still observed although the brilliance of the sun was much lower. The techniques of this operation are described in the eighth progress report.

Combustion in Fluorine

Aluminum was burned in fluorine to give a dazzling white flame. This experiment as well as some general

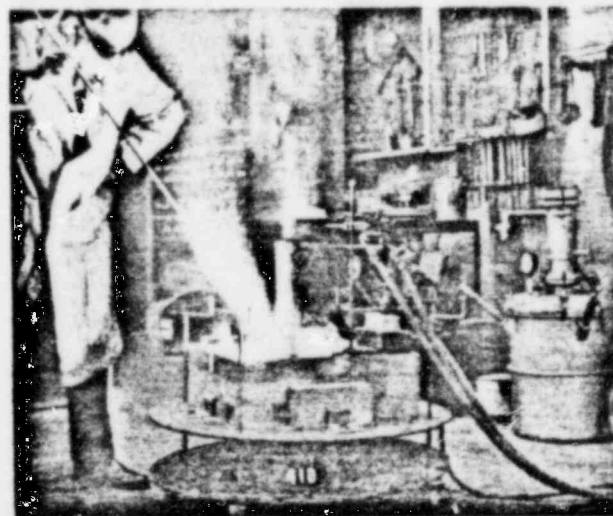


FIGURE 2. The same type of pot shown in Figure 1 is provided with a water-cooled sight-glass to observe the aluminum "skating-sun" phenomenon; (i.e., a boiling pool of aluminum metal floating on molten alumina and burning in oxygen at the rate of about 100 grams of aluminum per minute).

considerations regarding combustion of metals in fluorine are described in the third progress report.

Combustion of Metal Vapors

Metal vapors can be fed to a torch with oxygen and operated in much the same way as the oxy-acetylene torch. It is not possible, however, to pre-mix since in-

stant ignition would result when the oxygen came into contact with the hot vapors (in general all metals ignite before they boil).

A torch was operated in which magnesium vapor was burned in conjunction with a jet of oxygen. These experiments are described in our second progress report.



FIGURE 3. Two skating suns of burning aluminum as observed through the port of Fig. 2.

Combustion of Liquid Metals

A pool of liquid aluminum at about 800 degrees C was atomized using a specially designed ejector system and sprayed into a preheated enclosure. The atomizing gas was preheated oxygen and although ignition was not spontaneous the spray was ignited by placing a pilot flame just inside the enclosure into which the metal was being sprayed. Particle size obtained by the spray nozzle and complete operating details are contained in the seventh progress report.

Combustion of Metal Powders (Oxy-Metal Flames)

Metal powders dispersed in oxygen or air are highly inflammable. A review of the inflammability and explosibility of metal powders is presented in the third technical report.

Powdered metal, usually finer than 200 mesh, was fed into a stream of oxygen and the dispersed phase was ignited as it left a specially designed torch to form a brilliant flame. This phenomenon has been termed "oxy-metal flame" and the work dealing with this subject is discussed in progress reports four to nine.

The feed devices used for the metal powders are described in the fourth and fifth progress reports. The torch designs are described in the fifth progress report together with some flame characteristics for the alum-

inum-oxygen system. Various metals have been burned in this manner and the details of these experiments are described as follows: aluminum [4-6], magnesium [4], iron [5], cast iron [5], manganese [6], silicon [4, 7], titanium [8, 9], calcium [9], and zirconium [13]. Mixtures of these metals, alloys and some metallic compounds are described in the final report.

Flame Temperatures were measured with an optical pyrometer and those for aluminum and iron are reported in the fifth progress report. Other flame temperatures are reported with the description of the particular metal-oxygen system (see previous paragraph).

The radiation from an oxy-aluminum torch was analyzed by means of a Beckman spectrophotometer. These results are reported in the fifth progress report.

Melting and Cutting oxy-metal flames are very hot and highly luminous. They have been found to be effective in the melting of various ceramic materials. In the case of the oxy-aluminum flame no material

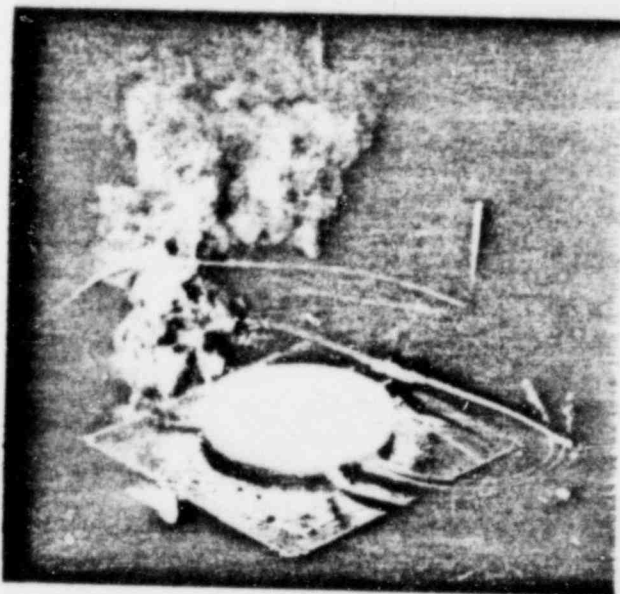


FIGURE 4. A water-cooled aluminum "skating-sun" furnace provides an intense source of radiant energy. The radiant-energy flux, above the quartz window (in center) and at a distance of $2\frac{1}{2}$ inches above the surface of the skating sun is approximately 30 kilocalories per square cm per sec.

has been found capable of resisting its intense heat. A bar of tungsten (melting point 3370 degrees C) disappeared in a few seconds after being placed in direct contact with the flame.

The oxy-metal torch has been used to cut holes in brick walls, in concrete walls up to 30 inches thick and in various other ceramic materials. Further, it has

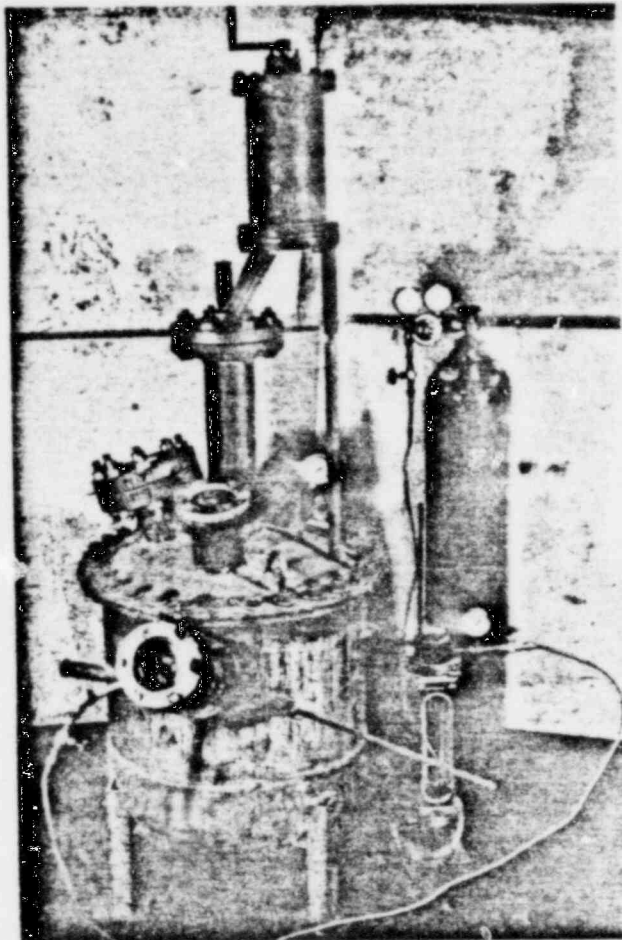


FIGURE 5. This is a pressure reactor for combustion of metals in oxygen under pressure. Metals can be fed, if available in the form of rods, through side stuffing box; if available in the form of balls, by means of a hand-driven gravity-feed ball machine shown above the autoclave.

been successfully used to cut various metals that cannot be cut with the oxy-acetylene cutting torch. Descriptions of various melting and cutting operations are found in various reports [5-8, 12]. Photographs are presented [12] showing large sections of concrete severed with an oxy-aluminum torch.

Mixtures of Metals, Alloys, and Metallic Compounds—Experiments dealing with the operation of oxy-metal torches fed with mixtures of metals are described in the fifth and sixth progress reports. Operations with various alloys and metallic compounds are described in the sixth progress report.

Radiation Measurements—The luminous nature of the oxy-aluminum flame suggested that measurements be made of this important characteristic. Measurements were made of the radiant flux density in calories per

sq cm per sec as a function of distance away from the torch and as a function of the distance along the length of the flame. At a distance of one foot from the centerline of the flame the radiation intensity was 0.9 cal per sq cm per sec. Readings were also made using a Norwood light meter and at a distance of 100 inches from the centerline of the torch a value of 1,860 foot candles was obtained. A description of this work is given in the seventh progress report.

Oxy-aluminum Torch Compared to Oxy-acetylene Torch—A comparison was made of the oxy-aluminum and oxy-acetylene torches and published in the fifth progress report. The flame temperatures of these two flames are very nearly the same but the highly luminous na-

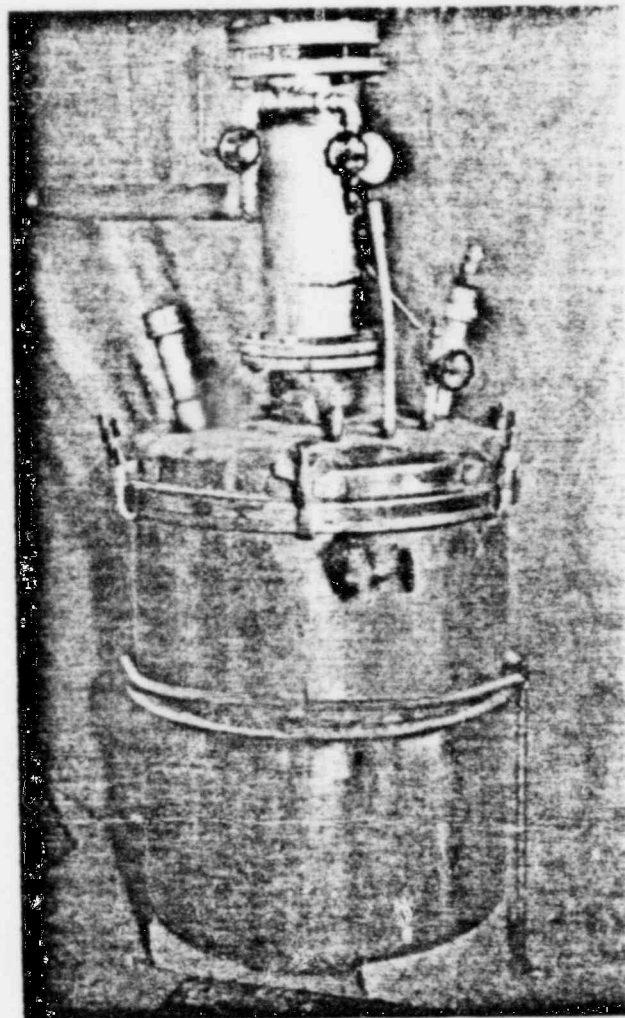


FIGURE 6. Autoclave for the combustion of metals either under pressure (up to 75 psi) or in a vacuum (down to 4 mm Hg). Metals are fed either in the form of rod through stuffing box or through side arm by gravity feed. Observation is through 4-inch sight-glass at top of autoclave.

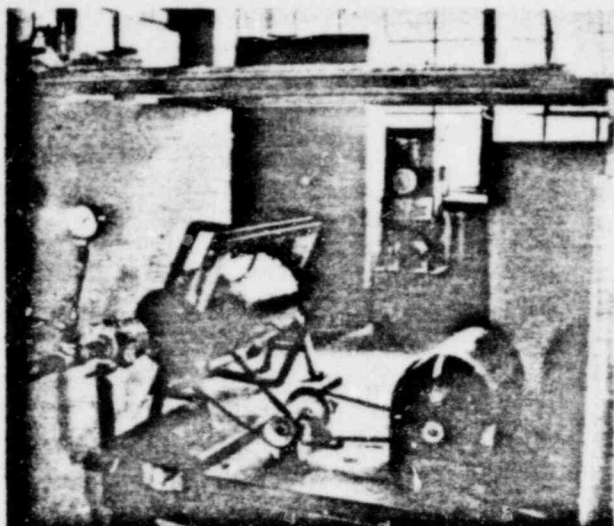


FIGURE 7. Centrifugal force is used to spread burning metal evenly over surface of hollow cylinder made out of desired oxide. Metal is fed in the form of rods through stuffing box shown below the gauge in the figure. The feed rate for aluminum is about 1 pound per minute; of oxygen 300 liters at normal pressure and temperature, per minute. Speed of rotation, about 300 rpm.



FIGURE 8. In operation of the centrifugal furnace a jet of aluminum oxide vapor emerges from the exit port of centrifugal reactor shown in Fig. 7. Alumina boils out at the rate of about 1 pound per minute.

ture of the oxy-aluminum flame together with the fact that an easily condensable combustion product is

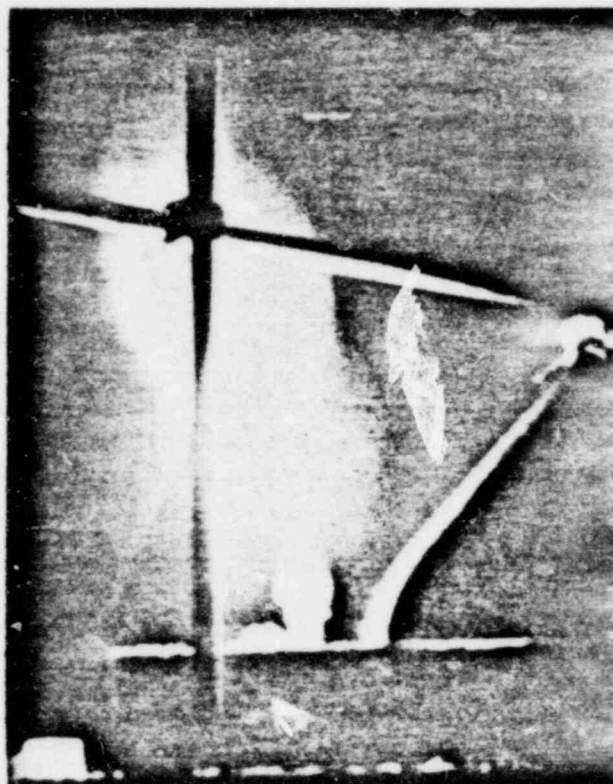


FIGURE 9. This is an electrical-resistance furnace for boiling magnesium metal at 1 atmosphere pressure. Magnesium vapor is shown burning in air as it emerges from the nozzle.

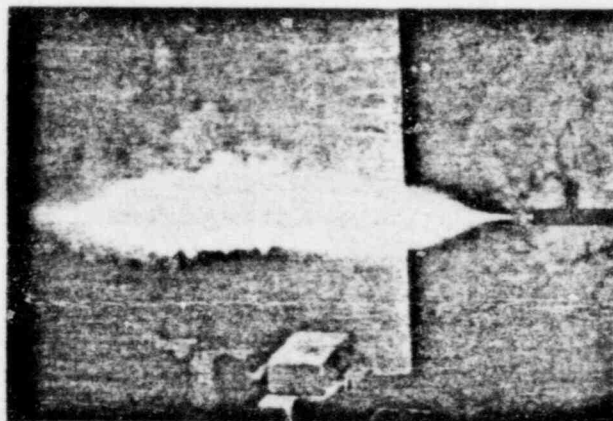


FIGURE 10. A typical metal-powder (oxy-aluminum) burning torch is shown. Three hundred grams of aluminum powder per minute are burned with 190 liters per minute of oxygen. Flame temperature is about 3000 degrees K.

formed gives rise to much more efficient heat transfer from flame to material. This explains why an oxy-acetylene torch is not effective in melting through ce-

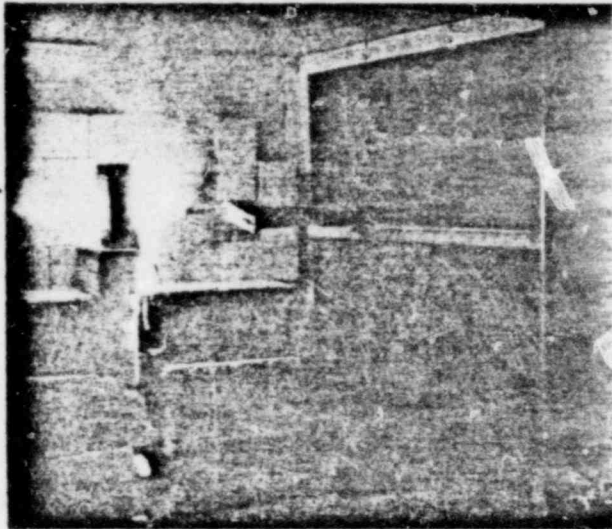


FIGURE 11. The torch of Fig. 10 is shown piercing a standard red brick. Piercing time from 20 to 50 seconds, depending on linear velocity of oxygen and aluminum powder.

ramic materials. The oxy-aluminum torch on the other hand melts through ceramic material with little difficulty.

Combustion of Metal Powders at High Pressures

A technique was developed for operating the oxy-aluminum flame at elevated pressures and is described in detail in our seventh progress report. Runs were made at pressures up to 75 psia. Radiation measurements at elevated pressures were also made and are described in our eighth progress report.



FIGURE 12. Oxy-aluminum torch cutting through cinder block.

Thermodynamics of Metal-Oxygen Systems

Several reports contain discussions dealing with the thermodynamics of metal-oxygen systems. Metallic

oxide stability is treated in the third technical report together with the methods employed in calculating flame temperatures. The titanium-oxygen system is treated in the eighth progress report and the zirconium-oxygen system in the final report. An extensive treatment of the aluminum-oxygen system is presented in the third progress report. A discussion similar to this is also given in the first technical report.

The Combustion of Gases

The oxy-acetylene flame is known to have a temperature of 3,140 degrees C. As such it represents the highest flame temperature among the commonly used gas flames.



FIGURE 13. The first hole cut through concrete slab using early model of oxy-aluminum torch. Diameter of hole about 2 feet.

The conditions necessary for obtaining high flame temperatures in gas flames are essentially the same as discussed previously when dealing with metal combustion. The reaction must be highly exothermic and the reaction products must be stable. Two gaseous systems possessing these characteristics are the hydrogen-fluorine and the cyanogen-oxygen flame. An investigation of these two flames was undertaken to measure the flame temperatures and to study some of the flame characteristics.

The Hydrogen-Fluorine Torch

Hydrogen and fluorine react spontaneously without the help of an ignition device. It is impossible, therefore, to operate a pre-mixed hydrogen-fluorine flame. Additional research may prove that various potential initiators of the reaction can be eliminated but from the experience obtained in this laboratory to

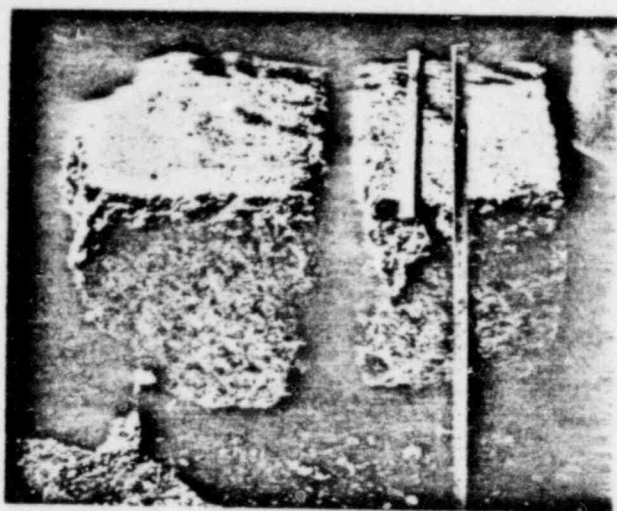


FIGURE 14. A one-ton concrete block cut in half by early model of oxy-aluminum iron torch.

date it has been found impossible to mix hydrogen and fluorine in an equimolar concentration at room temperature and atmospheric pressure without spontaneous ignition. A diffusion-type flame, therefore, was operated and the flame temperature was measured to be 4,300 degrees K. This temperature was measured by a modified line reversal method using a lithium salt instead of the commonly used sodium salt; the sun in the heavens served as the comparison indicator. This work is described in the literature [16, 17].



FIGURE 15. A 3-inch hole cut through 30-inch thick concrete slab.

The Cyanogen-Oxygen Torch

The combustion products of the $(CN_2)-O_2$ flame, i.e., CO and N_2 are the stablest molecules known.

The modified line-reversal method developed in conjunction with the work on the hydrogen-fluorine

torch was used to measure the temperature of the flame. A temperature of 4,640 degrees K \pm 150 degrees K was obtained. The theoretical flame temperature was calculated to be 4,835 degrees K at one atmosphere pressure.

It was possible to operate the cyanogen-oxygen system as a pre-mixed flame since no spontaneous ignition occurs as with hydrogen and fluorine. Blow-off and flashback velocities were determined and compared with the values for other pre-mixed gas flames. This work is described in a special report [18] and in the final report [13] in the section on the Cyanogen-Oxygen flame.

A pre-mixed cyanogen-oxygen flame was operated at pressures up to 100 psia. Although the flame temperature was not measured experimentally the theoretical calculations show the flame temperature to be about 5,000 degrees K. Until recently this represented the highest flame temperature ever produced.

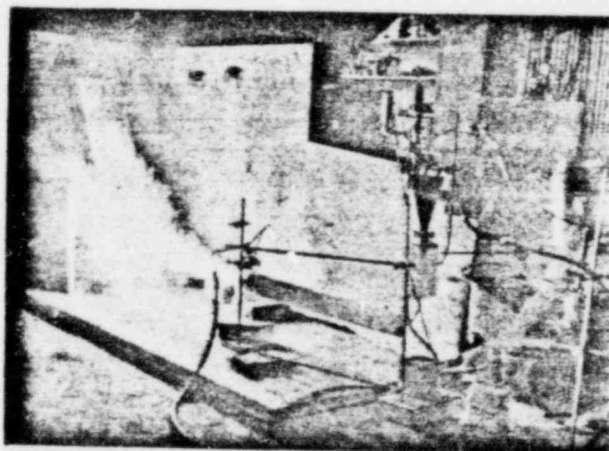


FIGURE 16. The combustion of zirconium powder in oxygen gives a temperature in excess of 4000 degrees K. An oxy-zirconium flame is much brighter than oxy-aluminum flame, due to its higher temperature.

The techniques developed for operating a pre-mixed cyanogen-oxygen flame at elevated pressures were employed to measure flashback and blow-off velocities as a function of pressure. This work is described in the final report [13].

Summaries of O.N.R. Technical Reports

Four technical reports were written pertaining to the work on this project during the O.N.R. period and copies of these reports are available upon request to this laboratory. The content of each of these reports is summarized below.

First Technical Report—"The Combustion of Metals," dated October 15, 1951[10]—this report de-

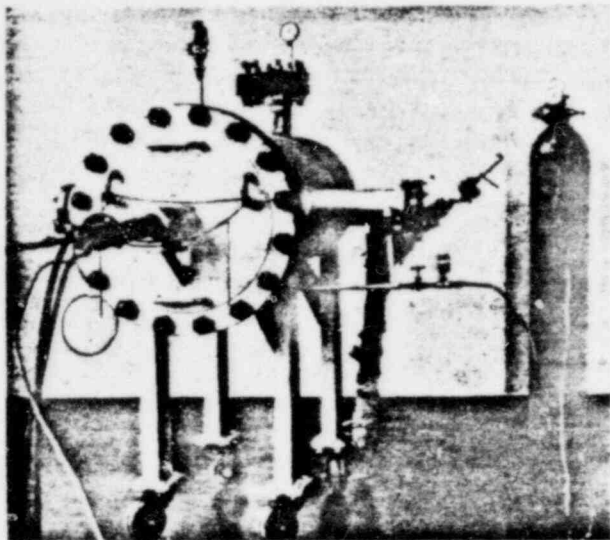


FIGURE 17. End view of pressure reactor for burning metal powders in oxygen fed by torch. Metal powder is fed through oxy-metal torch shown inserted in a standard stuffing box at end of reactor. Maximum pressure is 750 psi.

scribed some of our first observations dealing with the combustion of various metals. The experimental techniques employed in this laboratory to combust various forms of metals are described in detail. The section describing the operation of powdered metal-oxygen torches contains photographs of some of the materials melted by these torches.

A section on combustion thermodynamics discusses the calculation of the temperatures obtainable by burning metals. A generalization is made in terms of

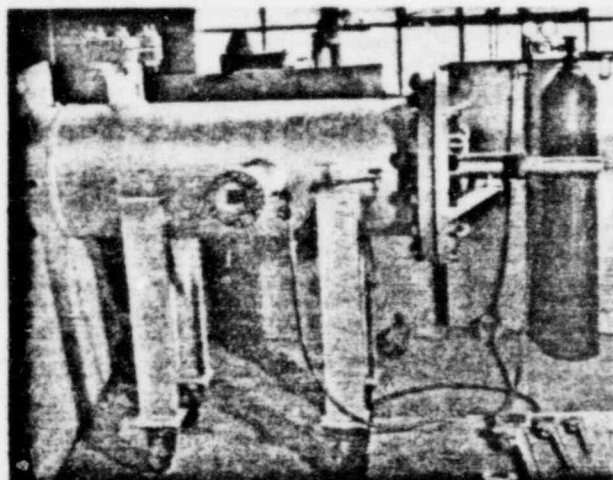


FIGURE 18. Side view of reactor of Fig. 17. Flame is observed through sight-glasses at each side of large reactor.



FIGURE 19. Fifty pounds of aluminum powder exploded in air. Diameter of mushroom, about 50 feet.

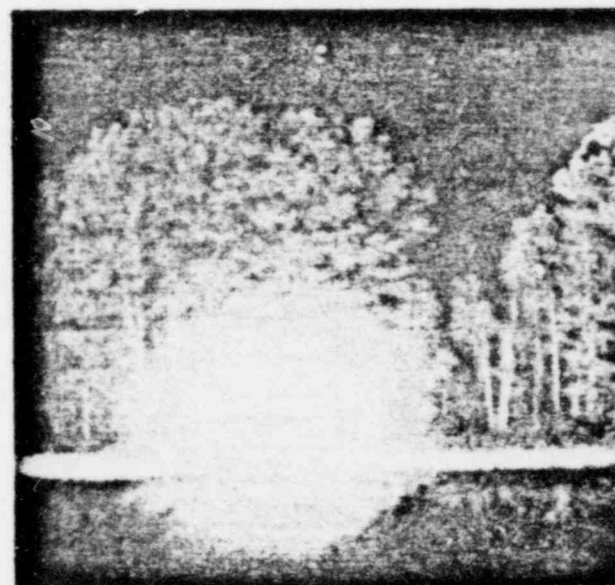


FIGURE 20. Detonation of charge 30 pounds of aluminum liquid-oxygen mixture.

the periodic table to show the location of the metals in the table that are capable of producing high temperatures.

Second Technical Report—"The Aluminum-Sun Furnace," dated July 1, 1952 [11].—A furnace was designed and constructed that serves as a source of high-intensity thermal radiation. It utilizes the combustion of aluminum and therefore generates a temperature of about 3,500 degrees C. The furnace represents a source of high-intensity radiation with a radiating area 12 to 15 inches in diameter. Intensities close to 30 cal per sq cm per sec have been obtained with this device.

The details of the development design and operation of this furnace are described in detail in the second technical report. The blueprints of this furnace are on file in this laboratory.

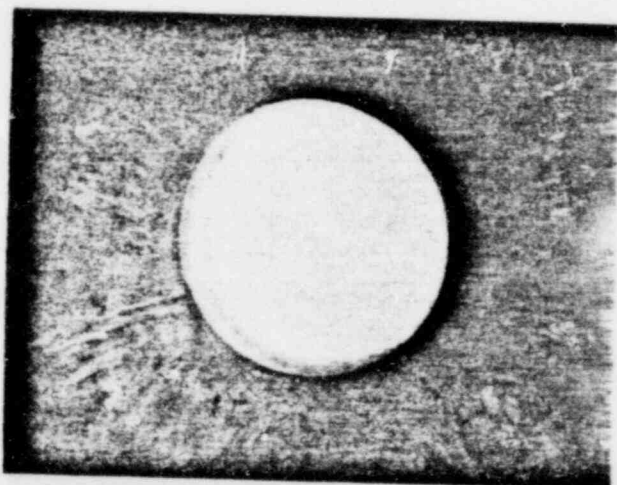


FIGURE 21. Typical brisance plate from aluminum-oxygen explosion. It shows the effect of detonating 100 grams of 53 percent aluminum, 47 percent liquid oxygen (stoichiometric mixture) on $\frac{1}{8}$ -inch steel plate.

Third Technical Report—"Powdered-Metal Flames," dated August 1, 1953 [12]—this report was written to summarize our work dealing with the combustion of metal powders dispersed in oxygen. It reviewed the previous work in this field, beginning with the first experiments of Von Ingenn-Hausz in 1782. A section dealing with the inflammability and explosibility of metal powders is presented which represents a condensation of the work of Hartmann and co-workers at the U.S. Bureau of Mines. A third section contains a fairly comprehensive treatment of the thermodynamics of metal combustion and a fair amount of the thermodynamic data of metallic oxides is tabulated. The final section describes the production of powdered-metal flames. This section deals with torch design, powder feed devices, torch operation, flame characteristics, melting and cutting operations, radiation effects, and high-pressure operation.

Chemical Means and the Combustion of Metals

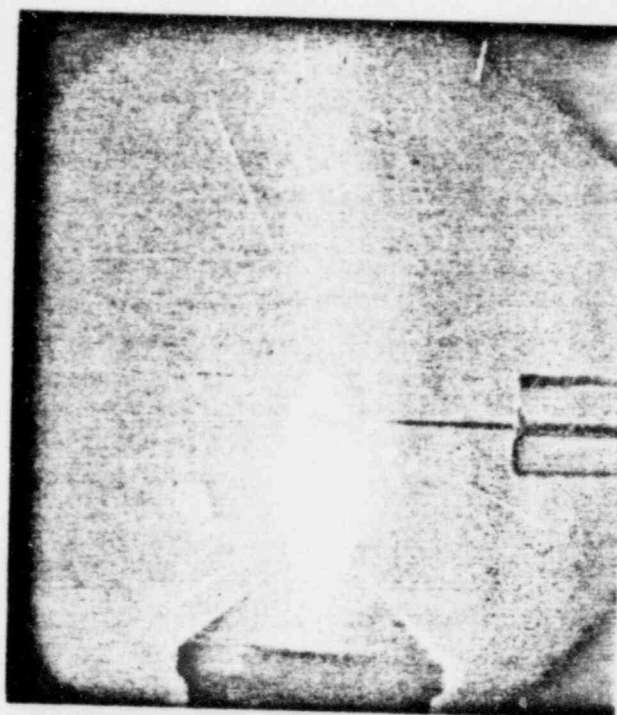


FIGURE 22. The boiling of iron in the tip of a premixed oxy-cyanogen flame cone at 1 atmosphere pressure. The flame temperature is about 4800 degrees K.



FIGURE 23. Flame produced by burning pure ozone to oxygen at 1 atmosphere pressure. Flame velocity, 475 cm per sec.; flame temperature, 2700 degrees K.

The report was written in considerable detail to serve as an excellent reference for anyone working with powdered metals.

The fourth, or Final Report [13], describes the combustion of zirconium powder in oxygen, the cyanogen-oxygen flame at high pressure, and a detailed summary of the work on the high-temperature project.

Whereas the above research pertains to continuous production of high temperatures, instantaneous methods such as explosions and detonations have also been included in our program. This research was primarily supported by the Office of Ordnance Research and a report on this work has recently become available [15].

Recent Work on the High-Temperature Project

At present the basic high-temperature project is being supported primarily by the Air Force Office of Scientific Research. A chemical method for producing continuous temperatures in the range of 5000-6000 degrees K has recently been described [14, 24].

A number of publications on high-temperature non-metallic flames have appeared in scientific periodicals and a list of them is included in References.

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