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VIOLENTLY SPRAYED SODIUM-AIR REACTION IN AN ENCLOSED VOLUME

by

Theresa S. Krolikowski

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Printed in the United States of America

Available from

Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

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Argonne, Illinois 60439

VIOLENTLY SPRAYED SODIUM-AIR REACTION
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by

Theresa S. Krolikowski

Chemical Engineering Division

Based on a thesis submitted to
the Office for Graduate Studies, Graduate Division,
Wayne State University,
Detroit, Michigan,
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

September 1968

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NOMENCLATURE

A_0	Total cross-sectional flow area of orifices, cm^2
c	Molar density, $\text{g-mol}/\text{cm}^3$
C_p	Heat capacity at constant pressure, $\text{cal}/(\text{g-mol})(^\circ\text{K})$
C'_p	Heat capacity at constant pressure, $\text{cal}/(\text{g})(^\circ\text{K})$
C'_v	Heat capacity at constant volume, $\text{cal}/(\text{g})(^\circ\text{K})$
d	Diameter, cm
D	Diffusion coefficient, cm^2/sec
ΔF	Free energy of reaction, $\text{cal}/\text{g-mol Na}_2\text{O}$
h	Heat-transfer coefficient, $\text{cal}/(\text{sec})(\text{cm}^2)(^\circ\text{K})$
H	Spray-chamber height, cm
ΔH^c	Heat of crystallization, $\text{cal}/\text{g-mol}$
ΔH^v	Heat of vaporization, $\text{cal}/\text{g-mol}$
k	Thermal conductivity, $\text{cal}/(\text{sec})(\text{cm})(^\circ\text{K})$
k_y	Mass-transfer coefficient, $\text{g-mol}/(\text{sec})(\text{cm}^2)$
K_p	Equilibrium constant
$\bar{m}$	Average mass, g
M	Molecular weight
n	Number of moles
N	Molar flux, $\text{g-mol}/(\text{sec})(\text{cm}^2)$
P	Pressure, atm
Q_T	Heat of reaction at temperature T , $\text{cal}/\text{g-mol O}_2$
Q_{TB}^*	Defined in Eq. 15
r	Particle radius, cm
R	Universal gas constant, $82.06 (\text{cm}^3)(\text{atm})/(\text{g-mol})(^\circ\text{K})$
t	Time, sec
T	Temperature, $^\circ\text{K}$

v	Velocity, cm/sec
Y	Gaseous mole fraction
ϵ	Emissivity
μ	Viscosity, poise
ν	Number of particles ejected in one time increment
ρ	Density, g/cm^3
σ	Stefan-Boltzmann constant, $1.356 \times 10^{-12} \text{ cal}/(\text{sec})(\text{cm}^2)(^\circ\text{K}^4)$
γ	Surface tension, dynes/cm

Dimensionless Groups

Nu	Nusselt number, hd/k
Pr	Prandtl number, $C_p\mu/k$
Re	Reynolds number, $dv\rho/\mu$
Sc	Schmidt number, $\mu/\rho D$
Sh	Sherwood number, $k_y d/cD$
We	Weber number, $dv^2\rho/\gamma$

Subscripts

A	Ambient conditions
B	Burning conditions
f	Diffusion film zone conditions
g	Gas
j	Jet
l	Liquid
n	Nozzle
N_2	Nitrogen
Na	Sodium
Na_2O	Sodium Oxide
O_2	Oxygen
p	Particle
t	Total

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SUMMARY

Ten-gram quantities of molten sodium (350-425°C) were injected by a pneumatic, piston spray-injector with drive pressures of 1000-1500 psig into a closed reaction chamber, 91.44 cm high and 15.24 cm in diameter, containing dry air or dry air-nitrogen mixtures. The sodium was sprayed through seven 0.0762- or 0.0254-cm-diam orifices. The rate of the pressure rise resulting from the sodium-air burning reaction was measured during the spraying interval. The pressure-rise rate was a measure of the reaction rate.

The pressure-rise rates ranged from 25 to 75 atm/sec, and the peak pressures attained were in the range 1.6 to 4.1 atm. The experimental results were compared on a reduced pressure-rise rate basis, (atm/sec)/(g Na/cm³). The pseudoconcentration term, g Na/cm³, was the weight of the in-flight burning sodium in the spray at any time after the spray reached the top of the chamber, divided by the volume of the chamber. This conversion eliminated the restrictions of the spray-chamber geometry and the sodium mass flowrate.

The spray particle size had the most pronounced effect on the reaction rate, which increased as the particle size decreased. Increasing the spray velocity resulted in a modest increase in the reaction rate. The reaction rate decreased slowly as the oxygen content of the atmosphere was lowered until, at an oxygen concentration of 4 m/o, there was no visible burning.

A mathematical model was developed to predict the burning rate and burning temperature of a single spherical sodium particle moving through air or air depleted in oxygen. The model was based on the assumption that the reaction rate was controlled by the diffusion of oxygen to a combustion zone surrounding the particle. A quasi-steady-state approach and an averaging technique were used to correlate the reaction rates of individual particles with the theoretical burning rate of a spray and the theoretical pressure rise in the enclosing volume.

The theory correctly predicted the direction and magnitude of the experimentally observed variations in reaction rate with respect to oxygen content, spray velocity, and particle size. The theory also predicted a cessation of vapor-phase combustion below an oxygen concentration of 4 m/o.

I. INTRODUCTION

Nuclear-power-reactor technology has progressed enough so that large reactors can be operated near metropolitan areas. The design of each reactor is accompanied by extensive accident analyses. These detailed analyses must establish that the probability of experiencing a major accident is extremely low and, moreover, that the consequences of such an occurrence would not constitute an undue public-safety hazard. Obviously, the accident analyses are meaningful only if the course of the hypothetical accidents and the individual accident steps have a sound scientific basis.

The fast power reactors currently under development use liquid sodium as a coolant. Sodium is an especially attractive heat-transfer medium because of its high thermal conductivity and its high boiling point, which makes operation under elevated pressures unnecessary.

Safety considerations require the enclosure of reactor systems in a containment shell. In the event of a nuclear accident or equipment failure, this structure must be capable of withstanding the resulting temperatures and pressures in order to isolate any scattered radioactive materials. During an accident, liquid sodium at a high temperature may be discharged from one of the sodium systems into the building atmosphere. Theoretically, there is a significant release of energy in the sodium-air reaction, which therefore is of major importance in reactor hazards analyses.

In this work, molten sodium (350-425°C) was injected into a closed reaction chamber containing dry air. A pneumatic, piston spray-injector was used to spray the sodium through a set of seven orifices. The pressure-rise rate resulting from the sodium-air reaction was measured. Since the injection interval was short, and the reaction occurred while the sodium was in flight, the initial loss of energy to the chamber walls was minimal and the reaction chamber approximated an adiabatic volume. Thus, the heat of reaction was primarily used in raising the temperature and pressure of the chamber atmosphere, and the pressure-rise rate was a true measure of the reaction rate. The effects of varying the spray velocity and the spray particle size, and of lowering the oxygen content of the chamber atmosphere, were investigated.

A mathematical model was developed to predict the burning rate and burning temperature of a single spherical sodium particle moving through air or air depleted in oxygen. The model was based on the assumption that the reaction rate is controlled by the diffusion of oxygen to a combustion zone surrounding the particle. A quasi-steady-state approach and an averaging technique were used to correlate the reaction rates of individual particles with the theoretical burning rate of a spray and the theoretical pressure rise in the enclosed volume. The experimentally observed variations in the pressure-rise rate were in good agreement with the theoretically predicted trends.

II. LITERATURE SURVEY

The literature survey is divided into three parts. The first part discusses the sodium oxidation reaction and the factors affecting it. The second part reviews previous studies of the sodium-air reaction, many of which are qualitative in nature. The final part briefly considers the disintegration of liquid jets.

A. Studies of Sodium Oxidation

Sodium is a waxy, lustrous, silvery metal, which melts at 370.98°K and boils at 1176.9°K.¹⁵ Sodium reacts with oxygen to form various oxides but only two, sodium oxide (Na₂O) and sodium peroxide (Na₂O₂), can be formed in significant amounts under combustion conditions.³² Sodium oxide formation may be represented by the reaction

Sodium oxide is a white powder, which melts at 1193°K and dissociates at approximately 2100°K.⁵ Sodium peroxide formation may be represented by the reaction

Pure sodium peroxide is a pale yellow powder, which melts at 948°K with decomposition.⁵ During sodium combustion, the presence of water vapor could result in the formation of sodium hydroxide by the reaction.

Sodium hydroxide is a white powder, which melts at 591.6°K and boils at 1663°K.¹⁷ The presence or absence of the above substances during combustion is dependent on the pressure, temperature, and humidity conditions during reaction.

Longton conducted a series of fundamental tests^{20,21} to determine the effects of pressure, temperature, and moisture content on the sodium oxidation reaction. Three distinct modes of reactivity were found, as shown in Tables I and II. When the ratio of the oxygen partial pressure to the water vapor partial pressure exceeded 5×10^5 , no detectable reaction (reaction rate $< 1 \times 10^{-6}$ g Na/(cm²)(min)) occurred up to 550°C, the maximum temperature employed. At intermediate pressure ratios in the range 9×10^3 to 4×10^5 , there was a region where the sodium did not react at a detectable rate below a certain temperature, the ignition temperature. At and above this ignition temperature, a vigorous combustion process developed.

TABLE I. Modes of Reactivity of Sodium at Various Water Vapor-Oxygen Levels²¹

Partial Pressure of Water Vapor, mm Hg	Partial Pressure of Oxygen, mm Hg ^a									
	10	50	100	200	300	400	500	600	700	900
0.00002	N	N	N	N	N	N	N	N	N	N
0.0001	I	N	N	N	N	N	N	N	N	N
0.001	I	I	I	I	I	I	N	N	N	N
0.01	R	R	I	I	I	I	I	I	I	I
0.1	R	R	R	R	R	R	R	R	R	I
0.25	R	R	R	R	R	R	R	R	R	R

^aN: No detectable reaction at any temperature up to 550°C; reaction rate $< 1 \times 10^{-6}$ g Na/(cm²)(min).

I: No reaction until a certain temperature, the ignition temperature, is exceeded.

R: Immediate reaction, without ignition at 105°C.

TABLE II. Temperatures Corresponding to the Sodium-reaction Modes²¹

Partial Pressure of Water Vapor, mm Hg	Partial Pressure of Oxygen, mm Hg									
	10	50	100	200	300	400	500	600	700	900
0.00002	550	550	550	550	550	550	550	550	550	550
0.00001	460	550	550	550	550	550	550	550	550	550
0.001	296	292	288	295	310	380	550	550	550	550
0.01	105	105	190	200	207	215	240	261	280	390
0.1	105	105	105	105	105	105	105	105	105	232
0.25	105	105	105	105	105	105	105	105	105	105 R

At pressure ratios of less than 7×10^3 , reaction occurred readily at 105°C, the minimum temperature used. Rate determinations in these instances indicated agreement with a parabolic reaction-rate law. Ignition temperatures were not determined under these conditions, because ignition appeared to depend upon the nature and thickness of the oxide film rather than on the temperature of the system.

Longton also found that hydrogen influences the reaction of sodium with oxygen in a manner directly comparable to that of water vapor. Tests²² were performed at a constant partial pressure of oxygen of 200 mm Hg. Table III shows the results, together with the results from the water vapor tests, under similar conditions, for comparison. Identical modes of reactivity are displayed as the hydrogen or water content of the oxygen gas is increased. The experimental hydrogen partial pressures were selected to have values exactly one-half of those used in the water vapor experiment because in the reaction

one-half mole of hydrogen is liberated for every mole of water vapor reacted. Longton postulated that the hydrogen assumed a catalytic role in the systems he studied.

TABLE III. Comparison of Effects of Water Vapor and of Hydrogen upon the Mode of Reaction of Sodium²²

$P_{\text{H}_2\text{O}}$, mm Hg	$P_{\text{O}_2}/P_{\text{H}_2\text{O}}$	Phenomenon	P_{H_2} , mm Hg	$P_{\text{O}_2}/P_{\text{H}_2}$	Phenomenon
0.00002	1×10^7	No detectable reaction at 550°C	nil	-	No detectable reaction at 550°C
0.0001	2×10^6	No detectable reaction at 550°C	0.00005	4×10^6	No detectable reaction at 550°C
0.001	2×10^5	Ignition at 295°C	0.0005	4×10^5	Ignition at 270°C
0.01	2×10^4	Ignition at 200°C	0.005	4×10^4	Ignition at 242°C
0.1	2×10^3	Immediate slow reaction at 105°C	0.05	4×10^3	Immediate slow reaction at 105°C

B. Studies of Sodium-Air Reaction

The types of accidents involving the release of sodium into the atmosphere surrounding a nuclear reactor can be divided into three broad categories: (1) explosive ejection, (2) pressurized spray, and (3) stagnant pool. Experimental investigations have generally dealt with one of these types of accidents; therefore the studies are discussed in the above order.

1. Explosive Ejection of Sodium

Of the three types of accidents, the explosive ejection of sodium results in the most severe reaction because of the potentially large mass of finely dispersed sodium discharged. Humphreys¹⁴ ejected variable amounts of 400°C sodium, by the detonation of a hydrogen-oxygen gas mixture, into a sealed reaction vessel containing air at normal ambient conditions, and measured the resulting internal peak pressures. Because his work is the most significant contribution in this area to date, the data are reproduced in Fig. 1.

Humphreys developed a theoretical model to predict the maximum temperatures and pressures resulting from the contained sodium-air reaction. This model is based on the assumption that the predominant reaction that occurs, when high-temperature molten sodium in a finely divided state is mixed with air, is the oxidation of sodium to form sodium peroxide:

It is assumed that this reaction proceeds until all of the oxygen is combined before additional sodium reduces the sodium peroxide to sodium monoxide:

The presence of water vapor results in the formation of sodium hydroxide:

Based on the energy derived from these reactions, the peak pressures and temperatures are calculated. Figure 1 shows the theoretical maximum

Fig. 1. Comparison of Theoretical and Experimental Maximum Pressures for the Sodium-Air Reaction

pressure as a function of the quantity of sodium ejected into the reaction vessel, assuming 100% reaction (of sodium or oxygen, whichever is limiting) and no heat loss to the vessel wall. The maximum pressures attained experimentally are substantially lower than those predicted by the theoretical model. Humphreys attributes the difference to a combination of incomplete sodium combustion and system heat losses. The theoretical maximum temperature curve has the same shape as the pressure curve with a peak value of approximately 3600°C at a sodium-to-oxygen ratio of 4.

In the opinion of Leibowitz¹⁹ and Baker and Tevebaugh,¹ the discrepancies between Humphreys' experimental and theoretical results were caused by the assumption that reaction is complete and that Na_2O_2 is the primary reaction

product. At the temperatures involved in a sodium-air reaction, the peroxide is highly unstable and the proposed reaction will probably not occur. Thus, the primary reaction product should consist entirely of sodium monoxide. In addition, Humphreys' model neglects the chemical equilibrium that exists between the products and the reactants. Regardless of the burning mechanism, the maximum pressures and temperatures are limited by the thermodynamic properties of the system.

Leibowitz calculated the equilibrium temperature, pressure, and composition conditions for sodium-air and sodium-air-water mixtures in an adiabatic volume, using a computer program designed to minimize free energy. The calculation was performed for dry air and for air saturated with water at 25°C. The species existing at equilibrium were considered to be $\text{N}_2(\text{g})$, $\text{O}_2(\text{g})$, $\text{Na}(\text{g})$, $\text{NaO}(\text{g})$, and $\text{Na}_2\text{O}(\ell)$. When water is

initially present, the additional species present at equilibrium are $\text{H}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and $\text{NaOH}(\text{g})$. As shown in Fig. 1, Humphreys' maximum experimental pressures are very near the theoretically possible maximum pressures, as calculated by Leibowitz. The theoretical maximum temperature had a peak value of 1987°C at a sodium-to-oxygen ratio of 5 for dry air. In this calculations, Leibowitz found that the effect of NaO formation is small; the largest change noted by excluding NaO was an increase of 40°C in the equilibrium temperature for a sodium-to-oxygen ratio of 5. The presence of water slightly lowered the maximum attainable temperature and pressure. Leibowitz's values are in good agreement with those of Baker and Tevebaugh¹ and Garelis and Nims,¹⁰ who used the classical equilibrium-constant method to calculate the equilibrium conditions. This method consists of solving the set of simultaneous equations involving equilibrium constants, material balances, and a heat balance, in a closed system.

Münster²⁶ also reported calculations for this system based on a sequential reaction scheme. The pressures agreed quite well with those of Leibowitz; however, the temperatures predicted by Münster for sodium-to-oxygen ratios greater than 2 exceeded the calculated maximums based on thermodynamics.

Moore²⁵ considered the formation of shock waves from the combustion of gaseous mixtures and used the sodium-air reaction as the basis for numerical calculations. He found that, under some conditions, the calculated transient peak pressures at the boundary walls greatly exceed the equilibrium adiabatic pressures. A high degree of dispersion is required to give the shock-wave effects predicted.

Charak and Smith⁷ reported some preliminary results in a study of sodium expulsion into air. The technique used involved firing a Teflon capsule containing 1-2-g quantities of sodium from a revolver, along an argon-filled firing chamber, at about 100 ft/sec. At the end of the firing chamber, a mechanical stop halted the capsule, and molten sodium was expelled into an air chamber with a volume such that the sodium-to-oxygen ratio was maintained at a stoichiometric value of 4. The sodium temperature was varied up to 650°C . Pressure rises on the order of 20-80 psig in 0.88 sec were obtained. In constant-volume air cells, the measured pressures were greater for cells with smaller diameters, probably because of improved sodium-to-air contact. The investigators also observed that a considerable fraction of the sodium did not ignite until it neared the top of the air chamber, and that a small quantity of sodium did not react with the air until the sodium droplets returned by gravity to the bottom of the air cell.

In a study of the behavior of fission iodine in the presence of sodium-air combustion, Rygaert and co-workers³¹ suddenly introduced

sodium vapor, with a small amount of iodine, at 1080°C into a closed volume containing atmospheric air (50% humidity). The sodium-to-oxygen ratio varied from 2.3 to 3.7. A maximum pressure rise of 23 psig was observed within 2 sec from the start of the reaction, and a maximum temperature between 1100 and 1300°C was reached during the explosion. The pressure in the reaction vessel after cooling indicated that 30-50% of the available oxygen had reacted.

2. Pressurized Sodium Sprays

The only effective difference between the explosive ejection and the pressurized spray of sodium is the reaction rate. At a given temperature, the rate of reaction is a function of the rate of sodium surface exposure, which depends on the mass flowrate and the particle size of the sodium. In a high-pressure spray, a very large discharge rate and a fine particle dispersion probably could not exist simultaneously.

Cowen and Vickers⁸ studied the ignition of liquid sodium which was forced with a pressure of 3-4 atm through a small hole (0.008-0.020 in. in diameter) into air. They found that, under these conditions, liquid sodium ignites at temperatures down to 120°C (the lowest temperature used in their work), irrespective of the atmosphere's moisture content. On the other hand, when sodium exposed to ordinary atmospheric conditions was gradually heated in an open dish, ignition did not occur until the sodium temperature reached 440-470°C. In the latter case, the formation of a thick oxide film on the sodium surface during heating probably inhibited ignition. Cowen and Vickers also observed that ignition did not occur when liquid sodium was injected into a nitrogen atmosphere, either moist or dry.

Nelson and Nelson²⁷ conducted large-scale tests in which they sprayed sodium into a chamber with varying oxygen content and made visual observations to determine the minimum oxygen concentration necessary to sustain combustion. Ejection pressures of 0.5-40 psig were used. Their results, based on initial oxygen content, are summarized as follows:

0-5% O ₂	No visual combustion
5-10% O ₂	Sparking only in cases of very fine dispersal
10-15% O ₂	Prompt combustion to be anticipated in most cases

The 5% oxygen limit set by Nelson and Nelson has been confirmed in measurements reported by Gracie and Droher,¹¹ who made the additional observation of the presence of very dense smoke at oxygen concentrations down to 0.1%.

Mangold and Tidball²³ injected various amounts of 455°C sodium through different nozzles, with a drive pressure of 50 psig, into a large

hemispherical chamber with varying oxygen concentrations. The purpose of the study was to determine effective methods of fire prevention. The investigators concluded that the most promising methods of preventing combustion were limiting the oxygen content to 5% and cooling the chamber walls to cause rapid cooling of the sodium.

Hines, Gemant, and Kelley¹³ measured the maximum pressures attained when 455°C sodium was sprayed through a nozzle into a tank (30 in. in diameter and 49 in. long) containing various concentrations of oxygen.

Fig. 2. Effect of Oxygen on Maximum Pressure Rise as Reported by Hines, Gemant, and Kelley¹³

In all the tests, pressurized nitrogen at 360 psig was used to drive 1 lb of sodium into the tank within 20 sec. The experiments showed that the maximum pressure decreased as the initial oxygen content was decreased. Figure 2 shows the effect of oxygen content upon the maximum pressure. In these tests, the pressure changes were also recorded as a function of time. When the initial oxygen content was 21 or 10.5%, an initial steep pressure-rise rate indicated that ignition occurred as soon as the sodium was introduced into the reaction vessel. At an initial oxygen content of 5.3%, the pressure did not rise until the last of the sodium entered the vessel. This delayed reaction was attributed to a failure of the sodium to

ignite readily in the oxygen-depleted atmosphere until the pressurized nitrogen propelling the sodium entered the reaction vessel at the end of the sodium spray and caused a markedly finer dispersion. The pressure rise with an initial oxygen content of 0.6% was slow and smooth.

Gracie and Droher¹¹ measured the pressure-rise rates in a chamber (3 x 4 x 4 ft) resulting from the injection of 0.5 lb of molten sodium through a narrow slit (0.001-0.006 in. wide). The oxygen concentration ranged from 0 to 5%, a zone of no combustion in the reports of the investigators cited earlier. The effects of varying several system variables were determined. The results indicate that the pressure-rise rate increased: (1) as the oxygen concentration was increased from 0 to 5 v/o; (2) as the initial sodium temperature was increased from 316 to 650°C; and (3) as the moisture content of the atmosphere was increased from less than 3 grains/lb of gas to 300 grains/lb of gas. There was no significant effect of spraying pressure between 30 and 60 psi. Placing a baffle near the entry point of the sodium interrupted the spray and resulted in a lower pressure-rise rate than would have been obtained with an unobstructed spray. The measured pressure-rise rates ranged from 0.08 to 4.8 psi/sec.

3. Stagnant Pools of Sodium

The studies of burning pools of sodium^{10,11,18} were conducted to provide qualitative information regarding burning rates and burning mechanisms. The reported average burning rates range from 5 to 10 lb/(hr)(ft²). These values tend to increase with an increase in the sodium pool depth and to decrease slightly with an increase in the surface area.¹¹ In most of the fires, the initial burning rate appeared to be higher than the average burning rate. Shallow pools burned as nodules on an irregular oxide surface, whereas deeper, well-insulated pools burned on the molten-metal surface.

Temperature measurements made during steady-state burning indicated that the sodium temperatures varied linearly with depth, as would be expected for a conducting medium, with a maximum temperature of about 700°C at the surface. In the flame at the liquid-air interface, there was a significant jump in the temperature to about 985°C. Temperatures in the gas phase above the flame decreased rapidly with distance from the flame.

The mechanism of extinction consisted of sodium oxide building up from the bottom of the pool, penetrating the surface, and finally forming a hard crust, which extinguished the fire. The appearance of oxide at the molten surface was accompanied by a considerable increase in temperature and oxygen consumption. It was postulated that the irregular surface temporarily provides a larger surface area for burning with the consequent liberation of more energy.

C. Disintegration of Liquid Jets

The phenomenon of jet disintegration has been a subject of theoretical and experimental investigation ever since Lord Rayleigh made his first analyses of jet instability in 1879.³⁰ The visual changes that occur in a jet, as the flowrate through a nozzle is increased, have been described by Keith and Hixson¹⁶ as follows:

"At low flowrates, drops form individually at the nozzle tip and grow in size until the weight or buoyance force overcomes the interfacial tension and the drop is released. At increased flowrate, a point is reached where a very short continuous neck of liquid exists between the nozzle tip and the point of drop detachment; this velocity is called the jetting point. Further increases rapidly lengthen the jet, which appears as a smooth column of liquid with occasional transient lumps (Rayleigh jet). Finally, the jet takes on a ruffled appearance at its outer end and the drops formed are less uniform than in the earlier stages; this occurs at or near the maximum length of the jet and will be called the critical velocity. Increasing the flow further decreases the jet length and increases drop

nonuniformity until the jet breakup point retreats to the nozzle tip and a nonuniform spray of rather small drops results; this last point is called the disruptive velocity or point of atomization."

Figure 3a is a relative plot of jet length versus liquid flowrate identifying the areas described above. The terms varicose region and sinuous region are used because of the occasional lumps in the jet and because of irregular weaving of the jet, respectively.

a. Jet Length as a Function of Liquid Flowrate

b. Flow Region Plot Suggested by Ohnesorge

Fig. 3. Flow Regimes in a Liquid Jet⁶

of 400°C, the experimental jet Reynolds number is 2.5×10^5 and the jet Weber number is 4.6×10^4 . Figure 3b shows that this is in the atomization region. Most of the available empirical correlations for predicting particle size as a function of Weber and Reynolds numbers are applicable only in the varicose and sinuous regions. Miesse²⁴ presents the one correlation that was developed for the atomization region from experimental data on jets of water and liquid nitrogen. The correlation is

$$\frac{d_p}{d_n} = We_j^{-1/3} (23.5 + 0.000395 Re_j). \quad (9)$$

Unfortunately, for Reynolds numbers greater than 1.2×10^5 (a value requiring extrapolation beyond Miesse's experimental data), this correlation predicts an increase in the particle size with an increase in spray velocity, an unreasonable result.

Ohnesorge²⁸ used dimensional analysis to differentiate between the several regions of drop formation. Using the jet Reynolds number

$$Re_j = \frac{d_n v \rho_l}{\mu_l} \quad (7)$$

and the group $We_j^{1/2}/Re_j$, where the jet Weber number is,

$$We_j = \frac{d_n v^2 \rho_l}{\gamma_l}, \quad (8)$$

Ohnesorge suggested the plot shown in Fig. 3b. Since the Weber number is a common term, the Weber number versus the Reynolds number is also shown.

In the present work, the spray particle size is of interest. At a spray velocity of 1.07×10^4 cm/sec (350 ft/sec) and a sodium temperature

An attempt was made to determine the spray particle size experimentally by using sodium at 150°C. Chapter V discusses the details of the method. Although the results were not completely satisfactory, they did indicate that about 65 w/o of the particles had diameters that varied uniformly over the range of 0-840 μ . For the test conditions, the Reynolds number was 1.37×10^5 , the Weber number was 4.25×10^4 , and Eq. 9 predicts a mean particle size of 1700 μ , which differs by a factor of at least 2 from the experimental results. It was concluded that an empirical prediction of the spray particle size is not possible with the currently available correlations.

III. THEORETICAL ANALYSIS

The theoretical analysis centers upon predicting the pressure rise in a closed volume due to the violently sprayed sodium-air reaction. The method can be divided into two parts. Initially, the steady-state burning rate of a single spherical particle of sodium moving through air or air depleted in oxygen is determined. Secondly, a quasi-steady-state approach and an averaging technique are used in correlating the reaction rates of the individual sodium particles forming a spray with the burning rate of the spray itself and the pressure rise in the enclosing volume.

A. Steady-state Combustion of a Single Spherical Particle of Sodium

The steady-state analysis of a single burning sodium droplet moving through an oxidizing atmosphere is based on the model shown in Fig. 4. The assumptions made in the development of this model are:

1. The combustion rate for the reaction

is controlled by the diffusion of oxygen from the surroundings through a stagnant nitrogen film to the burning zone, which is a flame front concentric with the sodium particle.

2. Sodium vaporizes at the droplet surface and diffuses to the flame front in a stoichiometric ratio to the oxygen.

3. Chemical equilibrium for the combustion reaction is maintained in the burning zone at the flame temperature.

COMBUSTION REACTION: $2\text{Na}(g) + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Na}_2\text{O}(\ell)$

Fig. 4. Combustion Model
for Sodium Particle

4. As a result of the two preceding specifications, sodium oxide must leave the burning zone in a stoichiometric ratio to the oxygen.

The rate of transport of oxygen to the burning zone can be expressed in terms of molar flux and gaseous mole fraction as

$$N_{\text{O}_2} = k_y(Y_{\text{O}_2,A} - Y_{\text{O}_2,B}) + Y_{\text{O}_2,B}(N_{\text{O}_2} + N_{\text{N}_2}), \quad (11)$$

which is a defining relationship for k_y in a binary system. The transport of each species is treated as the sum of a diffusional contribution and a bulk-flow contribution,² the first and second terms, respectively, on the

right-hand side of Eq. 11. Since the nitrogen is assumed to be stagnant, $N_{N_2} = 0$ and Eq. 11 can be rewritten as

$$N_{O_2} = \frac{k_y (Y_{O_2,A} - Y_{O_2,B})}{1 - Y_{O_2,B}} \quad (12)$$

A heat balance is obtained by equating the heat generation rate, due to reaction at the flame front, to the heat transfer rate by radiation, convection, and mass transport in the film zones:

$$\begin{aligned} N_{O_2} (-Q_{T_B}) &= \sigma \epsilon (T_B^4 - T_A^4) + h (T_B - T_A) \\ &+ 4N_{O_2} [\Delta H_{Na}^V + C_{p,Na} (T_B - T_{Na})] \\ &+ N_{O_2} C_{p,O_2} (T_B - T_A) \\ &+ 2N_{O_2} [C_{p,Na_2O} (T_A - T_B) + \Delta H_{Na_2O}^C] \end{aligned} \quad (13)$$

For the combustion reaction given in Eq. 10, the heat of reaction per mole of oxygen at the burning temperature, Q_{T_B} , is determined from

$$Q_{T_B} = Q_{298} + (2C_{p,Na_2O} - 4C_{p,Na} - C_{p,O_2}) (T_B - 298), \quad (14)$$

where Q_{298} , the heat of reaction at 298°K, is easily calculated from readily available heat-of-formation data.

To present the heat balance in a more compact form, define

$$\begin{aligned} Q_{T_B}^* &= -Q_{T_B} - 4[\Delta H_{Na}^V + C_{p,Na} (T_B - T_{Na})] \\ &- C_{p,O_2} (T_B - T_A) \\ &- 2[C_{p,Na_2O} (T_A - T_B) + \Delta H_{Na_2O}^C] \end{aligned} \quad (15)$$

Then Eq. 13 may be rewritten as

$$N_{O_2} Q_{T_B}^* = \sigma \epsilon (T_B^4 - T_A^4) + h (T_B - T_A), \quad (16)$$

and combining Eqs 12 and 16 yields

$$\frac{k_y (Y_{O_2,A} - Y_{O_2,B})}{1 - Y_{O_2,B}} Q_{T_B}^* = \sigma \epsilon (T_B^4 - T_A^4) + h (T_B - T_A). \quad (17)$$

The heat-transfer coefficient, h , and the mass-transfer coefficient, k_y , are obtained in the following fashion by introducing the Nusselt number,

$$Nu = \left(\frac{hd_p}{k} \right)_f, \quad (18)$$

and the Sherwood number,

$$Sh = \left(\frac{k_y d_p}{cD} \right)_f. \quad (19)$$

The heat-transfer correlation for forced convection around a sphere³ is

$$Nu = 2.0 + 0.6Re^{1/2}Pr^{1/3}, \quad (20)$$

and by analogy to the heat-transfer phenomena,² the mass-transfer correlation is

$$Sh = 2.0 + 0.6Re^{1/2}Sc^{1/3}, \quad (21)$$

where the Reynolds number, the Prandtl number, and the Schmidt number are defined as

$$\left. \begin{aligned} Re &= \left(\frac{d_p v_f \rho}{\mu} \right)_f, \\ Pr &= \left(\frac{C_p \mu}{k} \right)_f, \\ \text{and} \\ Sc &= \left(\frac{\mu}{\rho D} \right)_f. \end{aligned} \right\} \quad (22)$$

It is assumed that chemical equilibrium exists in the combustion zone; therefore, by definition, the partial pressures of the gaseous reactants in the burning zone are related to the equilibrium constant for Na_2O formation in the following manner:

$$K_p = \left(\frac{1}{P_{Na}^2 P_{O_2}^{1/2}} \right)_B, \quad (23)$$

which can be simplified to

$$\begin{aligned}
\frac{1}{K_p} &= P_t^{5/2} \left(Y_{Na}^2 Y_{O_2}^{1/2} \right)_B \\
&= P_t^{5/2} \left(4 Y_{O_2,B} \right)^2 Y_{O_2,B}^{1/2} \\
&= 16 \left(P_t Y_{O_2,B} \right)^{5/2}.
\end{aligned} \tag{24}$$

The relationship between the equilibrium constant and the standard free-energy change for the combustion reaction is

$$\Delta F = -RT_B \ln K_p, \tag{25}$$

which, combined with Eq. 24, becomes

$$\Delta F = RT_B \ln \left[16 \left(P_t Y_{O_2,B} \right)^{5/2} \right]. \tag{26}$$

Thus, the model results in two equations, Eqs. 17 and 26, containing two unknowns, T_B and $Y_{O_2,B}$. The equations are solved numerically by using the Newton-Raphson method²⁹ and a CDC-3600 computer. Appendix A discusses details of the solution.

Table IV shows the results of a typical calculation. The equilibrium oxygen concentration in the burning zone does not have a significant effect

TABLE IV. Typical Results of the Combustion Calculation for a Single Spherical Particle of Sodium

Ambient Oxygen Mole Fraction	Equilibrium Oxygen Mole Fraction	Burning Temperature, °K	Burning Rate $10^4 \text{ g-mol O}_2/(\text{sec})(\text{cm}^2)$
0.20	0.1308	2065	4.24
0.19	0.1208	2052	4.19
0.18	0.1108	2038	4.14
0.17	0.1009	2023	4.09
0.16	0.0911	2007	4.03
0.15	0.0814	1989	3.96
0.14	0.0718	1970	3.90
0.13	0.0623	1949	3.82
0.12	0.0530	1926	3.74
0.11	0.0439	1899	3.65
0.10	0.0350	1868	3.55
0.09	0.0265	1831	3.43
0.08	0.0185	1786	3.28
0.07	0.0113	1727	3.10
0.06	0.0053	1644	2.86
0.05	0.0015	1518	2.52
0.04	0.0001	1332	2.05
0.03	-	(1104)	-
Sodium temperature 775°K			
Particle diameter 500 μ			
Ambient temperature 298°K			
Particle velocity $9.14 \times 10^3 \text{ cm/sec (300 ft/sec)}$			
Ambient pressure 1.0 atm			
Emissivity 0.5			

on the burning rate until the ambient oxygen mole fraction is greater than 0.06. When the oxygen concentration in the atmosphere falls below a mole fraction of 0.04, the burning temperature rapidly approaches the boiling point of sodium (1177°K) and the melting point of sodium oxide (1193°K), and thus the vapor-phase combustion model is no longer valid. At the higher oxygen concentrations, the burning temperature is below the dissociation temperature of liquid sodium oxide (2100°K), so that the proposed combustion reaction is feasible.

The parameters in the theoretical model were varied over a wide range of values. Sections 1-4 below discuss the effects of these variations on the solutions.

1. Effect of Variations in Emissivity

Since it was difficult to choose an accurate value for the emissivity, calculations were carried out for emissivities ranging from 0.1 to 0.9. Figure 5 shows the results for the extreme values. A ninefold increase

Fig. 5. Effect of Emissivity on Theoretical Burning Temperature and Burning Rate of Sodium Spheres

or

$$\left(\frac{\partial K_p}{\partial T_B} \right)_P < 0. \quad (29)$$

When the equilibrium constant K_p (defined in Eq. 24) is substituted in the above expression, the result is

in the emissivity only produces a maximum decrease in the burning temperature of 83°K. This indicates that radiation is not the predominant mode of heat transfer from the burning particle. The decrease in the burning temperature is accompanied by a decrease in the equilibrium mole fraction of oxygen in the burning zone. This is in agreement with chemical equilibrium theory, as can be seen by examination of the van't Hoff Equation.⁹

$$\left(\frac{\partial \ln K_p}{\partial T_B} \right)_P = \frac{Q_{T_B}}{RT_B}. \quad (27)$$

The combustion reaction considered in this work is exothermic; therefore

$$\left(\frac{\partial \ln K_p}{\partial T_B} \right)_P < 0 \quad (28)$$

$$\left[\frac{\partial \left(\frac{1}{16P_t^{5/2} Y_{O_2,B}^{5/2}} \right)}{\partial T_B} \right]_P < 0, \quad (30)$$

which upon simplification becomes

$$\left(\frac{\partial Y_{O_2,B}}{\partial T_B} \right)_P > 0. \quad (31)$$

Thus, as the burning temperature decreases, the equilibrium mole fraction of oxygen in the burning zone also decreases with a corresponding increase in the burning rate. In the present case of emissivity variation, the burning rate has a maximum increase of 27%.

Since varying the emissivity does not greatly alter the burning rate and burning temperature, a value of 0.5 was used in all the subsequent work.

2. Effect of Sodium Temperature and Ambient Temperature

Increasing the initial sodium temperature or the ambient temperature reduces the driving forces for heat transfer. To maintain the heat balance described in Eq. 13, the burning temperature increases, as shown in Figs. 6 and 7. The increase in the burning temperature results in a decreased burning rate, as was explained in Section 1 above.

Fig. 6. Effect of Sodium Temperature on Theoretical Burning Temperature and Burning Rate of Sodium Spheres

Fig. 7. Effect of Ambient Temperature on Theoretical Burning Temperature and Burning Rate of Sodium Spheres

For the sodium temperatures and ambient temperatures considered, there is not a significant variation in the burning temperatures or burning rates.

3. Effect of Ambient Pressure

Figure 8 indicates that an increase in the ambient pressure increases both the burning temperatures and the burning rate. The equilibrium constant, K_p , is independent of pressure;⁹ therefore,

$$\left(\frac{\partial K_p}{\partial P}\right)_{T_B} = 0. \quad (32)$$

Substituting the definition of K_p from Eq. 24 yields

$$\left[\frac{\partial \left(\frac{1}{16 P_t^{5/2} Y_{O_2,B}^{5/2}} \right)}{\partial P} \right]_{T_B} = 0, \quad (33)$$

or

$$\Delta(P_t Y_{O_2,B})_{T_B} = 0. \quad (34)$$

Fig. 8. Effect of Ambient Pressure on Theoretical Burning Temperature and Burning Rate of Sodium Spheres

Thus, if the burning temperature remained constant, an increase in the total pressure would be accompanied by a proportional decrease in the equilibrium mole fraction of oxygen in the burning zone, $Y_{O_2,B}$. But a decrease in $Y_{O_2,B}$ increases the burning rate and, therefore, the heat-generation rate. The burning temperature will increase until a heat balance has been achieved. This increase in the burning temperature will, in turn, affect $Y_{O_2,B}$ as shown above. The net result of these simultaneous interactions is an increase in the burning temperature and the burning rate.

There is not much variation in the burning temperature with pressure at the lower ambient oxygen concentrations. But as the pressure increases, the minimum oxygen

concentration at which vapor-phase combustion occurs increases because of the rise in the sodium boiling point.

4. Effect of Particle Velocity and Size

Variations in the particle velocity or in the particle size have an important effect on the heat- and mass-transfer coefficients. When the velocity is increased or the particle size is reduced, these coefficients become appreciably larger. As a result, the burning rate is significantly increased, while the burning temperature remains essentially unaltered, which indicates that heat transfer by forced convection is the predominant mode of energy transmission from the flame front. Figures 9 and 10 show these results.

Fig. 9. Effect of Particle Velocity on Theoretical Burning Temperature and Burning Rate of Sodium Spheres

Fig. 10. Effect of Particle Size on Theoretical Burning Temperature and Burning Rate of Sodium Spheres

B. Combustion of a Sodium Spray in an Enclosed Volume

In the determination of the burning rate of a sodium spray in an enclosed volume, the following assumptions are made:

1. All the sodium particles in the entering sodium spray are spherical in shape and of the same size. The particle diameter is specified somewhat arbitrarily as either a fractional or integer multiple of the diameter of the orifices in the spray-injector. As was pointed out in

Section II.C above, the available empirical correlations of particle size with respect to jet Reynolds and Weber numbers are not applicable in this work.

2. The spherical particles originate at the orifices. This agrees with the description of the atomization region given in Section II.C above.

3. The particles are distributed equally over any cross section of the chamber. This assumption becomes invalid for spray chambers with extremely large cross-sectional areas with respect to the spray outlet area.

4. Ignition of the spray is instantaneous at the point of origin.

5. Combustion ceases when the spray impinges on the top of the spray chamber.

6. The spray chamber is an adiabatic volume.

A quasi-steady-state approach is used in the calculation. A spray chamber with a definite geometry is divided into an integral number of vertically stacked subvolumes. The spray velocity and the initial particle size are specified. A time increment Δt is defined as the time required for a particle to pass through a subvolume. In a time interval Δt , ν particles are ejected, where ν is determined from the spray rate and the particle size. Since it would not be practical to consider each particle individually, the ν particles are represented by the average particle ejected at $\Delta t/2$, so that now the problem is reduced to considering ν particles ejected simultaneously at the midpoint of the time interval. At the beginning of each time increment, the steady-state burning rate is calculated for each subvolume that contains or will contain particles. These calculations are based on the existing pressure, temperature, and composition conditions, and on the diameter of a particle entering the subvolume. Using this burning rate, the decrease in size experienced by the reacting particles and the heat generated in each subvolume due to reaction in the time Δt are calculated. Then the temperature, pressure, and composition changes in each subvolume during the time interval Δt are determined. These calculations are repeated for as many time increments as the spray is in existence. Appendix A shows a detailed listing of the FORTRAN computer program used in this work.

The above calculation was carried out for conditions that approximated the experimental portion of this work, and the parameters that might have an important effect on the rate of the sprayed sodium-air reaction were varied. A total spraying time of 50 msec was used. From the results of these computer calculations, which provide total pressure values as a function of time, theoretical pressure-rise rates were determined, since this was the experimentally measured variable. The theoretical

pressure-rise rates were essentially constant over the 50-msec spraying time. (For longer spraying times, this would not be valid because the pressure-rise rate begins to decrease when the ambient conditions have been altered significantly due to reaction.)

To remove the restrictions of the spray-chamber geometry and the sodium mass flowrate, the results are presented in terms of a reduced pressure-rise rate, $(\text{atm/sec})/(\text{g Na/cm}^3)$. The psuedoconcentration term, g Na/cm^3 , is the weight of the in-flight burning sodium in the spray at any time after the spray reaches the top of the chamber, divided by the volume of the chamber. At a spray velocity of 350 ft/sec in a 3-ft-high spray chamber, a spray particle will be in flight and available for reaction with oxygen for 8.6 msec, reaction ceasing when it impinges on the top of the chamber by assumption. Calculations revealed that under these conditions the diameter of a 572- μ particle will decrease by less than 2%. (In the theoretical calculations, the particle diameter was arbitrarily set equal to three-quarters of the orifice diameter.) Therefore, the weight of in-flight burning sodium is adequately approximated by the weight of sodium in a nonreactive spray existing between the injector and the top of the chamber. For a specific physical system, this weight has a constant value,

$$\text{weight of in-flight sodium} = \rho_{\text{Na}} A_0 H. \quad (35)$$

Fig. 11. Effect of Spray Particle Size on Theoretical Reduced Pressure-rise Rate

Figures 11 and 12 show the results of the calculations. The spray particle size has the most significant effect on the pressure-rise rate. The reduced pressure-rise rate is inversely proportional to the particle diameter to the 1.47 power. Increasing the spray velocity or the initial sodium temperature results in a modest increase in the reduced pressure-rise rate. The variation with initial sodium temperature is primarily due to density differences, which affect the amount of in-flight sodium. The relationship of the pressure-rise rate to the ambient oxygen concentration has the same characteristics as the burning rate of a single sodium sphere.

In addition to providing total pressure values as a function of time, the calculation described above also supplies the transient values for

Fig. 12

Effect of Several System Variables on Theoretical Reduced Pressure-rise Rate

the following: ambient temperature, ambient oxygen mole fraction, burning rate, burning temperature, and variation of particle size during flight and reaction. Table V shows how these values vary after a 50-msec spraying time.

TABLE V. Typical Results of the Combustion Calculation for a Sodium Spray in an Enclosed Volume

System Specifications:

Spray chamber height, 91.44 cm (3.0 ft)
 Spray chamber diameter, 15.24 cm (0.5 ft)
 Spray velocity, 9.14×10^3 cm/sec (300 ft/sec)
 Seven orifices, 0.0762-cm diameter each
 Initial sodium temperature, 775°K

	Initial Value	Average Values after 50 msec
Ambient pressure, atm	1.0	2.26
Ambient temperature, °K	298	679
Ambient oxygen mole fraction	0.20	0.1923
Particle burning rate, g-mol O ₂ /(sec)(cm ²)	3.98×10^{-4}	5.27×10^{-4}
Burning temperature, °K	2065	2199
Total amount of gas in chamber, g-mol	0.682	0.676
Weight of sodium ejected, g	-	12.2
Initial spray particle diameter, μ	572	572
Spray particle diameter after reaction, μ	-	562
Oxygen reacted, m/o	-	4.4

C. Summary of Theoretical Results

The steady-state combustion calculation for a single spherical particle of sodium predicts that the burning rate and burning temperature decrease slowly, as the ambient-oxygen concentration decreases from 20 to 4 m/o. As the ambient-oxygen concentration decreases from 8 to 4 m/o, the burning temperature and burning rate decrease at a sharper rate. For ambient-oxygen concentrations less than 4 m/o, the burning temperature falls below the boiling point of sodium (1177°K) and the melting point of sodium oxide (1193°K), and the vapor-phase combustion model is not valid.

The burning rate increases significantly when the particle diameter is decreased or the particle velocity is increased. The burning temperature is essentially insensitive to variations in the particle diameter and particle velocity, which indicates that heat transfer by forced convection is the predominant mode of energy transmission. Variations in the emissivity, ambient temperature, and sodium temperature produce a small change in the burning rate and burning temperature. Increasing the ambient pressure increases the burning temperature and the burning rate.

The combustion calculation for a sodium spray in an enclosed volume reveals that the spray particle size is the most important parameter. As the spray particle size decreases, the burning rate and the sodium surface area available for reaction increase, thereby significantly affecting the pressure rise due to reaction in the enclosed volume. The theoretical reduced pressure-rise rate is inversely proportional to the particle diameter to the 1.47 power.

Increasing the spray velocity or the initial sodium temperature results in a modest increase in the reduced pressure-rise rate. The relationship of the pressure-rise rate to the ambient-oxygen concentration has the same characteristics as the burning rate of a single sodium particle.

IV. EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 13 shows the experimental system used in this investigation. The basic components included a piston spray-injector, a spray chamber, an oscillograph for recording temperature and pressure data, and a controller to regulate the heating of the sodium.

Fig. 13. Experimental System for Sprayed Sodium-Air Reaction Studies

A. Spray-injector

Figure 14 is a cross section of the piston spray-injector. The injector was fabricated of Type 304 stainless steel. The inner surfaces of the sodium chamber and of the piston chambers were vapor-honed and electrolyzed with a chromium alloy coating (1 to 2 mils thick) using a process of The Electrolyzing Corporation.*

The injector shown in Figs. 15 and 16 operated in the following manner: The lower piston was driven by pressurized nitrogen (1000-1500 psig) introduced from a ballast tank through a solenoid valve (Asco Valve, 0.375-in. orifice, for pressures of 25-1500 psig). This piston pushed the upper piston to drive molten sodium upward into the reaction chamber through a discharge disc containing suitable orifices. The orifice pattern

*The Electrolyzing Corporation, 1505 East End Avenue, Chicago Heights, Illinois.

Fig. 14. Cross Section of Sodium Piston Spray-injector

Fig. 15. Component Parts of Sodium Piston Spray-injector

Fig. 16. Assembled Sodium Piston Spray-injector

For the remaining 0.125-in (0.318-cm) depth, drills of the hole sizes specified above were used.

To protect the sodium from contact with the atmosphere before ejection, the discharge disc was covered with a 0.0005-in. (0.0013-cm)-thick foil seal and a top plate. The top plate had the same orifice pattern as the discharge disc with 0.0625-in. (0.159-cm)-diam holes. Foil seals of annealed copper and of gold were equally satisfactory. The top plate, the foil seal, the discharge disc, and a spacer were bolted to the injector body as a layered set. The gasket cut from a sheet of 0.125-in. (0.318-cm)-thick, high-temperature silicon rubber provided a good seal when the sodium was heated to 350°C and the total heating time did not exceed 30 min. For longer heating times and higher temperatures, the gasket was partially melted when the injector was dismantled at the end of the run.

A narrow-banded cylindrical heater (115 V, 275 W) was used to heat the sodium chamber. The power leads from the heater and the leads from a Chromel-Alumel thermocouple, inserted between the heater and the outer wall of the sodium chamber, passed out of the injector through standard Conax fittings. The thermocouple was used to control the heating of the sodium, which will be discussed in Section IV.C below. The heater was surrounded by firebrick insulation to minimize heat losses.

Two types of heaters, differing in height by 0.5 in. (1.27 cm), were used during this work. The shorter heater fit snugly around the sodium chamber enabling the heating-control thermocouple to be inserted in a fairly reproducible position. The higher heater enclosed the discharge disc assembly as well as the sodium chamber. The spacer extended $1/32$ in. (0.079 cm) beyond the discharge disc and produced a gap between the heater and the sodium chamber wall. Thus, the position of the heating-control thermocouple varied, and the heated discharge disc assembly decreased axial heat losses. The net result was a higher initial sodium temperature. This was confirmed by heating the sodium with both types of heaters and measuring the sodium temperature. A temperature difference of 75°C was determined.

(see Fig. 15) consisted of six holes equally spaced on a 0.25-in. (0.635-cm)-diam circle. A seventh hole at the center of the circle coincided with the center of the disc. One discharge disc had 0.010-in. (0.0254-cm)-diam holes, and another had 0.030-in. (0.0762-cm)-diam holes. Drilling such small holes to a depth of 0.375 in. (0.935 cm) in stainless steel would be difficult. Therefore, 0.62-in. (1.57-cm)-diam drill was used to drill holes 0.25 in. (0.635 cm) deep from the bottom of the disc.

The injector was filled with molten sodium and sealed in a $2 \times 1\frac{1}{2}$ -module glovebox containing a high-purity helium atmosphere. The glovebox had safety-glass panels equipped with glove ports, grounded electrical outlets inside the box, an airlock to introduce materials into the box without contaminating the atmosphere, and a regulator to maintain a positive internal pressure of 1 in. of water. A purification system maintained both the oxygen and water-vapor content of the helium below 5 ppm.

The sodium used in the experiment was reagent grade, purchased from the Baker and Adamson Co. Table VI gives the limits of impurities that could have been present in the sodium as specified by the manufacturer. The percentage of other impurities such as SO_4 and nitrogen was less than that specified by the ACS Code 2188.

TABLE VI. Limits of Sodium Impurities

Substance	Chlorine	PO_4	Iron	Heavy Metals
Limit of Impurity, %	0.0015	0.0005	0.001	0.0005

B. Spray Chamber

The spray chamber and its auxiliary members are pictured schematically in Fig. 17. The spray chamber was a 36-in. (91.44-cm)-long, 6-in. (15.24-cm)-diam Pyrex pipe, with standard aluminum Pyrex pipe flanges at the top and bottom. It was mounted vertically on a stand which consisted of two stainless steel plates, 0.75 in. (1.91 cm) thick and 12 in. (30.48 cm) square, separated by four steel support tubes at the corners (1.75 in. [4.45 cm] OD, 0.75 in. [1.91 cm] ID, 24 in. [60.96 cm] long). The bottom plate of the stand was bolted to the floor. The upper plate had a 6-in. (15.24-cm)-diam hole at the center. The bottom flange of the pipe was bolted to the upper plate of the stand, and a Teflon gasket formed a pressure-tight seal. The injector was also fastened to this plate from below, and a Viton A O ring effected a seal. Figure 18 shows the mounting of the spray chamber and the injector on the stand, as well as the piping between the pressurized nitrogen ballast tank and the injector. Thick-walled copper tubing, 0.5 in. (1.27 cm) ID and 0.625 in. (1.59 cm) OD, was used.

Fig. 17. Schematic Representation of Sodium Spray Chamber

Fig. 18. Detailed View of Spray Chamber and Injector Mounting

The top of the spray chamber was a 6-in. (15.24-cm)-diam blind flange, 0.5 in. (1.27 cm) thick, of stainless steel, which was bolted to the upper pipe flange. A Teflon gas-gasket formed a pressure-tight seal. Evacuation of the chamber, the admission of nitrogen or dry air, and sampling of the chamber atmosphere were accomplished through separate branch lines along a common access line to the top of the chamber.

A Duo-Seal vacuum pump (Model No. 1405B, W. M. Welch Manufacturing Corp.) was used to evacuate the spray chamber. The manufacturer's specifications list a capacity of 58 liters/min (2.05 cfm) and a guaranteed ultimate vacuum of 10^{-4} mm Hg. The gas-sampling loop could be evacuated independently of the chamber.

Spray-chamber atmospheres used were dry air and dry air depleted in oxygen by the addition of nitrogen. The dry air and the nitrogen were obtained from commercially supplied cylinders. Table VII lists the properties of these gases.

TABLE VII. Properties of Dry Air and Nitrogen

Dry Air	Nitrogen	
Dew point: -75°F	Purity:	99.997%
	Dew point:	-85°F
	Oxygen content:	8 ppm

To ensure that the air-nitrogen gas mixtures were well mixed, they were circulated in and out of the chamber by using a diaphragm pump (Model G3, Air Control, Inc.). The absolute pressure of the system was read from a Heise gauge having divisions of 0.1 psi. Figure 19 is a detailed view of the top of the spray chamber.

Fig. 19. Detailed View of Top of Spray Chamber

C. Measurement and Control Instrumentation

Two pressure transducers were mounted in the top of the spray chamber. One was a quartz-crystal pressure transducer with a range of 10-3000 psi (Model 601, Kistler Instrument Corp.). This type of transducer is noted for its high sensitivity and rapid response. The other transducer was a variable-resistance, unbonded strain-gauge pressure transducer with a range of 0-1000 psig (Type No. 4-360-0108, Consolidated Electrodynamics Corp.). A baffle was placed 1.25 in. (3.18 cm) below the top of the chamber to protect the transducers from direct contact with the burning sodium spray. Two Chromel-Alumel thermocouples entered at the top of the chamber through a standard Conax fitting. One was taped to the bottom of the baffle; the other was set freely in the space above the baffle.

The output signals of the spray-chamber thermocouples and pressure transducers were recorded on a Midwestern Model 1210 Direct-Recording Oscillograph. This instrument uses galvanometers to achieve accurate response to rapidly changing input signals. The response of the galvanometer used in this work was flat to $180 \text{ Hz} \pm 5\%$. The recording medium was a light-sensitive paper, which moved at 160 in./sec. Timing lines were automatically registered at 0.1-sec intervals. Figure 20 is a schematic

Fig. 20
Schematic Representation of Pressure- and Temperature-measuring Networks

representation of the complete pressure- and temperature-measuring networks. A Kistler Charge Amplifier, Model 503, converted the charge signals from the quartz-crystal pressure transducer to voltage outputs. A simple potentiometric circuit initially zeroed the signal from the strain-gauge pressure transducer. The input signals to all of the galvanometers were amplified with Dana Model 3400 Amplifiers. To protect the galvanometers from an overload, a simple two-resistor damping circuit was placed between the galvanometers and the amplifiers.

Fig. 21. Schematic Representation of Pressure-transducer Calibration System

The pressure transducers were statically calibrated up to 50 psia after each run by using the system shown in Fig. 21. The Heise gauge used as a standard had 0.1-psi divisions. The calibration data were linear and reproducible.

The heating of the sodium was regulated with a Brown Elektronik strip-chart controller (Model 153, Minneapolis-Honeywell Regulator Co.). A range-expanding potentiometric circuit amplified the controller's base range, -0.5 to 10.5 mV. The design of the injector did not permit direct measurement of the sodium temperature during a run. But even if it had been possible to measure the sodium temperature directly, this would not have been a satisfactory control variable. The heating method produced a temperature gradient in the 0.5-in. (1.27-cm)-thick sodium chamber wall, which would result in additional heating of the sodium beyond a set point when the heater power was shut off. Thus maintaining a constant sodium temperature would have been difficult. Therefore, the control variable was the temperature measured by the Chromel-Alumel thermocouple between the heater and the outer wall of the sodium chamber. The set point was 525°C.

High-speed movies at 6000 frames/sec were taken of each experimental run with a Wollensak Fastax 16-mm camera, Model WF17. A 35-mm f/2.5 lens and a 17-mm f/2.0 lens were used during the experiments with equal success. Kodak Ektachrome ER film, Type B, was used, and a Wollensak Pulse Generator, Model 3106A, recorded 1-msec timing marks on the film. The Fastax Control Unit, Model WF301, synchronized the operation of the camera with the event being photographed. This unit provided for a 0.3-sec delay between the time when the camera began to operate and the time when the solenoid valve at the pressurized nitrogen ballast tank was activated, thus ejecting the sodium. The delay between these two operations ensured that the camera was functioning at the required speed. Two pen-type flashlights were positioned 18 in. (45.72 cm) apart along the side of the spray chamber for distance references in viewing the films.

D. Gas Analysis

Oxygen and nitrogen gas analyses were performed with a gas chromatograph. Samples were taken of the spray-chamber atmosphere, before

Fig. 22. Schematic Representation of Gas-analysis System

and after reaction, by expansion into an evacuated 10-ml sample loop with a four-way stopcock. The sample loop was then transferred to the chromatographic unit where it became an integral part of the system, as shown in Fig. 22. The gas in the sample loop was passed onto a 3-ft (91.44-cm)-long, 0.25-in. (0.635-cm)-diam, 70-80 mesh molecular sieve 5A column by using a purified-helium carrier gas. The oxygen and nitrogen were separated by selective adsorption and eluted individually. Under the conditions employed, argon was not separated from oxygen, and the two gases were released from the column simultaneously.

The chromatographic column was connected to a thermal-conductivity cell containing two sets of tungsten filaments, which served as legs of a Wheatstone Bridge circuit. The helium carrier gas constantly flowed over these filaments and, at a rate proportional to its thermal conductivity, removed the heat generated by the electrical current flowing in the circuit. Oxygen and nitrogen have thermal conductivities lower than that of helium, so that when oxygen and nitrogen entered the cell, less heat was removed from the filaments than with helium. The resulting rise in the temperatures of the filaments increased their resistance and caused a potential imbalance in the Wheatstone Bridge circuit. The degree of this imbalance was indicated on a strip-chart recorder as a peak above a baseline.

The sample response was compared to the response of suitable standards. The relative peak heights provided a measure of sample concentrations. Standards were made by preparing mixtures of gases with known concentrations of oxygen and nitrogen.

E. Experimental Procedure

The initial step in an experimental run consisted of filling the piston spray-injector with sodium in the glovebox. The sodium was heated to approximately 135°C in a stainless steel beaker on a hot plate. Any oxide film was removed from the molten sodium so that a shiny surface remained.

The preheated sodium chamber was then filled to a depth of $1\frac{1}{16}$ in. (2.70 cm) with 12.6 g of sodium, which allowed for expansion when the sodium was heated to higher temperatures. Next, the discharge-disc assembly was bolted into place. After sufficient time (at least 1 hr) had passed to permit cooling of the sodium, the injector was removed from the glovebox and attached to the spray chamber.

The spray chamber was evacuated and filled with the desired gas mixture to a total pressure of 1 atm. The dry air-nitrogen mixtures were formed on a partial-pressure basis. The evacuation and filling procedure was repeated three times. The dry air and nitrogen were mixed for 5 min after the second filling, in order to purge the mixing lines, and a 30-min mixing period followed the final filling.

After a gas sample was taken, heating of the sodium began. Thirty minutes was required to reach the set point of 525°C on the controller. When the controller had maintained the set point for 5 min, the sodium was injected into the spray chamber, and the pressure and temperature changes were recorded as functions of time. Samples of the spray-chamber atmosphere were taken immediately after and 10 min after injection of the sodium.

After the spray-injector had cooled, it was removed from the spray chamber and disassembled. All the component parts of the system were left exposed to the room atmosphere overnight. During this time, most of the unreacted sodium was slowly oxidized. The following day, the system was successively washed with isopropyl alcohol, ethyl alcohol, methyl alcohol, water, and acetone.

V. PRESENTATION AND DISCUSSION OF EXPERIMENTAL RESULTS

In the initial phases of the experimental work, an attempt was made to determine the particle-size distribution of the sodium spray. Following that, combustion experiments were performed, and the data from 34 experimental runs were analyzed to determine the effects of ambient oxygen concentration, orifice size, and spray velocity on the pressure-rise rate in the spray chamber. This chapter presents these results and other experimental observations.

A. Particle-size Distribution

The spray-chamber assembly was rearranged in the experimental runs for the determination of the spray particle-size distribution. The piston spray-injector was mounted on top of the Pyrex pipe. A stainless steel dewar filled with liquid nitrogen to a depth of 48 cm was placed at the outlet of the pipe. The pipe was continuously purged with gaseous nitrogen, which had been circulated through a 12-m copper coil submerged in liquid nitrogen. Sodium at 150°C was sprayed with a drive pressure of 1000 psig through the nonreactive nitrogen atmosphere in the pipe into the dewar. Sieve analyses on the quenched spray were performed in the glovebox.

Four experimental runs of this type were made. The results of the sieve analyses, shown in Table VIII, did not indicate a predominant particle size. About 65 w/o of the particles had diameters that varied rather uniformly over the range 0-840 μ with a mean particle size of 420 μ . Visual observation of the particles larger than 840 μ revealed that they were agglomerates of smaller particles.

TABLE VIII. Experimentally Determined Particle-size
Distributions of a Sodium Spray

Particle Diameter, μ	Weight Fraction			
	Run 1	Run 2	Run 3	Run 4
0-210	0.150	0.172	0.162	0.116
210-420	0.269	0.215	0.172	0.100
420-590 } 590-840 }	0.304	0.119	0.113	0.146
		0.168	0.186	0.219
840-1680 } 1680-~3500 }	0.277	0.193	0.173	0.241
		0.133	0.193	0.178
Initial sodium temperature:		150°C		
Drive pressure on piston:		1000 psig.		
Discharge disc with seven orifices:		0.0762-cm diameter		

Some doubt exists as to whether the above results are truly representative of the spray-particle size. When the sodium spray encountered the liquid nitrogen surface, the spray particles may have undergone additional breakup. A drive pressure of 1000 psig corresponds to a spray velocity of 1.07×10^4 cm/sec (350 ft/sec). (This velocity was determined from the high-speed movies of the combustion runs.) At this velocity, the impact force would have been sizable. Furthermore, about one-third of the sprayed sodium was recovered as a frozen mass stuck to the bottom of the dewar. The particles composing this mass of sodium could have a significant effect on the size distribution. Therefore, this method of determining the particle-size distribution of the sodium spray was abandoned.

At this point, it became apparent that particle sizes could not be readily determined. Since this research was the initial phase in a series of sprayed sodium-air reaction studies, it was decided that the burning phenomena were of primary interest and would be examined first. Detailed characterization of the spray particle size would be a suitable subject for future investigation.

B. Sodium Combustion Data

Initially, some exploratory experiments were run to test the injection apparatus using a steel spray chamber 36 in. (91.44 cm) high and 6 in. (15.24 cm) in diameter. Several observations were made during these experiments:

(1) Mounting a pressure transducer on the side instead of on the top of the spray chamber did not alter the measured pressure-rise rate.

(2) Increasing the number of orifices to 37 and thereby broadening the sodium spray did not alter the peak pressure attained. This indicated that the 7- and 37-orifice discharge discs provided the same sodium-to-oxygen contact. Since the pressure-rise rate could be more easily determined for longer spraying periods, seven-orifice discharge discs were used in the rest of this work.

(3) Shielded thermocouples of 10-ml wire, platinum/90% platinum-10% rhodium, placed along the length of the spray chamber to measure gas temperatures, showed no response during the injection period. Apparently, there was not sufficient time for the gas and the thermocouples to achieve equilibrium. This same lack of response was obtained with the thermocouple above the baffle in the later runs in the glass spray chamber.

Appendix B presents the data from 34 experimental runs in the glass spray chamber. In the first four runs, 3G1-3G4, a set point of 421°C controlled the heating of the sodium (sodium temperature: ~250°C). The sodium spray burned in dry air, but burning failed to occur when the initial ambient

oxygen concentration in the spray chamber was lowered to 18 m/o. It was postulated that the sodium was not hot enough to ignite in the oxygen-depleted atmosphere during the 8.6-msec flight time of a spray particle. Therefore, the heating set point was raised to 525°C in all subsequent runs. The hotter

sodium eliminated the nonignition phenomena. In two other runs, 3G14 and 3G22, complete pressure and temperature records were not obtained. Thus, only the data from 28 runs were analyzed for the results presented here.

Fig. 23. Typical Temperature and Pressure Records

Figure 23 is a typical pressure and temperature record. The injection interval shown is the time required for the injection of 10 g of sodium at 1.07×10^4 cm/sec (350 ft/sec) relative to the initial thermocouple response. The 12.5 g of sodium loaded in the injector was never fully expelled. During the 44-msec spraying period, the spray chamber approximated an adiabatic volume; the heat of reaction was almost totally used in raising the temperature and pressure of the spray-chamber atmosphere. The pressure-rise rate, which is indicative of the reaction rate of the spray, was determined from the linear portion of the pressure trace. The pressure-rise rates ranged from 25 to 75 atm/sec. The experimental results were compared on the reduced pressure-rise rate basis (atm/sec)/(g Na/cm³), de-

defined in Chapter III (p. 30). For each discharge disc, a constant value was used for the concentration term, g Na/cm³, which implied that the sprayed sodium adhered to the baffle at the top of the chamber and stopped burning. This conversion eliminated the restrictions of the spray-chamber geometry and the sodium mass flowrate.

1. Effect of Ambient Oxygen Concentration

Figure 24 shows the experimental, reduced pressure-rise rate for two orifice sizes as a function of the initial oxygen concentration in the spray chamber. The designated initial sodium temperatures are based on the measurements made with both types of heaters. The scatter in the data is attributed to fluctuations in the temperature.

Fig. 24. Effect of Ambient Oxygen Concentration on Experimental Pressure-rise Rate (Experimental spray particle size unknown)

The experimental pressure-rise rates varied with ambient oxygen concentration, as predicted by the theory; the rates decreased as the oxygen concentration decreased. The effect of the initial sodium temperature on the experimental pressure-rise rate was much greater than predicted in the theoretical analysis. But the influence of the temperature-dependent density, viscosity, and surface tension of the sodium on the spray-particle size was not considered in the development of the theory, because the currently available correlations were not applicable in this work. As the temperature increased, the kinematic viscosity and the surface tension of the sodium decreased with a resultant decrease in particle size. The pressure-rise rate increased significantly as the particle size decreased (as shown in Fig. 11). Thus, qualitative agreement exists between the experimental results and the theo-

retical predictions, since most of the experimental variation with sodium temperature can be attributed to variations in particle size.

Figure 24 compares theoretically predicted curves with the experimental data. The theoretical curve for a spray with an initial particle size of 470μ approximated the data for sodium ($\sim 350^\circ\text{C}$) sprayed through the 0.0762-cm orifices. When the initial sodium temperature was 425°C , agreement with theory occurred at an initial spray-particle size of 360μ . These particle sizes are consistent with the experimentally determined average particle size of 420μ . For the 0.0254-cm orifices, the theoretical, best-fit curve corresponded to an initial spray-particle size of 90μ . When all the above particle sizes are considered, another factor must be noted. Most of the sprayed sodium adhered to the top baffle and upper inch of the chamber wall, where burning ceased because of heat dissipation. But a small amount of finely divided burning sodium was dispersed toward the lower chamber wall after impact at the baffle and thereby contributed to the pressure rise. If the contribution of this dispersed sodium could be excluded from the observed pressure-rise rate, the agreement between the theory and the experimental data would occur at a slightly larger particle size, i.e., lower reduced pressure-rise rates.

When the spray-chamber atmosphere was 4 m/o oxygen, no visible burning occurred. This corresponds to the observations of the investigators cited previously.^{11,23,27} The theoretical analysis predicted that vapor-phase combustion ceased below 4 m/o oxygen. This agreement lends further support to the vapor-phase combustion model developed.

Fig. 25. Effect of Orifice Size on Experimental Pressure-rise Rate

2. Effect of Orifice Size

Figure 24 also clearly demonstrates that as the orifice size was decreased, the reduced pressure-rise rate was significantly increased because of a decrease in particle size. The reduced pressure-rise rates for all the runs in which sodium was sprayed into dry air were plotted against the orifice diameter, as shown in Fig. 25. The line between the two sets of data was based on the dry-air values of the curves shown in Fig. 24. It indicates that the experimental reduced pressure-rise rates were inversely proportional to the orifice diameter to the 2.2 ± 0.6 power. More data at other orifice sizes are required to determine an accurate relationship.

Theoretically, the reduced pressure-rise rate was inversely proportional to the particle diameter to the 1.47 power. Since a one-to-one correspondence between particle size and orifice size was not expected, this was considered reasonably good agreement.

3. Effect of Spray Velocity

The spray velocity was varied in several experimental runs by changing the drive pressure on the piston. Figure 26 shows the resultant reduced pressure-rise rates. The velocities corresponding to the drive pressures were determined from the high-speed movies. The experimental reduced pressure-rise rates increased gradually as the spray velocity was increased, which is in agreement with the theoretically predicted response. Once again, the scatter in the data may be attributed to a decrease in the spray particle size as the velocity and the initial sodium temperature increased.

4. Other Experimental Observations

This experimental investigation yielded other results worthy of comment.

Fig. 26. Effect of Spray Velocity on Experimental Pressure-rise Rate

five percent of the temperature data were in the range of 750-1000°K. Even though the thermocouple was covered with a mass of sodium, these temperatures were probably proportional to the burning temperature. The temperature gradually decreased as the oxygen concentration decreased. There was not much variation with respect to spray velocity, orifice size, or initial sodium temperatures; therefore these factors were not differentiated in the plot. The theoretical burning temperature displayed the same general trends, as was shown in Chapter III.

c. Oxygen Consumption.

Figure 28 shows the total amount of oxygen reacted in each experimental run as a function of the initial ambient-oxygen concentration. As would be expected, the oxygen-consumption curve has the same characteristics as the pressure-rise rate relationship. Increasing the initial sodium temperature or the spray velocity and decreasing the orifice size resulted in greater oxygen consumption. In considering the data in Fig. 28, one must remember that, although burning ceased after injection, the sodium-oxygen reaction did not. Part of the oxygen depletion was due to the reaction between oxygen and

a. Peak Pressures. The peak pressures attained in the experimental runs exhibited the same trends as the pressure-rise rates, but there was more scatter in the data. This is because the final pressure was dependent, not only on the pressure-rise rate, but also on the total amount of sodium injected into the spray chamber. Upon disassembly of the injector, varying amounts of unexpelled sodium remained; an amount as small as 0.5 g was equivalent to 4 w/o of the total. The peak pressures ranged from 1.13 atm in a nonburning run to a maximum of 4.1 atm.

b. Temperatures at the Baffle.

Figure 27 shows the peak temperatures measured by the thermocouple below the baffle during the injection interval for all the experimental runs. Seventy-

Fig. 27. Peak Temperatures at Baffle during Injection

Fig. 28. Experimental Oxygen Consumption

dispersed upon impact. Eventually, burning sodium particles filled the entire chamber. Burning ceased soon after injection ended. When the sodium was sprayed through the smaller-diameter orifices, the burning displayed greater turbulence and intensity.

the exposed surfaces of the sodium adhering to the baffle and the chamber wall. This was reflected in the values for the higher-velocity runs, in which the adhered sodium was spread over a larger area and thereby provided more reaction surface.

d. High-speed Movies. Figures 29 and 30 are photographic time sequences of experimental runs taken from the high-speed movies. Initially, the burning was confined to the center of the spray chamber. As the spray impinged on the top baffle, the burning intensity appeared to increase because of the finely divided sodium

Fig. 29. Injection of Sodium into Dry Air; 0.0762-cm-diam Orifices

Fig. 30. Injection of Sodium into Dry Air; 0.0254-cm-diam Orifices

e. Reaction-product Fallout. When the spray chamber was opened after an experimental run, most of the unreacted sodium was found on the top baffle and upper inch of the chamber wall. The inner surface of the chamber was covered with a thin, white oxide film. Essentially all the reaction product was found on the bottom of the chamber as a light, fluffy white powder. Upon exposure to the room atmosphere, this powder rapidly absorbed water.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

This investigation has provided basic information, in terms of pressure-rise rate data, about the reaction rate of a high-velocity, molten sodium spray with dry air and dry air-nitrogen mixtures. The spray particle size had the most pronounced effect on the reaction rate, which increased markedly as the particle size decreased. The experimental reduced pressure-rise rate (defined in Section III.B) was inversely proportional to the orifice diameter to the 2.2 ± 0.6 power, for orifice diameters of 0.0254 and 0.0762 cm. Increasing the spray velocity resulted in a modest increase in the reaction rate. When the drive pressure on the piston of the spray-injector was varied from 1000 to 1500 psig, which increased the spray velocity from 1.07×10^4 cm/sec (350 ft/sec) to 1.31×10^4 cm/sec (430 ft/sec), the experimental reduced pressure-rise rate increased by 10%. The reaction rate decreased slowly as the oxygen content of the atmosphere was lowered until, at an oxygen concentration of 4 m/o, there was no visible burning.

A theoretical model was developed, based on the assumption that the reaction rate is controlled by the diffusion of oxygen to a combustion zone surrounding the particle. The theory correctly predicted the direction and magnitude of the experimentally observed variations in reaction rate with respect to oxygen content, spray velocity, and particle size. The theoretical curves, which fit the experimental reduced pressure-rise rate data, were for initial spray particle sizes that were in reasonable agreement with the available experimental particle-size data. The theory also predicted a cessation of vapor-phase combustion below an oxygen concentration of 4 m/o. The agreement between the theoretical and experimental results indicates that the theoretical model is a good representation of the burning phenomenon.

B. Recommendations

Additional experimental work is required in this field. There are several possible areas for future study.

1. A detailed determination of the spray-particle-size distribution, considering the effects of the initial sodium temperature, the spray velocity, and the orifice size, would make possible a precise comparison of theoretical and experimental results.

2. An alternate approach entails collecting reaction-rate data for a wide range of orifice sizes and orifice patterns. These data could then be correlated in terms of equivalent particle sizes that produce agreement with the theory. This correlation, combined with the basic theory, would be of value in reactor safety analyses.

3. Future studies of the sprayed sodium-air reaction could also include the effects of the water-vapor content of the atmosphere, examination and identification of the reaction products, and optical measurements of the flame temperature.

4. A study of the reaction of single drops of molten sodium with air would provide valuable basic information relative to the prediction of ignition temperatures and reaction rates for sodium droplets.

APPENDIX A

Details on the Solution of the Theoretical Model

A theoretical model was developed in Chapter III to predict the pressure rise in a closed volume due to the violently sprayed sodium-air reaction. Initially, the steady-state burning rate of a single spherical particle of sodium moving through air or air depleted in oxygen is determined. Then, a quasi-steady-state approach and an averaging technique are used in correlating the reaction rates of the individual sodium particles forming a spray with the burning rate of the spray itself and the pressure rise in the enclosing volume.

This appendix discusses the mechanics of solving the equations in the model.

1. Steady-state Combustion of a Single Spherical Particle of Sodium

The model for the combustion of a single spherical particle of sodium presented in Section III.A uses two key equations in terms of the two unknowns T_B and $Y_{O_2,B}$, namely, the heat balance,

$$k_y \left[\frac{Y_{O_2,A} - Y_{O_2,B}}{1 - Y_{O_2,B}} \right] Q_{T_B}^* = \sigma \epsilon (T_B^4 - T_A^4) + h(T_B - T_A), \quad (A.1)$$

and the chemical-equilibrium relationship,

$$\Delta F = RT_B \ln [16(P_t Y_{O_2,B})^{5/2}]. \quad (A.2)$$

A computer is used to solve these equations; therefore the temperature dependence of the heat capacity, thermal conductivity, and viscosity in the diffusion zone is represented by empirical equations determined from plots of tabulated data.¹² Similarly, an empirical equation for the temperature dependence of the product, cD , of the molar density and the diffusion coefficient for oxygen-nitrogen mixtures was determined from values calculated with a Chapman-Enskog formula.⁴ The empirical relationships are

$$\left. \begin{aligned} C_p' &= 0.0883 T^{0.165}, \\ k &= 1.77 \times 10^{-6} T^{0.65}, \\ \mu &= 5.245 \times 10^{-6} T^{0.629}, \\ \text{and} \\ cD &= 1.788 \times 10^{-7} T^{0.678}. \end{aligned} \right\} \quad (A.3)$$

The relationships are most accurate in the region of 300-2000°K. These properties are required to determine the heat- and mass-transfer

coefficients from the Nusselt- and Sherwood-number correlations. Likewise, the empirically determined relationship between the standard free energy of reaction and temperature¹⁵ is

$$\Delta F = 57.41 T_B - 128030 \text{ cal/g-mol Na}_2\text{O}. \quad (\text{A.4})$$

Equation 15 defined the modified heat of reaction at the burning temperature, $Q_{T_B}^*$. Using average values for the heat capacities, this expression becomes

$$Q_{T_B}^* = 217872 - 26(T_B - 298) - 24(T_B - T_{Na}) - 8(T_B - T_A) - 48(T_A - T_B). \quad (\text{A.5})$$

The Newton-Raphson method²⁹ is used to determine the values of the unknown quantities. For a system of two equations, f_1 and f_2 , in two unknowns, x_1 and x_2 , the successive approximations to the solution in this iterative procedure can be represented in matrix notation as

$$\begin{bmatrix} x_1 \\ x_2 \end{bmatrix}_{j+1} = \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}_j - \left\{ \frac{1}{J} \begin{bmatrix} \frac{\partial f_2}{\partial x_2} & -\frac{\partial f_1}{\partial x_2} \\ -\frac{\partial f_2}{\partial x_1} & \frac{\partial f_1}{\partial x_1} \end{bmatrix} \begin{bmatrix} f_1 \\ f_2 \end{bmatrix}_j \right\}, \quad (\text{A.6})$$

where

$$J = \begin{vmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} \end{vmatrix}, \quad (\text{A.7})$$

and j is the iteration index.

The procedure used in the solution is as follows:

1. Specify the sodium particle size, sodium temperature, particle velocity, ambient temperature, ambient pressure, and ambient oxygen concentration.
2. As the initial assumptions for the values of $Y_{O_2,B}$ and T_B , set $Y_{O_2,B}$ equal to $0.5Y_{O_2,A}$ and solve for T_B from Eqs. A.2 and A.4.
3. Define an average temperature as $0.5(T_A + T_B)$, and calculate the physical properties of the system in the diffusion zone by using this

average temperature and Eqs. A.3. Then calculate the heat- and mass-transfer coefficients from the Nusselt- and Sherwood-number correlations (Eqs. 20 and 21, respectively), and the heat of reaction from Eq. A.5.

4. Check the equality in Eqs. A.1 and A.2. The convergence limit is set at a difference of ± 0.00005 between the right- and left-hand sides of the equations.

5. If convergence is attained, then the current values of $Y_{O_2,B}$ and T_B are the desired solution and the burning rate can be determined from Eq. 12.

6. If convergence is not attained, calculate new trial values for $Y_{O_2,B}$ and T_B by using the method of Eq. A.6, and repeat Steps 3 and 4. In determining the required partial derivatives, neglect the temperature dependence of h , k_y , and Q_{T_B} .

Table IX is a listing of the FORTRAN computer program, SUBROUTINE RXRATE, for carrying out the above procedure. On the CDC-3600 computer, a computing time of approximately 0.125 sec is required for convergence.

TABLE IX. FORTRAN Computer Program for Combustion
Calculation for a Single Sodium Particle

FORTRAN 5.301

06/06/68

```

SUBROUTINE RXRATE(TB,TA,P,DIAM,VEL,YO,EMISS,YO1,CHECK,J,ORATE,
1F1,F2,TNA)
C
C   STEADY STATE COMBUSTION CALCULATION FOR A SINGLE SPHERICAL
C   PARTICLE OF SODIUM
C
C   NOMENCLATURE
C   CD      = PRODUCT OF THE MOLAR GAS CONCENTRATION AND THE
C             DIFFUSION COEFFICIENT, (GMOLS/CM**3)(CM**2/SEC)
C   CHECK   = CONVERGENCE INDICATOR,
C             CHECK=0, CONVERGENCE
C             CHECK=100, NONCONVERGENCE AFTER 20 ITERATIONS
C   CP      = HEAT CAPACITY, CAL/(GM)(DEG.KELVIN)
C   DENS    = DENSITY, GM/CM**3
C   DFCO    = DIFFUSION COEFFICIENT, CM**2/SEC
C   DF1T    = PARTIAL DERIVATIVE OF F1 WITH RESPECT TO TB
C   DF1Y    = PARTIAL DERIVATIVE OF F1 WITH RESPECT TO YO1
C   DF2T    = PARTIAL DERIVATIVE OF F2 WITH RESPECT TO TB
C   DF2Y    = PARTIAL DERIVATIVE OF F2 WITH RESPECT TO YO1
C   DIAM    = PARTICLE DIAMETER, CM
C   EMISS   = EMISSIVITY
C   F1,F2   = FUNCTIONS USED FOR THE NEWTON-RAPHSON ITERATION
C             PROCEDURE
C   H       = HEAT TRANSFER COEFFICIENT, CAL/(SEC)(CM**2)(DEG.KELVIN)
C   HNU     = NUSSLETT NUMBER FOR HEAT TRANSFER
C   J       = ITERATION INDEX, INDICATES NUMBER OF ITERATIONS
C             PERFORMED
C   ORATE   = REACTION RATE, GMOLS OXYGEN/(SEC)(CM**2)
C   P       = AMBIENT PRESSURE, ATM
C   PR      = PRANDTL NUMBER
C   QRX     = MODIFIED HEAT OF REACTION, CAL/GMOL OXYGEN

```

TABLE IX (Contd.)

```

C      RE      = REYNOLDS NUMBER
C      SC      = SCHMIDT NUMBER
C      SH      = SHERWOOD NUMBER
C      TA      = AMBIENT TEMPERATURE, DEG.KELVIN
C      TB      = BURNING TEMPERATURE, DEG.KELVIN
C      TCON    = THERMAL CONDUCTIVITY, CAL/(SEC)(CM)(DEG.KELVIN)
C      TNA     = INITIAL SODIUM TEMPERATURE, DEG.KELVIN
C      VEL     = PARTICLE VELOCITY, CM/SEC
C      VISC    = VISCOSITY, POISE
C      YK      = MASS TRANSFER COEFFICIENT, GMOLS/(SEC)(CM**2)
C      YO      = AMBIENT MOLE FRACTION OXYGEN
C      YOI     = EQUILIBRIUM MOLE FRACTION OXYGEN IN THE BURNING ZONE
C
C      DIMENSION TB(25),YOI(25),F1(25),F2(25)
C      CHECK=0
C
C      SPECIFICATION OF INITIAL VALUES FOR THE UNKNOWN QUANTITIES
C
C      YOI(1)=YO/2,
C      TB(1)=128030./(57.41-1.986*LOGF(16.*(P*YOI(1))**2.5))
C
C      NEWTON-RAPHSON ITERATION PROCEDURE
C
C      DO 100, I=1,20
C
C      CALCULATION OF REQUIRED COEFFICIENTS AT THE SPECIFIED CONDITIONS
C
C      T=(TA+TB(I))/2.
C      CP=0.0883*T**0.165
C      TCON=1.77*10.**(-6.)*T**0.65
C      CD=1.788*10.**(-7.)*T**0.678
C      VISC=5.245*10.**(-6.)*T**0.629
C      DENS=28.5*P/(T*82.06)
C      DFCO=CD*T*82.06/P
C      RE=DIAM*VEL*DENS/VISC
C      PR=CP*VISC/TCON
C      SC=VISC/(DENS*DFCO)
C      HNU=2.0+0.6*RE**0.5*PR**(1./3.)
C      SH=2.0+0.6*RE**0.5*SC**(1./3.)
C      YK=SH*CD/DIAM
C      H=HNU*TCON/DIAM
C      QRX=217872.-24.*(TB(I)-TNA)-8.*(TB(I)-TA)-26.*(TB(I)-298.)
C      1=48.*(TA-TB(I))
C
C      CHECK FOR CONVERGENCE OF THE FUNCTIONS DEFINING RELATIONSHIP
C      BETWEEN THE UNKNOWN QUANTITIES
C
C      F1(I)=YK*(YO-YOI(I))*QRX/(1.-YOI(I))
C      1=1.356*10.**(-12.)*EMISS*(TB(I)**4.-TA**4.)-H*(TB(I)-TA)
C      F2(I)=57.41*TB(I)-128030.-1.986*TB(I)*
C      1LOGF(16.*(P*YOI(I))**2.5)
C      IF(ABS(F1(I))-.00005)50,50,75
C      50 IF(ABS(F2(I))-.00005)150,150,75
C
C      CALCULATION OF NEW TRIAL VALUES FOR THE UNKNOWN QUANTITIES
C
C      75 DF1Y=YK*QRX*(YO-1.)/((1.-YOI(I))**2)
C      DF1T=(-1.)*1.356*10.**(-12.)*EMISS*4.*TB(I)**3.-H
C      DF2Y=(-1.)*1.986*TB(I)*2.5/YOI(I)
C      DF2T=57.41-1.986*LOGF(16.*(P*YOI(I))**2.5)
C      DET=DF1T*DF2Y-DF1Y*DF2T
C      TB(I+1)=TB(I)-(DF2Y*F1(I)-DF1Y*F2(I))/DET
C      DELY=(DF1T*F2(I)-DF2T*F1(I))/DET
C      20 YOI(I+1)=YOI(I)-DELY
C      IF(YOI(I+1))25,25,100
C      25 DELY=DELY/2.
C      GO TO 20
C      100 CONTINUE

```

TABLE IX (Contd.)

```

C
C      NONCONVERGENCE IN TWENTY ITERATIONS
C
      CHECK=100,
      J=I-1
      RETURN
C
C      CONVERGENCE
C
150 ORATE=YK*(Y0-YOI(1))/(1.-Y0)
      J=I
      RETURN
      END

```

2. Combustion of a Sodium Spray in an Enclosed Volume

Section II.B outlined the assumptions in the quasi-steady-state approach used to calculate the pressure changes in an enclosed volume due to the sodium-air (depleted air) reaction. The method consists of dividing a spray chamber into an integral number of vertically stacked subvolumes; for the chamber used in the experimental portion of this work, ten divisions was satisfactory. A spray velocity, an initial spray particle size, and the initial physical properties of the system (i.e., the initial ambient pressure, temperature, and oxygen concentration, sodium temperature, and the number and size of the orifices) are specified. A time increment, Δt , is defined as the time required for a particle to pass through a subvolume. The ν particles ejected in the time interval Δt are represented by the average particle ejected at $\Delta t/2$, which is equivalent to considering a group of ν particles ejected simultaneously at the midpoint of the time increment. These particles will have traveled to the center of the first subvolume at the end of the time increment in which they were ejected, to the center of the second subvolume at the end of the next time increment, and so on.

Now consider the system during the $i + 1$ time interval. With SUB-ROUTINE RXRATE (Table IX), the steady-state burning rate N_{O_2} is calculated for each volume increment that contains or will contain particles for $i\Delta t < t < (i+1)\Delta t$. These calculations are based on the pressure, temperature, and composition conditions that exist at $t = i\Delta t$ and on the diameter of a particle entering the subvolume at $t = i\Delta t$. The decrease in size experienced by a reacting particle is determined as follows:

$$\left. \begin{aligned} \frac{dn_{Na}}{dt} &= \frac{d}{dt} \left[\frac{4}{3} \pi r^3 \left(\frac{\rho}{M} \right)_{Na} \right] = -4N_{O_2}(4\pi r^2); \\ \frac{dr}{dt} &= -4 \left(\frac{M}{\rho} \right)_{Na} N_{O_2}. \end{aligned} \right\} \quad (A.8)$$

For sufficiently small time increments, N_{O_2} is essentially constant, and integration of Eq. A.8 yields

$$\Delta r = -4 \left(\frac{M}{\rho} \right)_{Na} N_{O_2} \Delta t. \quad (A.9)$$

Therefore, using Eq. A.9 and the subscript k to designate the subvolume (recalling that in the time between $i\Delta t$ and $(i+1)\Delta t$, each group of particles will move from the center of one subvolume to the center of the next subvolume, spending a time $\Delta t/2$ in each section), the change in the radii of each group of particles can be expressed as

$$r_{k+1,(i+1)\Delta t} = r_{k,i\Delta t} - 4 \left(\frac{M}{\rho} \right)_{Na} \left[(N_{O_2})_{k,i\Delta t} + (N_{O_2})_{k+1,i\Delta t} \right] \left(\frac{\Delta t}{2} \right). \quad (A.10)$$

The amount of oxygen that reacts with a single particle in time t is

$$\int dn_{O_2} = \Delta n_{O_2} = \int_0^t N_{O_2} 4\pi r^2 dt. \quad (A.11)$$

If t is sufficiently small, N_{O_2} is essentially constant and Eq. A.9 gives the dependence of r on t . Substituting the appropriate form of Eq. A.9 into Eq. A.11 produces

$$\Delta n_{O_2} = 4\pi N_{O_2} \int_0^t \left[(r)_{t=0} - 4 \left(\frac{M}{\rho} \right)_{Na} N_{O_2} t \right]^2 dt, \quad (A.12)$$

so that the amount of oxygen reacted in any subvolume in the time interval $i\Delta t$ to $(i+1)\Delta t$ is

$$\begin{aligned} (\Delta n_{O_2})_k = & 4\pi \nu (N_{O_2})_{k,i\Delta t} \left\{ \int_0^{\Delta t/2} \left[r_{k,i\Delta t} - 4 \left(\frac{M}{\rho} \right)_{Na} (N_{O_2})_{k,i\Delta t} t \right]^2 dt \right. \\ & \left. + \int_0^{\Delta t/2} \left[r_{k-1,i\Delta t} - 4 \left(\frac{M}{\rho} \right)_{Na} \left\{ (N_{O_2})_{k-1,i\Delta t} \frac{\Delta t}{2} + (N_{O_2})_{k,i\Delta t} t \right\} \right]^2 dt \right\}, \end{aligned} \quad (A.13)$$

where the first integral accounts for reaction with the group of particles originally in the center of the subvolume at $i\Delta t$, and the second integral accounts for reaction with the group of particles that enters the subvolume at $(i+1/2)\Delta t$.

The temperature change ΔT_A is calculated from the heat transferred from the burning particles to the gas in the subvolume, as follows:

$$(\bar{m}_g C_v \Delta T_A)_k = (Q_{TB}^* \Delta n_{O_2})_k \quad (A.14)$$

Subsequently, the pressure is determined from the ideal gas law.

Table X lists the FORTRAN computer program NARX for performing the above calculations. On the CDC-3600 computer, a computing time of 58 sec is required for a spray chamber with ten volume increments, time increments of 1 msec, and a total spraying time of 50 msec.

TABLE X. FORTRAN Computer Program for Combustion
Calculation for a Sodium Spray in an Enclosed Volume

FORTRAN 5,301

06/06/68

PROGRAM NARX

```

C
C   DETERMINATION OF THE PRESSURE AND TEMPERATURE CHANGES IN AN
C   ENCLOSED VOLUME DUE TO THE SODIUM-AIR(DEPLETED AIR) REACTION AS
C   A FUNCTION OF TIME
C
C   NOMENCLATURE
C   CHECK      = QUANTITY WHICH INDICATES CONVERGENCE OR NONCONVERGENCE
C               IN SUBROUTINE RXRATE
C   CV          = HEAT CAPACITY AT CONSTANT VOLUME, CAL/(GM)(DEG.KELVIN)
C   DCOL        = DIAMETER OF SPRAY CHAMBER, CM
C   DIAM        = DIAP=DDIAP=SPRAY PARTICLE DIAMETER, CM
C   DIAMO       = ORIFICE DIAMETER, CM
C   DTIME       = TIME INCREMENT-TIME REQUIRED FOR A PARTICLE TO PASS
C               THROUGH A VOLUME INCREMENT, SEC
C   EJNA        = TOTAL WEIGHT OF SODIUM EJECTED UNTIL TIME INCREMENT
C               UNDER CONSIDERATION, GMS
C   EMISS       = EMISSIVITY OF A BURNING SODIUM PARTICLE
C   ETIME       = TOTAL EJECTION TIME, SEC
C   F1,F2       = FUNCTIONS USED FOR THE NEWTON-RAPHSON ITERATION
C               PROCEDURE IN SUBROUTINE RXRATE
C   GASML       = MOLES OF GAS PER VOLUME INCREMENT
C   GASMW       = GAS MOLECULAR WEIGHT
C   HCOL        = HEIGHT OF SPRAY CHAMBER, CM
C   J           = INDEX INDICATING THE NUMBER OF ITERATIONS PERFORMED IN
C               SUBROUTINE RXRATE
C   N=AN        = NUMBER OF VOLUME INCREMENTS IN THE SPRAY CHAMBER
C   NT          = TIME INCREMENT INDEX
C   NZ          = VOLUME INCREMENT INDEX, VALUES RANGE FROM 1 TO (N+1).
C               NZ=1 DENOTES THE INJECTOR-A NO-REACTION VOLUME
C   ONUM        = NUMBER OF ORIFICES IN THE ORIFICE PLATE OF THE INJECTOR
C   OXLOSS      = GMOLS OF OXYGEN REACTED
C   OXRATE      = ORATE=REACTION RATE, GMOLS OXYGEN/(SEC)(CM**2)
C   P=PA        = AMBIENT PRESSURE, ATM
C   PARTS       = NUMBER OF PARTICLES EJECTED IN ONE TIME INCREMENT
C   PI          = INITIAL AMBIENT PRESSURE, ATM
C   QRX         = MODIFIED HEAT OF REACTION, CAL/GMOL OXYGEN
C   RAD         = RRAD=PARTICLE RADIUS, CM
C   SODMW       = SODIUM MOLECULAR WEIGHT
C   SPRT        = SPRAY RATE, GMS/SEC
C   T=TA        = AMBIENT TEMPERATURE, DEG.KELVIN
C   TAI         = INITIAL AMBIENT TEMPERATURE, DEG.KELVIN
C   TB=BT       = BURNING TEMPERATURE, DEG.KELVIN
C   VEL         = SPRAY VELOCITY, CM/SEC
C   VCL         = INCREMENTAL VOLUME, CM**3
C   X           = GASML

```

TABLE X (Contd.)

```

C      YO      = INITIAL AMBIENT MOLE FRACTION OXYGEN
C      YOA=YOX  = AMBIENT MOLE FRACTION OXYGEN
C      YOI      = EQUILIBRIUM MOLE FRACTION OXYGEN IN THE BURNING ZONE
C
      DIMENSION TB(25),YOI(25),F1(25),F2(25),T(15),PA(15),YOA(15),
1DIAP(15),OXRATE(15),RAD(15),RRAD(15),GASML(15),BT(15),DDIAP(15)
C
      READ 900, N,TAI,PI,DIAMO,ONUM,VEL,YO,EMISS,TNAI,HTCOL,DCOL,
1SODMW,ETIME
C
C      CALCULATION OF CONSTANT FACTORS AND SPECIFICATION OF INITIAL
C      CONDITIONS
C
      AN=N
      N1=N+1
      VOL=3.1416*DCOL*DCOL*HTCOL/(4.*AN)
      X=PI*VOL/(TAI*82.06)
      DIAMP=0.75*DIAMO
150 DTIME=HTCOL/(AN*VEL)
      DNSNA=0.9490*22.3*10.**(-5)*(TNAI-273.)-1.75*10.**(-8)*(TNAI-
1273.)**2
      SPRT=DNSNA*ONUM*3.1416*DIAMO*DIAMO*VEL/4,
      PARTS=(SPRT*DTIME)/(DNSNA*3.1416*DIAMP**3/6,)
      DC 100, NZ=2,N1
      T(NZ)=TAI
      PA(NZ)=PI
      YOA(NZ)=YO
      RAD(NZ)=0
      GASML(NZ)=X
100 CONTINUE
      DIAP(2)=DIAMP
      DDIAP(1)=DIAMP
      RAD(1)=DIAMP/2.
      RRAD(1)=RAD(1)
      OXRATE(1)=0
      EJNA=0
      NZ1=2
      NZ2=2
      NT=1
      TIME=0
      PRINT 901, HTCOL,DCOL,N,VOL,X,DIAMO,ONUM,TAI,PI,YO,TNAI,VEL,
1 DTIME,SPRT,PARTS,DIAMP,EMISS
C
C      DETERMINATION OF REACTION RATE AND CHANGES IN OXYGEN
C      CONCENTRATION, PRESSURE, TEMPERATURE, AND PARTICLE SIZE
C      IN EACH VOLUME INCREMENT
C
175 DC 250, NZ=NZ1,NZ2
      TA=T(NZ)
      RRAD(NZ)=RAD(NZ)
      DDIAP(NZ)=DIAP(NZ)
      P=PA(NZ)
      YOX=YOA(NZ)
      DIAM=DIAP(NZ)
      CALL RXRATE(TB,TA,P,DIAM,VEL,YOX,EMISS,YOI,CHECK,J,ORATE,F1,F2,
1TNAI)
      IF(100.-CHECK)800,800,200
200 OXRATE(NZ)=ORATE
      BT(NZ)=TB(J)
250 CONTINUE
      DC 350, NZ=NZ1,NZ2
      OXLOSS=((RAD(NZ-1)-4.*SODMW*OXRATE(NZ-1)*DTIME/(2.*DNSNA))**3-
1(RAD(NZ-1)-4.*SODMW*(OXRATE(NZ-1)+OXRATE(NZ))*DTIME/(2.*DNSNA)
2)**3)/(3.*4.*SODMW*OXRATE(NZ)/DNSNA)
      IF(RAD(NZ))275,300,275
275 OXLOSS=OXLOSS+((RAD(NZ))**3-(RAD(NZ)-4.*SODMW*OXRATE(NZ)*DTIME/
1(2.*DNSNA))**3)/(3.*4.*SODMW*OXRATE(NZ)/DNSNA)

```

TABLE X (Contd.)

```

300 OXLOSS=OXLOSS*OXRATE(NZ)*4.*3.1416*PARTS
    ORX=217872.-24.*(BT(NZ)-TNAI)-8.*(HT(NZ)-T(NZ))-
1 26.*(RT(NZ)-298.)-48.*(T(NZ)-BT(NZ))
    CV=.0883*T(NZ)+.0.165/1.39
    GASMW=32.*YOA(NZ)+28.16*(1.-YOA(NZ))
    T(NZ)=T(NZ)+ORX*OXLOSS/(CV*GASMW*(GASML(NZ)-OXLOSS/2.))
    YOA(NZ)=(YOA(NZ)*GASML(NZ)-OXLOSS)/(GASML(NZ)-OXLOSS)
    GASML(NZ)=GASML(NZ)-OXLOSS
    PA(NZ)=GASML(NZ)*T(NZ)*.08205/(VOL*28.32)
350 CONTINUE
    DO 450, NZ=NZ1,NZ2
    RAD(NZ)=RRAD(NZ-1)-4.*SODMW*(OXRATE(NZ-1)+OXRATE(NZ))*DTIME/
1 (2.*DNSNA)
    DIAP(NZ)=DDIAP(NZ-1)-8.*SODMW*OXRATE(NZ-1)*DTIME/DNSNA
450 CONTINUE
    TIME=TIME+DTIME
    EJNA=EJNA+SPRT*DTIME
474 PRINT 902, TIME,EJNA
    DO 475, NZ=NZ1,NZ2
    NNZ=NZ-1
    PRINT 903, NNZ,GASML(NZ),T(NZ),PA(NZ),YOA(NZ),OXRATE(NZ),BT(NZ),
1RAD(NZ),DIAP(NZ)
475 CONTINUE
476 IF(ETIME-TIME)850,850,500
500 NT=NT+1
    IF(NT-N)510,510,520
510 NZ2=NZ2+1
    DIAP(NZ2)=DDIAP(NZ2-1)-8.*SODMW*OXRATE(NZ2-1)*DTIME/DNSNA
520 GO TO 175
800 NNZ=NZ-1
    PRINT 904, NNZ,GASML(NZ),T(NZ),PA(NZ),YOA(NZ),DIAP(NZ)
    DO 805, I=1,J
    PRINT 905, YOI(I),TB(I),F1(I),F2(I)
805 CONTINUE
850 CCNTINUE
900 FORMAT(15/(4E15.5))
901 FORMAT(1H14X,10H COLUMN HEIGHT,CM,25X,E20.5/5X,20H COLUMN DIAMETER
1,CM,23X,E20.5/5X,28H NUMBER OF HEIGHT INCREMENTS15X, 115/5X,29H I
2NCREMENTAL VOLUME,CUBIC CM,14X,E20.5/5X,24H GMOLS GAS PER INCREMEN
3T19X,E20.5/5X,21H ORIFICE DIAMETER,CM,22X,E20.5/5X,19H NUMBER OF O
4RIFICES24X,E20.5/5X,27H AMBIENT TEMPERATURE,KELVIN16X, E20.5/5X,22
5H AMBIENT PRESSURE,ATM,21X,E20.5/5X,29H AMBIENT MOLE FRACTION OXYG
6EN14X,E20.5/5X,34H INITIAL SODIUM TEMPERATURE,KELVIN9X,E20.5/5X,22
7H SPRAY VELOCITY,CM/SEC21X,E20.5/5X,20H TIME INCREMENT,SEC.23X,
8E20.5/5X,19H SPRAY RATE,GMS/SEC24X,E20.5/5X,33H NO. PARTICLES PER
9TIME INCREMENT10X,E20.5/5X,30H INITIAL PARTICLE DIAMETER,CM,13X,
1E20.5/5X,11H EMISSIVITY32X,E20.5/)
902 FORMAT(1H14X,10H TIME,SEC,36X,E20.5/5X,36H TOTAL WEIGHT OF EJECTED
1 SODIUM,GMS,10X,E20.5/2X,8H INCREM,5X,10H GMOLS-GAS3X,12H TEMPERA
2TURE6X,9H PRESSURE8X,7H OXYGEN8X,7H OXYGEN7X,8H BURNING7X,8H AVERA
3GE6X,9H ENTERING/28X,7H KELVIN11X,5H ATM,12X,5H MOLE9X,8H RX-RATE3
4X,12H TEMPERATURE7X,7H RADIUS7X,9H PARTICLE/61X,9H FRACTION2X,13H
5GMOL/SEC-CM27X,7H KELVIN8X,4H CM,10X,9H DIAM-CM,/)
903 FORMAT(110,8E15.5)
905 FORMAT(4E25.5)
904 FORMAT(1H14X,15H NONCONVERGENCE/5X,10H INCREMENT22X,116/5X,10H GMO
1LS-GAS22X,E20.5/5X,19H TEMPERATURE,KELVIN13X,E20.5/5X,14H PRESSURE
2,ATM,18X,E20.5/5X,21H OXYGEN MOLE FRACTION11X,E20.5/5X,22H PARTICL
3E DIAMETER,CM,10X,E20.5/5X,19H EQUILIBRIUM OXYGEN5X,20H BURNING T
4EMPERATURE12X,13H FUNCTION ONE12X,13H FUNCTION TWO/6X,14H MOLE FRA
5CTION10X,15H DEGREES KELVIN/)
    END

```


APPENDIX B

Experimental Data

TABLE XI. Experimental Conditions and Experimental Oxygen Consumption

Run No.	Temp at Heater, °C	Sodium Temp, °C	Orifice Diam, cm	Drive Pressure, psig	Initial Oxygen Conc, m/o	Reacted Oxygen	
						g-mol	m/o
3G1	421	250	0.0762	1000	21.0 (dry air)	0.082	55
3G2	421	250	0.0762	1000	21.0 (dry air)	0.077	52
3G3	421	250	0.0762	1000	~18.0	~0.016	13
3G4	421	250	0.0762	1000	~18.0	~0.016	13
3G5	525	350	0.0762	1000	17.1 ± 0.9	0.052	44
3G6	525	350	0.0762	1000	10.0 ± 0.5	0.021	30
3G7	525	350	0.0762	1000	10.0 ± 0.5	0.031	46
3G8	525	350	0.0762	1000	~4.0	-	-
3G9	525	350	0.0762	1000	21.0 (dry air)	-	-
3G10	525	425	0.0762	1000	18.5 ± 1.0	0.064	51
3G11	525	350	0.0762	1000	12.6 ± 0.6	0.051	59
3G12	525	350	0.0762	1000	8.7 ± 0.5	0.035	59
3G13	525	350	0.0762	1000	~16.0	-	-
3G14	525	350	0.0762	1000	6.2 ± 0.3	0.027	65
3G15	525	425	0.0762	1000	6.2 ± 0.3	0.035	82
3G16	525	350	0.0762	1000	14.6 ± 0.7	0.043	43
3G17	525	350	0.0762	1500	21.0 (dry air)	0.087	58
3G18	525	350	0.0762	1250	21.0 (dry air)	0.091	60
3G19	525	350	0.0254	1500	21.0 (dry air)	0.127	90
3G20	525	350	0.0254	1500	10.6 ± 0.6	0.067	92
3G21	525	425	0.0762	1000	3.8 ± 0.2	0.012	46
3G22	525	350	0.0762	1000	6.3 ± 0.3	0.028	65
3G23	525	350	0.0762	1000	6.1 ± 0.3	0.015	36
3G24	525	425	0.0762	1000	9.9 ± 0.5	0.043	63
3G25	525	425	0.0762	1000	15.0 ± 0.8	0.059	57
3G26	525	350	0.0762	1000	17.1 ± 0.9	0.042	36
3G27	525	350	0.0762	1000	21.0 (dry air)	0.038	25
3G28	525	350	0.0762	1500	21.0 (dry air)	0.059	39
3G29	525	425	0.0762	1000	21.0 (dry air)	0.060	40
3G30	525	425	0.0762	1500	21.0 (dry air)	0.100	65
3G31	525	425	0.0762	1250	21.0 (dry air)	0.110	72
3G32	525	425	0.0254	1500	21.0 (dry air)	0.116	76
3G33	525	350	0.0254	1500	10.7 ± 0.5	0.059	80
3G34	525	350	0.0254	1500	21.0 (dry air)	0.126	85

TABLE XII. Experimental Pressure and Temperature Data

Run No.	Pressure-rise Rate, psi/sec	Reduced Pressure-rise Rate, $(10^5 \text{ atm/sec})/(\text{g Na/cm}^3)$	Pressure Rise, psig	Peak Temp at Baffle, °C	Comments
3G1	-	-	-	-	No oscillograph record.
3G2	362	1.70	17.2	387	
3G3	100	0.47	3.0	228	No visible burning.
3G4	-	-	3.6	90	No visible burning.
3G5	584	2.75	17.0	507	
3G6	419	1.97	8.7	281	
3G7	393	1.85	14.2	541	
3G8	47	0.22	2.0	282	No visible burning; no oxygen analysis.
3G9	560	2.63	18.8	693	No oxygen analysis.
3G10	686	3.22	26.6	675	
3G11	539	2.53	20.7	552	
3G12	473	2.22	14.6	510	
3G13	493	2.31	17.4	592	No oxygen analysis.
3G14	-	-	-	-	No oscillograph record.
3G15	654	3.07	17.3	531	
3G16	496	2.33	18.2	571	
3G17	646	3.04	21.1	684	
3G18	623	2.93	22.0	571	
3G19	495	20.9	29.0	-	
3G20	800	33.8	39.1	767	
3G21	180	0.85	3.8	387	No visible burning.
3G22	-	-	20.6	397	Incomplete oscillograph record.
3G23	407	1.91	10.0	397	
3G24	858	4.03	31.7	531	
3G25	775	3.64	33.1	592	
3G26	544	2.56	19.0	641	
3G27	430	2.02	14.8	618	
3G28	466	2.19	16.2	581	
3G29	676	3.18	28.5	217	
3G30	974	4.58	45.5	505	
3G31	1560	7.33	42.5	-	
3G32	1101	46.6	43.0	581	
3G33	563	23.8	33.8	779	
3G34	830	35.1	35.0	715	

ACKNOWLEDGMENTS

I would like to express my gratitude to all who have given encouragement and assistance during this study.

Dr. Stanley K. Stynes of the Chemical Engineering Department, Wayne State University, served as graduate advisor. His interest in this project is sincerely appreciated.

The staff of the Chemical Engineering Division, Argonne National Laboratory, furnished a great deal of assistance. Dr. Leonard Leibowitz, as research advisor, provided advice on both the experimental and theoretical aspects of this study, and on the interpretation of the experimental data. Dr. Richard E. Wilson and Mr. Richard O. Ivins willingly served as consultants at various stages in this work. Mr. John C. Cassulo and Mr. John R. Pavlik provided technical assistance in the experimental work. Mrs. Ruth C. Hanna and Mr. Alan F. Panek performed the many oxygen analyses required.

The financial support given by Argonne National Laboratory is gratefully acknowledged.

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