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Phase I - Final Report
No. 3982
April 8 to December 31, 1965

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Phase I - Final Report
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INTRODUCTION

With the advent of space propulsion, combustion physics has undergone drastic innovations, concerned primarily with transient combustion phenomena and more specifically with problems of rocket engine combustion instability. Although the bulk of this research has been devoted to post-ignition instability, more recent studies have been directed toward the pre-ignition stages, primarily because of the catastrophic pressure spiking (hard start) experienced during vacuum starts for low thrust, hypergolic bipropellant rocket engines. Ignition pressure spikes as large as 4000 psia have been observed in prototype 100-lb thrust Apollo RCS engines fueled with Aerozine-50/nitrogen tetroxide (NTO) and started at a pressure corresponding to an altitude of 300,000 feet. Pressure spiking of this magnitude generally reduces engine performance and/or engine life. Although it is often possible to circumvent such problems by means of a hardware fix, this is usually a temperary solution, specific to a given engine. Consequently, it is of more value to the engine developer to understand the basic mechanism responsible for the spike so as to effectively evaluate the potential of the proposed system and achieve a more realistic design. With this in view, the Bureau of Mines supported by the Manned Spacecraft Center, Houston, Texas, has entered into an investigation of the mechanism of such hard-start phenomena. It is not the purpose of this investigation to generate rocket engine design criteria but to delineate those processes in the engine complex which contribute to the ignition spike. The program is divided into two phases: a six-month survey of the literature and industry to acquire all information currently available on the problem, and a proposed 18-month experimental and theoretical investigation designed to provide the additional information necessary to resolve the problem.

The present report summarizes the results of the first phase - the six-month search of the literature and industry. Section I defines the problem and discusses the various physical and chemical processes occurring in the engine complex that could contribute to a hard start. Section II describes the mechanics and scope of the industry survey and literature search. Sections III, IV and V deal with physics of spray formation, chemistry of combustion, physicochemistry, and gas dynamics and transport. They summarize the information currently available in the literature on these subjects and discuss the information gaps in each problem area.

I. The Problem of Hard Start

It is the purpose of this study to delineate the physicochemical processes in hypergolic engines that could be responsible for hard start. Specifically, it is concerned with those processes which occur from the time of engine energization up to and including the spike phenomena. Although it is not the intention of this report to discuss the engineering aspects of hypergolic liquid propellant engines, it is essential for report continuity to recognize the basic hardware that contributes to the state of the system prior to ignition. Figure 1 shows a sketch of an idealized hypergolic rocket engine employing a single doublet injector; although the majority of such engines normally use a number of these doublet injectors, this should not affect the salient features of the discussion. Following engine energization, the sequence of processes is the following: liquid fuel and oxidant flow through previously evacuated lines and exit into the combustion chamber from the injector head; the two fluid streams impinge at a preferred angle a short distance from the injector; the integrity of the liquid streams is destroyed on or before impingement, depending on the state of the fluid in the chamber, resulting in the formation of propellant sprays which then commence to vaporize and mix; the gaseous fuel and oxidant react chemically and the heterogeneous reacting mass moves through the combustion chamber and exits from the exhaust nozzle. The events in the combustion chamber following fluid injection and prior to ignition are complicated by such factors as the distribution of droplet sizes and velocities in the spray; the effect of pressure, temperature, size, and gas concentration on the rate of droplet vaporization; the effect of pressure, temperature and concentration on the chemical and physical reactions; and the spatial and temporal dependence of the fluid dynamics. It is apparent that one cannot hope to factually delineate such a complex aggregate of processes, but must be content with an overall understanding of the underlying mechanism.

II. Literature and Industry Survey Program

The problem of hard start having been defined, a list of all related processes was compiled and supplemented subsequently by a more extensive listing of key words for the literature search.

The survey itself was begun in April 1965. The first two months of this survey were spent largely in searching the various library facilities in the Pittsburgh area and making arrangements with information retrieval agencies such as the Chemical Propulsion Information Agency, the NASA Scientific and Technical Information Facility, the Library of Congress, the Science Information Exchange of the Smithsonian Institution, and the Defense Documentation Center, to conduct searches of their "libraries" based on the key word list. The next few months were spent contacting various private and governmental agencies to acquire the pertinent reports which were recorded and catalogued upon receipt. The influx of documents appeared to reach its peak around the end of July, at which time the present report was begun. Unfortunately, most of the documents relating directly to pressure spiking were not received until late in December, thus delaying its completion.

Concurrently, a number of industrial agencies engaged in rocket engine development were visited. These included: Martin-Marietta Corporation, Marquardt Corporation, Rocketdyne Corporation, and the Reaction Motors Division of Thiokol Chemical Corporation. Although further visits to other

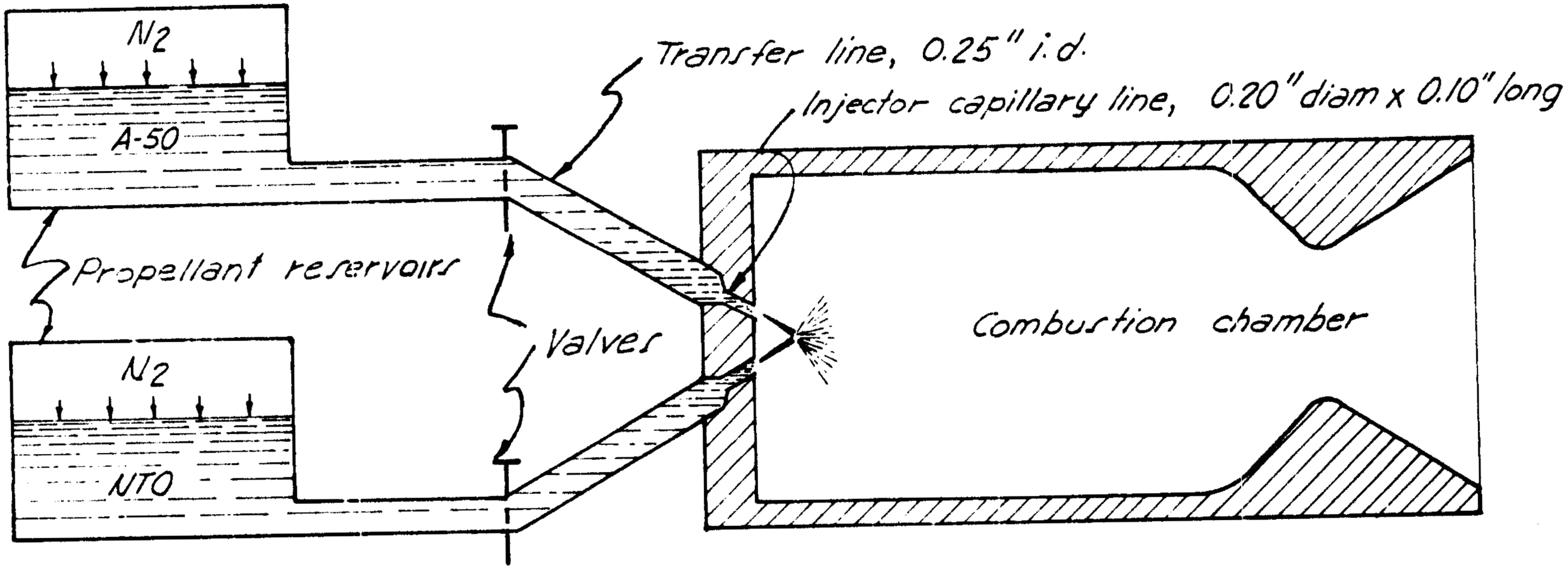

Figure 1. - Idealized hypergolic bi-propellant rocket engine complex.

agencies were planned, the urgency of the Phase I final report made it necessary to defer these to a later date.

It is difficult to estimate the extent of the coverage attained in surveys such as this. However, thanks to the searching facilities of the above information retrieval agencies, it seems unlikely that many pertinent documents were overlooked.

III. Physics of Spray Formation

This section is primarily concerned with events in the engine complex immediately following engine energization, up to and including spray formation in the combustion chamber. In a liquid rocket engine, a very large number of processes occur simultaneously. Each of these processes has its own series of antecedents and, in turn, effects a series of following processes. Since these processes are not uniformly dispersed in either time or space, a complete mathematical description or model of the engine is not possible in the present state of information. However, a quantitative description of the main effects contributing to engine operation make it possible to evaluate the part played by each of these effects and to study the role of any particular engine or system parameter in the ignition process. The present discussion follows a particular element of fluid in a Stokesian manner through the various changes of state from engine energization up to and including droplet formation. It will show, among other things, that although each of these processes has been the subject of numerous investigations, the present quantitative global description is still inadequate. Much experimental and theoretical work is still needed to achieve an adequate description of the preignition engine history.

There are two publications that treat the problem of spray formation in its entirety. "Spray Formation and Breakup and Spray Combustion" by A. E. Fuhs,[1/] and "Hydraulic Gas-Liquid Systems" by Kutateladze and Styrikovich.[2/] In addition, in 1953 the Pennsylvania State University published an extensive bibliography on sprays[3/] which includes abstracts of articles pertinent to spray formation published prior to 1953. An excellent survey of spray formation and breakup, including spreading and mixing, is given by Bixson and Deboi.[4/] Finally, "Basic Considerations in the Combustion of Hydrocarbon Fuels in Air" edited by Barnett and Hibbard[5/] appears to be the bible of spray physics. The majority of the material examined deals with some special aspect of the production of an atomized fuel (spray) which normally involves the following sequence:

(a) Fluid flow through the injector feed lines,

(b) kinetic energy imparted to the fluid stream on exit from the orifice,

(c) disintegration of the fluid stream into filaments or droplets by instability phenomena, stream interaction with the ambient fluid or stream-stream interaction,

(d) droplet (filament) disintegration due to interaction with the ambient fluid,

(e) droplet (filament) disintegration due to droplet-droplet interaction or internal energy droplet conversion, and

(f) interaction of the combustion process with the spray.

III(1). Hydrodynamics of Fluid Streams and Jets in Initially Low Pressure Environments

Although the dynamics of nonviscous incompressible fluids has reached the level of mathematical maturity[6] the same cannot be said for viscous, compressible systems. The problem is further complicated by the heterogeneity of the system which introduces many additional coupling phenomena, making a mathematical solution ever more difficult. Although there are numerous articles pertaining to heterogeneous flow, these are primarily of a semi-empirical nature and have limited use in temporal problems such as encountered here.

III(1)(a). Volatile Liquid Flow in Initially Low Pressure Piping

The dynamic response of a liquid that fills an inelastic pipe and is suddenly released at one end into a low pressure environment can adequately be described by wave diagram techniques. Although such a calculation is beyond the scope of this monograph, the solution is not very difficult if viscous effects are ignored. Problems such as this have long attracted the attention of researchers and numerous investigations have been conducted in this area.[7]

For the problem of liquid escaping from an inelastic pipe, the process starts with a rarefaction wave at the exposed liquid interface which propagates into the liquid column at the speed of sound in the liquid (about 4000 ft/sec). The expansion of the liquid across this interface causes the liquid to flow toward the injector at a linear velocity equal to the product of the sound velocity and the liquid's expansion coefficient; about 4 ft/sec for A-50 corresponding to a mass flow rate of 0.07 lb/sec in a quarter inch ID line. If the line's ullage, for this example, is initially less than 2.5×10^{-4}, liquid emits from the orifice before the rarefaction reaches the reservoir. Furthermore, as the expanding liquid column moves through the line, the flow is resisted by the viscous drag on the walls resulting in a pressure gradient opposing the liquid's motion. This pressure gradient causes a decrease in the pressure drop across the receding rarefaction. If the head pressure is large and the transfer line relatively short, the rarefaction reaches the fuel reservoir before its pressure differential becomes negligibly small. At the reservoir, the rarefaction reverts to a compression wave that travels back down the liquid-filled line toward the orifice. On crossing this compression wave, the liquid flow velocity again increases by an amount determined by the liquid's change in density. At the orifice the compression reverts to a rarefaction which moves back up the line as before and the process begins a new cycle.

With each cycle, the liquid's velocity increases by a discrete but smaller amount until eventually a steady state flow is established by virtue of the dissipative forces. As a rough estimate, the time required to reach steady state is normally assumed to be the time necessary for a sonic wave to traverse twice the length of the feed line (about 5 milliseconds for every 10 feet of line). Such factors as cross-sectional area reduction, transfer line irregularities and geometry, and fluid viscosity, prohibit any realistic calculations for this process except in the most trivial of situations.

Although this description is admittedly oversimplified, it does illustrate some important temporal features of the fluid flow during the first 10 or 20 milliseconds following valve opening. In particular, it shows that the transient flow characteristics depend not only on the injector head but in addition on the fluid control and transfer devices remote to the engine. These can have an adverse influence on the initial oxidizer to fuel ratio, the mixing efficiency of impinging jets and/or the mechanical response of the system complex.

III(1)(b). Heterogeneous Pipe Flow

The previous section was concerned with the temporal flow characteristics of noncavitating liquid in transfer lines. The present section considers cavitating flow in such lines, especially its genetics and transport phenomena.

Although two-phase systems had been studied sporadically for over sixty years, it was not until about 1935 that researchers were attracted to this subject in any numbers. Initially, Naval architects and engineers were concerned with the adverse effects of cavitation phenomena on hydrosurfaces. At present, cavitation studies are divided into two distinct areas. The first concerns the genetic or nucleation and growth processes of individual cavities (bubbles). A considerable amount of the theoretical and experimental work conducted in this area is reported in an excellent collection of articles published by R. Davies[8] in 1964. The second area concerns the transport properties associated with heterogeneous (vapor-liquid) systems in pipes. Because of the complexity of this problem, no direct mathematical attack has been possible. However, similitude arguments have been used to develop a number of useful relationships capable of generating design criteria. Reference (2) gives an excellent account of the dimensional relations and numerous experimental findings associated with two-phase pipe flow.

The presence of cavities in liquid systems has been of considerable interest to rocket engine developers for some time, primarily because various types of rocket combustion instability have been attributed to the compressible nature of these cavities.[9] This particular aspect is not of immediate interest here as it is primarily a postignition process; however, there are other aspects of cavitation that relate to the hard-start problem. In particular, cavities in the feed line can significantly affect the flow characteristics of the liquid propellants. It is generally agreed that there exist four types of two-phase (vapor-liquid) pipe flow,[2] (1) bubbly flow, in which discrete bubbles are dispersed in the liquid stream, (2) slug flow, with alternating regions of gas or liquid passing a given point in the pipe, (3) annular or core flow in which a thin layer of liquid is established along the wall with a core of flow containing a dispersion of liquid and gas, and (4) mist flow, in which liquid drops are dispersed in a main gas stream. Although all four flow types can exist at one time or another in our engine complex, bubbly and slug flow are probably the most prevalent and will be discussed at some length.

It is now generally agreed that cavitation is due to the growth of undissolved vapor or gas nuclei suspended in the liquid or trapped on microscopic foreign particles. It is well known that the rupture forces of very clean denucleated liquids are of the order of those predicted by kinetic theory (several hundred atmospheres).[7] Thus, the presence of nuclei is essential for caviation at pressures of the order of the liquid's vapor pressure. In the absence of a pressure gradient, a bubble once nucleated grows by the separate or combined action of two mechanisms: vaporization of liquid from the bubble surface into the cavity, and/or outgassing of dissolved gases from the bubble surface into the cavity. Since bubble growth by vaporization does not require mass transport through the liquid phase to the bubble surface, this mechanism is relatively rapid; typically, a bubble radius increases at a rate of 3 ft/sec.[10] At this rate, a bubble will completely fill the cross-section of the 0.02-inch diameter injector capillary of our ideal engine in approximately 0.5 millisec. On the other hand, the growth rate of a gas bubble in a quiescent liquid is controlled by the relatively slow diffusion of the dissolved gases through the bulk liquid to the bubble surface. The radius of the growing bubble is proportional to the square root of the product of the diffusion coefficient and the time[11] following the inception. For example, carbon dioxide bubbles growing in a supersaturated water solution of 15 psia (supersaturated at a CO_2 pressure of 55.9 psia) reach a diameter of 0.02 inches in about 5 seconds,[10] which is 10,000 times slower than the vapor bubble growth rate. Similar results have been reported by Westwater[11] for hydrogen bubble growth during electrolysis. When the bubble and liquid phase are in relative motion, the transport expression must contain a convection term, a problem which does not appear to have been considered so far.

There exists yet another bubble growth mechanism of significance to our system that has not been given much consideration in the literature. This concerns the expansion of a bubble as it moves through a decreasing pressure gradient. As the expanding bubble must displace the liquid, the rate of bubble growth by this mechanism depends on the viscosity and inertia of the liquid.

With the exception of the latter mechanism, bubble growth in quiescent liquids appears to be reasonably well understood, as theory and experiment appear to be in accord. Before discussing the application of these concepts to our particular engine, let us continue this discussion of the generalities of two-phase flow by considering the transport properties.

The motion of bubbles in quiescent liquids has received considerable attention since the pioneering work of Stokes, who showed that bubble dynamics in quiescent liquids is controlled by the balance of the buoyant and viscous forces as long as the bubble diameter remains below a critical size (about 0.08 inches for an air bubble in water). Larger bubbles lose their spherical shape and their dynamics are not well understood. Rybchinsky-Hadamand[12] derived an expression for the rate of bubble rise in quiescent liquids which is applicable for a Reynolds number of less than 2. For higher Reynolds numbers the mobility of the interface produces a flow which is different from the flow past a solid surface; the separation point for a mobile boundary is displaced nearer to the wake of the flow. With increasing Reynolds number, the bubble becomes distorted and the resulting dynamics have not yet been described mathematically.

Another cavitation reaction that has received some attention recently is bubble collapse. It has attracted the attention of many investigators, including Lord Rayleigh, and has been shown to produce extremely large shock pressures capable of considerable mechanical damage.[11] Although this phenomenon is of interest to rocket engine developers, it has no apparent immediate bearing on the present problem and will not be considered further.

Two-phase flow in horizontal circular tubes has received considerable attention by both Russian and American investigators. Reference (2) gives an excellent review of this subject. Because of its extent and its mathematical similarity with single-phase flow, no attempt will be made here to review the subject. It should simply be noted that due to the presence of the bubbles, such systems cannot be treated as incompressible fluids. Moreover, as will be shown later, the cavitation process is strongly dependent on the combustion chamber pressure and thus the flow characteristics change continuously during the preignition chamber pressurization stage. As the extent and type of cavitation affects the relative amounts of fuel and oxidant as well as the spray formation or mixing process, it is apparent that cavitation could be instrumental in the ignition delay process.

In Section III(1)(a) it was shown that as the rarefaction wave moving upstream overtakes a volume of liquid, the hydrostatic pressure of the liquid drops sharply. This is probably when gas bubbles begin to form. Furthermore if, as previously mentioned, vapor cavities form in the feed line at the point where the hydrostatic pressure equals the liquid's vapor pressure, bubbles will normally begin to form at a point in the injector capillary line very near the orifice. Assuming an NTO mass flow rate of 0.22 lb/sec and a capillary line and orifice diameter of 0.024 inches, the liquid would have a linear flow velocity of 1120 ft/sec. In addition if, as we have shown, the vapor bubble requires 0.5 msec to grow to the injector capillary diameter, then it would require approximately 3.4 inches of linear travel (assuming there is no relative motion between the liquid and bubble) in the capillary line before the bubble would completely fill the line cross-section. Since such capillary lines are normally about 0.1 inch in length, it seems reasonable to conclude that slug flow would not result from this mechanism alone. In the case of gas bubble growth, the problem is to determine the maximum size the bubble will attain in the 4 msec period prior to ignition. Further, since we have growth rate data for carbon dioxide at 55.6 psia[11] it will be assumed that CO_2 is the pressurizing gas. Using this data and assuming that bubble nucleation immediately follows the passage of the rarefaction, it can be shown that a carbon dioxide gas bubble will grow to a diameter 0.004 inches in 4 msec. This is not sufficient to fill the cross-section of the orifice, however, a high nucleation rate makes the number density of these bubbles sufficiently large that they could still contribute to the overall problem.

A more realistic interpretation of bubble growth involves the combines effects of outgassing and vaporization. The actual contribution of each process to the final cavity size depends on the state of the system and on the length of time during which each process is operative. The major difference is that the vaporization process is a sensitive function of the combustion chamber pressure whereas bubble growth by the outgassing mechanism is little influenced by this small increase in pressure. It should also be noted that during the 4 milliseconds before ignition, only a small fraction of the cavitating liquid contained in the larger tributary line actually reaches the combustion chamber.

Although the purely physical process of bubble growth by expansion does not involve mass transport into the cavity, it is limited by the inertial and viscous forces of the surrounding liquid. For example, if the hydrostatic pressure is 150 psig at the entrance to the capillary injector line and 0.1 psia at the orifice, then on traversing this pressure gradient the bubble's diameter would adiabatically increase by a factor of 5.5. Consequently, a 0.004-inch diameter bubble entering the 0.024-inch diameter capillary line will completely fill this line when it arrives at the orifice.

To sum up, it seems reasonable to conclude that the bubble starts by the combined action of outgassing and vaporization after passage of the rarefaction wave reaches a diameter of say 0.005 inch at the entrance to the 0.024-inch in jector capillary line and expands adiabatically as it traverses this line to a final value at the orifice which is determined by the injector pressure drop and the physical properties of the surrounding liquids.

In addition to bubble nucleation by microscopic particles and cavities, there is another mechanism which forces nucleation and which involves flow separation. Flow separation occurs at points in a liquid stream where, due to sharp changes in the bounding surface, the inertia of the liquid prevents it from following the contour,6/ as for example when the cross-section of the feed line changes abruptly. Normally, for pure liquids, the hydrodynamics of the stream will determine the geometry of such a cavity. However, for real liquids both outgassing and vaporization into the cavity causes a bubble to grow beyond its normal size, after which the stream drags it away from the wall and carries it downstream; then another bubble grows in its place and the process repeats itself. The number density of bubbles generated by such a mechanism is apparently a function of the boundary surface condition and geometry and of the kinetics of the gas and vapor bubble growth mechanism previously discussed. Reference (2) discusses the fluid flow characteristics of heterogeneous liquid systems in detail. The flow characteristics of cavitated systems depends on whether the bubble in the dispersion is a gas or vapor bubble. The complexity of such systems is attributable to the fact that in addition to the compressibility of the bubbles, both inertia and thermal trasnport must be taken into account. As it is not possible to do justice to this topic in the limited space of this report and since reference (2) essentially contains all the pertinent information currently available on the subject, it will not be discussed further here.

III(1)(c). Hydrodynamic Instability Criteria of Liquid Jets

A liquid jet moving into a quiescent environment normally retains its integrity for a finite distance and then breaks up into droplets forming a spray. This section is concerned with the disintegration of the jet as a function of its initial state and environment. The physical characteristics of the spray resulting from jet disintegration are discussed in Section III(2). Due to the complexity of the mathematics describing jet instability, there are at present no satisfactory theoretical representations of jet disintegration in liquid rocket engines. Because of this, most of the research on jet instability has been experimental in nature.

It was shown in Section III(1)(b), that cavitating flow normally exists in the fluid streams prior to discharge.[9] It was also shown that gas bubble formation by outgassing of dissolved gases in the propellant is relatively unaffected by preignition combustion chamber pressurization. However, it was noted that cavitation due to liquid vaporization is strongly pressure-dependent. Consequently, the cavitation process should change abruptly as the chamber pressure approaches the vapor pressure of the injected liquid. As cavitating and noncavitating flows exhibit different initial jet configurations, they result in different spray configurations. As a result, the physical and chemical state of this heterogeneous system changes continuously as the chamber pressure increases.

The three configurations of liquid streams most often used in rocket engine spray formation devices are the jet, the cone and the sheet. Although this report is primarily concerned with liquid jets, the other two geometries must also be considered. The energy necessary to break up a large liquid volume into small drops represents only a very small fraction of the energy available in the pressure drop across an injector (about 0.05 percent);[13] most of the energy is accountable in the kinetic energy of the drops. Haenlein,[14] in experiments with jets emitted into air from nozzles with a length-to-bore ratio of 10:1, observed four stages in jet disintegration: (1) At low stream velocities, varicose or radially symmetric disturbances occurred as a result of the jet surface energies; (2) at increased stream velocities, the varicose instability was accentuated by aerodynamic interaction of the surrounding air with the jet surface; (3) at still higher stream velocities (intermediate velocities), increased aerodynamic interaction produced a sinuous or snake-like jet instability; and (4) at high stream velocities the jet started disintegrating rather chaotically near the nozzle (jet atomization).

Rayleigh[15] conducted the first theoretical investigation of jet disintegration in 1878. He showed that for low velocity jets the wave length of the varicose disturbance is 4.51 times the diameter of the orifice and is independent of the jet density and velocity. Such a disturbance created at the orifice grows exponentially as it travels down the jet and finally disrupts it. In 1933 Tyler[16] conducted experiments with jets of water, mercury and aniline, at jet velocities from 3 to 6 ft/sec. In each case he found satisfactory agreement between Rayleigh's theoretical values and his experimental data for the resulting drop diameter.

In practice, Rayleigh break-up of a plain jet only occurs if the relative velocity between the jet and the surrounding atmosphere is low and if the surface tension forces are adequate. As the jet velocity for a given nozzle configuration increases, two processes tend to predominate: (1) The Reynolds number of the liquid jet increases, eventually causing the stream to acquire a turbulent boundary layer which grows with increasing orifice length; and (2) the aerodynamic forces start interacting with the jet surface. Rayleigh extended his investigation to include the effect of this latter factor on jet instability. Neglecting surface forces, he found that a sinuous or snake-like unstable mode results. In a later paper published in 1892, Rayleigh extended his previous studies to include the viscosity of the jet. He found that within the limits of his calculations, the stream viscosity had little effect on the resultant droplet size,[17] although the rate of growth of the unstable disturbance increased.

Weber, in 1931,[18] extended Rayleigh's treatment of the problem to include the combined effects of both surface tension and viscosity as well as jet velocity and aerodynamic drag. The most recent theoretical investigation was conducted in 1935 by Tomotika[19] who was primarily interested in low velocity liquid jets injected into a liquid environment. Consequently, he neglected the surface energy and studied only viscosity effects. As a result of these investigations, four dimensionless groups have been defined that appear to characterize the various stages of jet instability phenomena in the intermediate velocity region.[20] The relation of these dimensionless groups to jet instability has been discussed by Miesse's[20](1955) who compared these earlier theoretical results with his own experiments using water and liquid nitrogen. Miesse concludes that Rayleigh's original theory is entirely inapplicable to the disintegration of the intermediate speed jets which he examined. Further he observes that Weber's analysis for a sinuous jet gives the best correlation of his experimental data. This is due to the fact that the jets considered by Miesse were rapid enough so that aerodynamic forces and surface energies both contributed to jet breakup. As regards Tomotika's theory, Miesse finds that the droplet size predicted by this theory from the wave length of the unstable disturbance is in almost quantitative agreement with the experimental values.

Merrington and Richardson,[21] in 1946, studied the effect of liquid viscosity on jet breakup length and resulting droplet diameter, using such materials as molasses, glycerin, water, zine chloride solutions, rubber dissolved in gasoline and mercury. Following the work of Smith and Moss in 1917, Merrington showed that jet length/jet diameter ratio varies linearly with the Weber number (W), for small values of W, reaches a maximum value at some critical value of W and then decreases hyperbolically for higher values of W.

In 1962, Rupe[22] published an interesting account of work done to measure the velocity profiles of liquid jets injected into air. He conducted a series of experiments bearing the same basic geometry but incorporating a turbulence-inducing section with varying degrees of roughness and provisions for varying the total length/diameter ratio. As expected, Rupe's results show that the velocity profile of a jet tends to become uniform as the distance from the orifice increases and the energy that becomes available as this occurs can be an important factor in jet breakup. Reference (22) contains numerous photographs of jet disintegration from fully developed laminar flow to fully developed turbulent flow, including Reynolds numbers from 1000 to 80,000.

Rupe also showed that the dynamic characteristics of liquid jets are largely determined by the physical properties of the orifice as well as by the dynamics of the upstream system. The effect of this latter factor was further investigated by McCormack,[23] and McCormack, Crane and Birch[24] and Dityakin and Yagodkin[25] using forced vibrations on cylindrical jets. They concluded that for low velocity jets, high induced vibration particle acceleration upstream of the orifice produced pronounced "bunching" of the liquid in the jet. This effect predominates over the normal Rayleigh-Weber capillary instability and decreases considerably the length of the jet before breakup (jet breakup length).

Schweitzer[26] and Lyshevskiy[27] studied the influence of the ambient atmosphere on jet instability, in conjunction with diesel injectors. They found that injecting nonvolatile liquids into a vacuum environment resulted in jet breakup that closely resembled aerodynamic disintegration. They concluded that the internal turbulence of the jet generated the instability because breakup became most pronounced as the Reynold number of the jet approached its critical value (2000). Corbett, Dawson, Seamans and Vanpee,[28] studied jets of liquid carbon tetrachloride, unsymmetrical dimethylhydrazine and nitrogen tetroxide injected into various inert low pressure environments. They found that higher environmental pressures and high flow rates lead to greater stream breakup. Furthermore, the distance to essentially complete stream breakup is only slightly affected by the injection velocity; ordinarily stream breakup was complete within a millisecond after leaving the orifice.

Similar experiments were conducted by Lee and Spencer at environmental pressures as high as 14.5 atmospheres. They showed that increasing environmental pressure markedly reduced the jet breakup length. In addition, they concluded that of all the liquid properties, viscosity has a most significant effect on jet instability. Schmidt[29] studied volatile liquid jets injected into low pressure environments whose total pressure was close to the vapor pressure of the emitted liquid. His results indicate that jet instability changes markedly as the environmental pressure approaches the liquid vapor pressure. This subject will be discussed further in the following section on cavitating flows. For high velocity jets (Reynold's number > 50,000) the breakup mechanism commences at the orifice and appears to be due to violent interaction of the jet surface with the gas environment. In the case of water, this interaction produces a very rough, opaque jet but the effective jet diameter does not change appreciably over a length equal to 100 diameters.

Breakup of liquid sheets into droplets has been studied by numerous investigators. Lewis[30/] in 1961 published photographs of such processes. On the basis of theoretical and experimental studies, York, Stubbs, and Tek[31/] conclude that instability and wave formation at the interface between the sprayed and ambient fluids are the major factors in sheet disintegration. Dombrowski and Hooper[32] (1961), studied the effect of the environment density on drop formation from flat sheet injectors. They found that a flat laminar sheet injected into a vacuum is quite stable and that drop formation occurs only at the edges. At higher environment pressures, disruption is caused by the aerodynamic forces. In addition, they developed theoretical expressions for the size of drops produced from such fan spray sheets. They found that under certain operating conditions, the drop size increases with density of the surrounding environment. Atomization from impinging jets appears to be intermediate between that of plain jets and sheets.[30/] At low injection velocities and large impinging angles, a well defined sheet is formed. However, the sheet becomes progressively less pronounced as the jet velocity increases or the impinging angle decreases. Atomization of sheets injected into environments having appreciable pressures appears to occur in two stages:[33/] (1) Breakup of the sheet into ligaments, and (2) subsequent breakup of the ligaments by Rayleigh-Weber instability into drops. Sheets injected into a vacuum do not exhibit ligament formation; instead perforations appear in the sheet which grow to coalescence and sheet destruction.[33/] This same phenomenon is exhibited by jets containing insoluble or unwettable impurities.

One further mechanism of jet disintegration that has received considerable attention in the last few years involves shock wave disruption. Morrell[34,35/] investigated this mechanism and developed scaling relationships for determining the jet breakup time as a function of liquid parameters and shock strength. However, this process is probably not operative during the preignition stage of rocket function, although it may play a part in heterogeneous combustion.[36/]

Cavitating liquid jets exhibit jet disruption phenomena that are different from those of noncavitating systems. As previously shown, cavitation is normally the result of three processes: (1) Outgassing of dissolved gases, (2) boiling of the jet liquid and (3) flow separation. For volatile liquids the jet stability (or instability) characteristics change drastically as the environmental pressure is gradually lowered to the vapor pressure of the liquid.[34,31/] In 1965, Simmons and Gift[37/] conducted an investigation on liquids debouched into a vacuum. They showed that volatile liquid jets, such as of cryogenic liquids, appear to disintegrate in the immediate vicinity of the orifice; in some cases cavitation may even occur within the orifice proper. For some materials the solid angle subtended by the resulting spray configuration approaches 180°; in this case, the process is primarily due to boiling within the liquid jet. Unfortunately, the boiling process due to vapor nucleation and growth is not sufficiently understood for a realistic estimate of the rates of bubble formation for such a process. Apparently it is markedly influenced by minute quantities of impurities. Simmons and Gift attempted to derive order-of-magnitude results for liquid jets of nitrogen, oxygen, nitrogen tetroxide, Aerozine-50 and water. They found that for the cryogenic liquids injected into a vacuum the jet length appears to be very short (< 0.1 inch) or even nonexistent. This presents a problem for impinging stream type injectors, as the efficiency of such a device is markedly impaired if the two streams lose their integrity and consequently fail to impinge. It would appear that if the rates of cavity nucleation and growth be controlled, it might be possible to select the spray angle and/or resulting spray droplet distribution for a given propellant combination.

Knox and Sund[9/] studied cavitation phenomena occurring in rocket engine propellant feed lines. In these experiments, flow separation and outgassing were primarily responsible for cavitation. However, these authors were concerned with cavitation during post ignition processes when the combustion chamber had reached its operating pressure. An excellent discussion of cavitating processes in liquids is given in reference (8). A short discussion dealing primarily with flow separation can be found in reference (6). Although there are many articles on the fluid dynamics of two-phase systems, no reference was found to studies involving the dynamics of jet disintegration of cavitated streams.

In spite of the numerous studies on jet disintegration processes, present knowledge of these phenomena is far from complete. It will be difficult to determine the necessary direction of further research efforts until a more detailed study has been made of this earlier work.

III(2). Single Particle Physics

To determine those factors that contribute to the pressure spike, it is important to have some definition of the temporal state of the propellant drops in the combustion chamber. In particular, vaporization and chemical reaction at the drop surface contribute to pressurization of the combustion chamber. Hypergolic drop agglomerates probably contribute to the intensity of the combustion. Consequently, it is anticipated that drop physics will prove to be a significant factor in the preignition process and conceivably a controlling one. Much has been published on the physical kinetics of drops. Prior to the liquid rocket programs, these studies were primarily concerned with improving the efficiency of diesel engine injectors or of fire-fighting equipment. A bibliography covering investigations up to 1953 has been published by Pennsylvania State University.[3/] To avoid duplication of effort, these articles will not be referenced here. In addition to the Pennsylvania State University report, in 1960 the Faraday Society published an excellent monograph, (No. 30, 1960) containing some two dozen articles on the physical chemistry of aerosols which are not included in this report.

Drops moving in an unbounded gaseous environment are subject to three main physical phenomena; (1) Cooperative phenomena involving dynamics of phase transitions (liquid, solid, or gas); (2) drop kinematics concerned with the internal and external fluid motion of the drops; and (3) energy and mass transport phenomena in the gaseous and condensed phases.

III(2)(a). Cooperative Phenomena

The term "cooperative phenomena" refers to those processes occurring during phase transitions, such as fusion (liquid $\rightleftharpoons$ solid) sublimation (solid $\rightleftharpoons$ gas) and vaporization (liquid $\rightleftharpoons$ gas). Cooperative phenomena are concerned primarily with drop nucleation and growth.

Nucleation is the formation of the least stable cluster of molecules of the new phase. In almost all cases, nuclei contain less than 100 atoms (molecules, ions, etc.) and in some cases they may contain less than 10 atoms. The actual stability of a particular drop also depends on its size relative to other drops in its environment. Although this subject has received considerable attention over the past twenty years, particularly since the advent of jet vapor trails and nuclear cloud and bubble chambers, it remains sufficiently obscure to prohibit an a priori estimation of nucleation rates. According to a recent article by Russell[38] there is a 1:7 order-of-magnitude difference between the experimentally determined and the theoretically predicted behavior of homogeneous nucleation in cloud chambers. Courtney[39] (1961) reviewed the state of the art and compiled an extensive bibliography pertaining to nucleation and growth phenomena. The problem is well stated by Courtney who writes: "Experimentally one observes that condensation from ordinary impure vapor often occurs readily, but condensation from the pure vapor usually takes place only after an appreciable and moderately critical supersaturation. Once condensation begins, a few large particles will be formed if nucleation is slow compared to growth or agglomeration, and many small particles are formed if nucleation is fast compared to growth and agglomeration. Nucleation can be either homogeneous or heterogeneous. Heterogeneous nucleation occurs when the new phase initially deposits onto foreign impurities (e.g., dust, salt particles, ions) and thus bypasses the more difficult homogeneous nucleation step. There is considerable uncertainty whether or not a truly homogeneous nucleation ever does occur, because the total absence of subtrace amounts of catalytic impurities is unlikely in nature and is difficult to prove even in the laboratory." It is estimated that approximately 100 heterogeneous nucleation sites per cubic centimeter occur in nature. Most experimental nucleation work has been conducted on water and various organic vapors in expansion-type cloud chambers.[39] As stable nuclei may contain up to 100 atoms, the mathematical description of this process involves at least 100 independent differential equations. To circumvent this gigantic mathematical problem, a number of simpler theories have been developed.[40-48]

Liquid condensation from vapor and fusion from liquid, although qualitatively similar, are quantitatively distinct. Fusion is of particular importance to hypergolic ignition during engine start in low pressure environments where solid formation in the propellant sprays has often been observed. Most materials exhibit supercooling, which is characterized by a marked lowering of the freezing temperature of the liquid below its normal or bulk freezing point, but this phenomena does not appear to be significant in contaminated systems. The extent of the freezing point depression is apparently determined by the rate of temperature lowering and the size of the drop. According to reference (49) hydrazine drops smaller than 10 microns can be supercooled as much as 129°C, if exceptional care is taken to exclude all foreign matter from the liquid. No supercooling studies appear to have been conducted with Aerozine-50 or NTO.

Drop growth rate theory on the other hand, is comparatively well understood, particularly for larger drops. The drop growth rate is influenced by seven mechanisms:[39/] (1) Transport of vapor to the drop surface, (2) adsorption, (3) surface diffusion, (4) chemical reaction if any, (5) incorporation of the molecule (or atom) into the structural lattice of the drop, (6) desorption of any vapor products, and (7) dissipation of thermal energies. Thus, drop growth involves both cooperative and transport phenomena. Mechanisms (2), (3), (5), and (6) above are considered to be cooperative, whereas (1) and (7) are transport phenomena and will be discussed in a later section.

The principle current problem in growth kinetics concerns the accommodation coefficient. Theoretically, the simple condensation of a material onto an infinite liquid surface has been interpreted[39,50/] in terms of the "free angle of rotation" in the liquid phase. This means that the vapor molecule must preserve its rotational energy during condensation and an adsorbed molecule tends to re-evaporate if it must lose some of this rotational energy in order to fit into a liquid lattice with restricted rotation. This can best be illustrated with water and carbon tetrachloride where the accommodation coefficient of water, an unsymmetrical molecule, is 0.04 whereas that of carbon tetrachloride, a symmetrical molecule, is 1. Paul[51/] has compiled accommodation coefficients for a wide variety of materials.

The other cooperative mechanisms of droplet growth kinetics are not yet sufficiently understood and little has been published on them.

III(2)(b). Drop Kinematics

Drop kinematics studies the internal and external dynamics of liquid drops immersed in a fluid environment. Drop ballistics, on the other hand, is concerned with the motion of rigid bodies moving through such environments. Although there have been numerous drop ballistics studies, little attention has been given to drop kinematics. The dynamic behavior of individual drops entrained by a gas stream depends on the drop strength as well as on the drop-environment interaction.

The drop-environment interaction is described by a complex set of partial differential equations developed by numerous investigators, starting with Stokes. Initially, investigations were confined to the motion of rigid spherical bodies falling through gaseous media under the action of a gravitational field. Later, primarily due to Rybezynski and Hadamard[12] in 1911, these studies were extended to include spherical liquid bodies with limited internal motion. A detailed study of drop-environment interaction has been published by Levich.[52]

Drop ballistics concerns the balance between the inertia of the drop and restoring or drag forces exerted on the drop by the environment. This problem is relatively straight-forward and has been investigated by many authors. Drag coefficients for various regular shaped solid bodies can be found in any physics or fluid mechanics text book such as the Handbook of Fluid Dynamics or the American Institute of Physics Handbook. Fledderman and Hensen[53] studied the effect of turbulence on the velocity and vaporization of drops and concluded that the drag coefficient varies inversely as the 3/2 power of the Reynold's number. A subsequent experimental study by Ingebo[54] showed that the drag coefficient varies inversely as the relative velocity, but its dependence upon the Reynold's number was not clearly defined. Theoretical drop ballistics studies were made by Langmuir and Blodgett[55] who neglected evaporation; by Hughes and Gilliland,[56] who stressed the importance of an acceleration drag; Ingebo,[54] who solved the evaporation and momentum equations simultaneously by numerical integration; and by Miesse,[57] who assumed a constant evaporation rate and Stokesian flow. Miesse[58] in a later study included the effect of velocity and evaporation. Wolfson[59] developed mathematical expressions for the motion of a drop in an oscillating environment. His principle objective was to relate combustion stability to injector design variables by considering the dynamics and combustion of rigid drops.

The classical treatment of drag is satisfactory as long as the body retains its shape. Because of the large number of articles pertaining to this problem, only a few can be mentioned here. Reference (60) gives graphical results for drag coefficient as a function of Reynold's number. Ingebo[61] in 1956 published the drag coefficients of drops and solid spheres in accelerating air streams - a work which is often cited.

When the drop shape is not invarient, its dynamic response is considerably more complicated. Once deformation occurs as a result of the aerodynamic forces, the internal motion of the liquid becomes intimately coupled to the motion of the surrounding atmosphere. If this interaction is sufficiently strong, the drop may break up into fragments. Some of the first work on drop break-up in air blasts was done by Lane[62] in 1950. Rubin, Schallenmuler and Lawhead,[60] Hanson and Domick,[63] and Rubin and Lawhead,[64] investigated the displacement and shattering of propellant drops behind shock waves. Two types of droplet break-up were observed in these studies - shear-type and bag-type. In the former, the drop is first flattened to a disk, and then the center of the disk is bowed out to form a thin, bag-like membrane attached to a heavy rim. The bag-like membrane finally bursts forming very small drops, while the rim breaks up into larger drops. In shear-type break-up, the drop is flattened to some extent but instead of forming a disk it assumes a saucer-like shape with the convex surface toward the air-flow. Progressively, the edges of the disk are drawn out into a thin sheet which breaks up into fine drops. The effect of wind velocity, wind duration, surface tension, and environmental pressure on break-up characteristics were investigated for both burning and nonburning drops. It was found that it is the gas flow behind the shock front which causes break-up, rather than any impulsive action of the front itself. It was further found that the product of the Weber number and the square root of the Reynold's number gave satisfactory correlation of break-up. Other investigators[2,20,60,61,66,65] have obtained slightly different dimensionless expressions. In particular, Morrell[66] in 1961 studied the two types of drop break-up and compared the results of dimensional arguments with experiment. The lack of agreement he found has been attributed to the drop-environment interactions.

Except for casual observations, drop rotation and internal vibration have not been studied. Simmons and Grift[37] and Rabin, et al.[64] have considered internal drop motion. In the former study, photographs of various liquid sprays (unsymmetrical dimethylhydrazine, Aerozine-50, and nitrogen tetroxide) debouching into a vacuum show a flickering of the light reflected from the drops which was attributed to the rotation of the drops. From such records the authors calculated drop rotational velocities as large as 50,000 revolutions per second. This is an exceedingly high speed and it is interesting to speculate on the stability of such a drop to retain its integrity. Harrje and Reardon[67] published high-speed photographs of shock wave-drop interactions which show a 400-micron diameter drop undergoing large internal vibrations which apparently terminate in its destruction.

III(2)(c). Transport Phenomena

As in the case of drop kinematics, transport processes are both internal and external to the drop. Internal transport is primarily concerned with the movement of molecular species between the interior of the drop and its surface, and the conduction of thermal energy from the drop surface to its interior. Either or both of these processes could be rate-controlling. With the exception of one report (37), no reference was found to any studies directly concerned with internal drop transport mechanics. In this report the investigation was primarily concerned with determining the spatial temperature distribution within an evaporating drop, and with calculating the time necessary to freeze drops of various materials in a vacuum environment as a function of their initial diameter. Experimental results of studies using sprays of water, liquid nitrogen, nitrogen tetroxide and Aerozine-50 were in satisfactory agreement with the calculated values. Except for this work, little or nothing has been done in this area.

Mass transport near slow drops has been treated in some detail by Levich.[52] As the drop velocity increases, the aerodynamics become increasingly complicated. So far the problem of fluid flow around moving rigid spheres has defied mathematical description, thus it is not surprising that a similar description for deformable bodies is completely lacking. Transport mechanics in the vicinity of the drop is usually incorporated in mathematical models by the use of dimensionless expressions. The use of such expressions is not objectionable if the transport time is relatively long and if the various processes occurring are not strongly coupled. Gaseous transport mechanics in the absence of drops, or far removed from drops, is mathematically quite sound, if the medium can be assumed to be incompressible. Otherwise one must again resort to dimensionless arguments. The vaporization of drops in motion relative to their environment has been considered by Fuhs.[1] Although the problem has not been satisfactorily solved for either small or large Reynolds numbers, there are a number of approximations that can be used.

In summary then, it can be said that sufficient information does not exist to permit reliable prediction of the detailed transport mechanics of high-speed deformable, volatile bodies moving relative to a gaseous environment.

III(3). Physics of Sprays

A spray is characterized by a distribution of the characteristics of its individual drops. Consequently, spray characteristics are not described by a single number, as are drop characteristics, but rather by a statistical distribution function. Drop-size, drop-velocity, and drop-number density are the most frequently measured spray characteristics and are the most significant of the characteristics necessary for postignition rocket engine analyses. It is anticipated that for each spray characteristic there exists a unique value or set of values necessary for optimum rocket engine performance. However, it is not immediately apparent that these unique values (or sets of values) are collectively coexistent. Furthermore, it is not obvious that the optimization of postignition engine performance also optimizes preignition performance. Consequently, although the literature is strewn with reports of investigations concerned with the effects of spray characteristics on postignition engine performance, little information is currently available concerning preignition studies.

Spray drop-size distributions have been more extensively studied than any other characteristic and four distribution functions have received general acceptance: The Nukiyama-Tanasawa, the Rosin-Rammler, the Logarithmic-Normal and Upper-Limit. As these distributions have already been reviewed in considerable detail,[1,5,62,68] the present discussion is limited to reports published subsequently.

In a study of impinging n-heptane jets, Ingebo[69] obtained drop-size distribution data as a function of orifice diameters, liquid-jet velocities, and jet velocities relative to the airstream. He showed that impinging jets produced a relatively coarse spray for the smallest orifice (0.029 inch) and the highest velocity (235 ft/sec). In addition, Ingebo found that of the four types of distributions examined, the Nukuyama-Tanasawa gave the best fit with his data. In 1960 and 1961, Foster and Heidmann[70,71] reported results of a similar study on spray formation from impinging jets. They also used heptane but included an additional factor corresponding to the angle of jet impingement. Their results showed that drop-size data fit a binominal distribution. Reexamination of Ingebo's data showed that a similar distribution could be fitted to his results. Eisenklam[33] studied liquid atomization in rocket engines using a wide variety of injectors. In addition to drop-size and spatial distribution studies, he also investigated the influence of liquid and environment viscosity on the resulting spray. Unfortunately, Eisenklam made no attempt to fit his experimental results to any of the four common distributions.

In 1956 Rupe[72] (apparently overlooked in reference (5)) studied the uniformity of the mixture-ratio resulting from a pair of impinging jets. He found that the spatial distribution of the two components of a bi-liquid spray from a pair of impinging streams attains its most uniform configuration (i.e., one component relative to the other) when the ratios' product of the velocity heads and stream diameters is equal to unity. He observed that this correlation appeared to be independent of the angle of impingement. Cohen and Webb,[73] using a swirl atomizer, concluded that the ambient gas density and the injector pressure drop are important factors in defining spray distributions although the gas viscosity has no apparent effect below a critical value. Bittker,[74] in 1958 conducted a theoretical study of the mixing of gaseous propellants emitted from a regular lattice of injectors. He showed that the contribution of molecular diffusion to the overall mixing is negligible compared with turbulence-controlled mixing.

Although additional work needs to be done in this area, most investigators appear to feel that the existing information satisfies their present needs and as a result current rocket engine model studies are not concerned with many of the more salient spray features. This is probably not the case for the preignition process where other spray characteristics may be significant.

Two additional spray characteristics, drop collision and coagulation have received comparatively limited attention. Smoluchowski first investigated the association (coagulation) of homogeneous aerosols in 1917.[75] His theoretical rate expressions were extended by Patterson and Cawood[76] in 1932 to include a drop-radius dependent term. Approximately 40 articles have appeared since Smoluchowski's and the majority of these consider only quiescent environments where the association rate is determined by the random collision of drops. Such a collision mechanism is probably not of prime importance in the high velocity sprays found in rocket engine combustion chambers.

In 1965 Gunn[77] published a report on the collision characteristics of rain drops. He points out that drop association is governed by three factors: (1) Intersection as a result of collision course, (2) Bernoulli pressure forces between moving bodies, and (3) electrostatic attraction. The magnitude of the Bernoulli pressure forces depends on the drop size, drop separation and relative velocity between drops and gaseous environment. Drop association does not imply coalescence which is a function of such factors as the drop surface energies, the relative velocity of drops prior to association, miscibility and chemical reactivity of the droplet pair. According to Gunn, drop association can be followed by:

(1) Recoil, (2) coalescence, and/or (3) drop disruption. Which of these events occur depends upon the precollision states of the two drops individually and collectively. In 1965, Nicholls, Dabora and Regland,[36] using monodispersed streams of droplets, found that nearest neighbor drop pairs often coalesced as a result of aerodynamic forces. In 1963, Devir[78] discussing the association of slightly charged aerosols in a quiescent environment, found satisfactory agreement between theory and experiments. Nicholls, Dabora and Ragland[36] also investigated the dynamics of charged drops. They found that by charging the drops in a monodispersed spray, the electrostatic repulsive forces between the drops caused them to disperse rapidly.

It is apparent that drop collision has been only sparsely investigated and that considerably more work needs to be done before one can evaluate the significance of this process in rocket engine dynamics, particularly preignition dynamics. Although numerous experiments have been directed toward the specification of size distribution of liquid drops from various injectors, it is not possible to completely predict a realistic distribution and to determine its statistical parameters based on given propellant properties and injector design.

IV. Chemistry of Combustion

Combustion involves three areas of development: (1) The preparation of combustible systems, (2) the physico-chemistry of the combustion process (ignition and flame propagation) and (3) the interaction of the released energies with the environment. The first of these has been discussed in the previous sections, the second is discussed in the present section and the third will be covered in Section V(2).

The physicochemistry of combustion includes the three distinct but related processes: ignition, flame propagation and flame extinguishment or termination. Although these three phenomena have been actively studied for the past forty-odd years, the current state of the art is such that, except for those involving only thermodynamic calculations, few combustion characteristics can be determined a priori. This is primarily attributable to the fact that the study of combustion is based on the two nonlinear processes of fluid dynamics and chemical kinetics. As combustion is very intimately associated with pressure spiking, more attention will be given to details in this section than in the previous sections. Because of the large volume of related literature, the discussion will be confined to those areas that are of immediate interest to hypergolic systems.

Of the numerous general texts on combustion, the most appropriate appear to be those of Lewis and von Elbe,[79] Jost,[80] and Gaydon and Wolfhard.[81] The AGARD series[82] and the Progress in Astronautics and Rocketry Series[83] contain excellent collections of articles by various authors on nearly every aspect of rocket propulsion. A number of translated Russian texts by Khitrin[84] and Sokolik[85] contain references to less familiar Russian work. The ten volumes of the Combustion Symposia papers probably offer the most extensive collection of the best in combustion. More recently, Barrere, Jaumotte, De Venbehe and Vandenkerck[86] have covered some of the more practical aspects of combustion as applied to space engines. Williams,[87] and Friestrom and Westenberg[88] have published more basic flame studies, and Markstein[89] has covered the field of flame stability. These publications contain a good deal of the material that will be discussed in the following sections.

The following paragraphs include the results of investigations concerned primarily with the combustion characteristics of hypergolic systems, more specifically nitrogen tetroxide hydrazine-type systems. For convenience, the basic concepts of ignition, flame propagation, and flame termination will be discussed here, deferring to a later section investigations concerned specifically with the combustion characteristics related to engines.

IV(a). Ignition

Ignition is probably the least well understood of the three combustion processes, although it has received as much attention as propagation and more than termination. A rather good discussion of the recent developments in spontaneous ignition is given by Sokolik.[85] Ignition constitutes the initial state of flame propagation and as such it is a major factor of the overall combustion process. Like most other originating processes, ignition exhibits two forms, spontaneous and induced. Classically, a gas mixture of combustible and oxidant ignite spontaneously when the heat generated by chemical reaction exceeds the heat loss. Induced ignition, on the other hand, is obtained by the application of an external energy source, such as hot surface, electric discharge, or shock wave. In spite of numerous attempts to develop a theory of spontaneous ignition, no adequate method has been developed for predicting ignition quantitatively. If for a given state of the gas it is assumed that there exists a certain probability that a unit volume of combustible will ignite per unit of time, then for a given vessel and initial gas state there must exist a specific ignition density rate. If this density of ignition rate greatly exceeds the rate of flame propagation, the gas mixture will appear to burn uniformly and homogeneously. Otherwise, if the mixture has a single ignition site, a flame propagates from this site throughout the combustible mixture. Obviously, the temporal nature of these two situations is very different. A uniform combustion process consumes the entire combustible mixture in the time necessary for an incremental volume of material to traverse the flame zone thickness, independent of the volume of the combustible mixture. In the converse situation, the burn time is equivalent to the time necessary for the flame zone to traverse the mixture's (vessel) maximum dimension. For example, in the case of a combustible gas mixture having a flame zone thickness of 0.04 and a burning velocity of 40 inches per second, the time to reach maximum combustion pressure by the homogeneous ignition mechanism is approximately one millisecond, whereas the flame propagation mechanism requires 25 milliseconds for each inch of flame travel or 75 milliseconds for a three-inch long combustion chamber. Although the rates of pressure rise for these two situations are considerably different, the resultant maximum combustion pressures will be very nearly the same, provided the gas density remains invarient.

Spontaneous ignition or autoignition, as it is sometimes called, is characterized by two observable system parameters - the state of the system conducive to ignition and the time delay between subjection of the system to this state and subsequent ignition. Unfortunately, the theory of spontaneous ignition has not matured sufficiently to predict either of these parameters a priori. Classically, the time delay is a result of the opposing thermal processes previously mentioned, although normally such delays include the physical processes of vaporization, mixing and heating. Consequently, unless the chemical induction delays are considerably longer than those physical processes, the chemical induction times are masked by the physical ones. These processes have attracted considerable attention, both in regard to rocket engine performance and industrial chemical engineering processes.

The earliest combustion studies involving these propellants concerned the measurement of the spontaneous decomposition and ignition temperatures of hydrazine-type fuels in various nonhypergolic atmospheres. Herickes, Damon, and Zabetakis[90/] determined the spontaneous ignition and decomposition temperatures of unsymmetrical dimethylhydrazine in air at 0 and 200 psig. Scott, Burns, and Lewis[91/] in 1949, and Burgess, Grumer and Zabetakis[92/] in 1960, conducted similar studies on hydrazine.

Later investigations involved the hydrazine-type/nitrogen tetroxide propellant combinations. These studies were primarily concerned with measuring the spontaneous ignition characteristics of vaporized hydrazine, unsymmetrical dimethylhydrazine and Aerozine-50 (A-50) in combination with gaseous nitrogen tetroxide (NTO).[92-97/] They showed that although a spontaneous reaction always results when any of these hydrazine-type fuels contacts NTO, the reaction does not always culminate in an ignition. Furthermore, it was shown[98,89/] that the products of the preignition and ignition reactions differ. Perlee, Imhof and Zabetakis[98/] in 1961 determined the hypergolic ignition characteristics of vaporized hydrazine, unsymmetrical dimethylhydrazine, and Aerozine-50 (A-50) in atmospheres consisting of various nitrogen tetroxide-air mixtures. They also determined the products of the low pressure (2 Torr) nonignition reaction of hydrazine and nitrogen tetroxide. Nitrous oxide, water vapor and nitrogen, were the major gas products with traces of ammonia. They showed that the solid reaction product was not ammonium nitrate as previously supposed, but it was not until 1965 that Weiss' report[97/] identified this solid product as hydrazinium nitrate, a relatively sensitive explosive with a detonation velocity of 19,000 fps and pressure of 10^6 psi.[99/] In a similar study on the unsymmetrical dimethylhydrazine-nitrogen tetroxide reaction, Perlee, et al.[99/] found similar gaseous reaction products and a solid product tentatively identified as the methylated derivative of hydrazinium nitrate.

In 1962, Skinner, Hedley, and Snyder,[100/] studying the reaction between argon-diluted mixtures of hydrazine and nitrogen tetroxide, found that the reaction products were a function of the concentration of the reactants. In particular, for reactant mixtures preheated to 85°C and containing less than 2 mole percent reactant, Skinner and coworkers found ammonium nitrate and nitrous oxide to be the major preignition reaction products. As the reactant concentration in the argon atmosphere increased above 2 mole percent, the preignition reaction product analysis indicated a regular increase in nitrogen and nitric oxide at the expense of nitrous oxide. At 3 mole percent reactant, the major products were nitrogen and nitric oxide, with minor quantities of nitrous oxide and ammonia. At 5 mole percent, ignition occurred. Based on these studies, Skinner, Hedley and Snyder developed a reaction mechanism for the hydrazine-NTO flame reaction. A similar study was conducted by Chuan, Everton, Merrijan, and Wilber,[96] using 0.1, 10, and 1600-liter spherical vessels. These experiments were conducted by continuously and simultaneously vaporizing liquid NTO and A-50 into the evacuated vessels and observing the pressure at which ignition occurred. Their results showed a strong pressure dependence of the ignition phenomena. They also found that in going from a 0.1-liter vessel to a 1600-liter vessel, the ignition pressure decreased by two orders of magnitude.

Burning characteristics of impinging jets of hypergolic liquids have been studied primarily by rocket engine developers. As we have seen in a previous reaction, the impact of two liquid streams produces a complex heterogeneous system. It has never been determined whether in such systems ignition originates in the gas or condensed phase. Most investigations to date have not studied the intimate details of the ignition process. They have been primarily concerned with global phenomena such as the explosive potential of gross hydrazine/NTO spills. Hatz, Chambers, and Suarez-Alfonso[101] in 1961, conducted the first spill experiment at Haystack Butte in using total propellant weights of 5 to 1800 pounds. In these experiments the propellants were simultaneously dumped into a diked area and the resultant blast pressures recorded. With small weights of propellant, they obtained TNT equivalents of less than 1 percent. For large spills having total dump times of less than two seconds, TNT equivalents of less than 1 percent were again observed. In similar experiments conducted with A-50/NTO, the highest TNT equivalents recorded were 0.5 percent. Markels, Friedman, Haggerty, and Dezubay,[102] in 1962, using 1 to 300-gram quantities of propellants and a rupture device to pierce a common wall separating the propellants, recorded TNT equivalents of about 3 percent for the larger quantities. In addition, they observed that occasionally a little water added to the hydrazine appeared to make the explosion more intense. In a later study,[103] the same authors injected liquid NTO into liquid hydrazine, using jet velocities of 38 ft/sec to obtain high-speed photographs (2600 frames/sec) that clearly show the liquid NTO stream penetrating the liquid hydrazine before ignition. Not all of these experiments resulted in an explosion and unfortunately they were not instrumented to record pressure histories, so TNT equivalents were not obtained. As a result of this study, Friedman, et al. proposed the existence of an adduct that forms on propellent contact and would be responsible for the explosive reaction. This is the first mention in the literature of such an intermediate, although other investigators have since arrived at a similar conclusion.

Wasko[104] in 1963, studied the ignition characteristics of the NTO/hydrazine system in an initially low pressure (4×10^{-4} Torr) environment. In these experiments, two glass vials containing various quantities of liquid NTO and hydrazine were broken simultaneously by means of a mechanical cleaver. When the total pressure of the resulting vapors exceeded 4 Torr, ignition occurred; when an ignition did not occur then the final chamber pressure corresponded to the unreacted reactants. This is contrary to what Perlee, et al.[98] found at 2 Torr; since if Perlee, et al. results are correct, hydrazine and NTO react according to the stoichiometry $2\ N_2O_4 + 3\ N_2H_4 \rightarrow H_2O + N_2O + N_2 + 2\ N_2H_5NO_3$ and a gas pressure reduction of 7/3 should have been observed (at these pressures $N_2O_4 \rightarrow 2\ NO_2$). At about this time, Chuan, Everton, Merrigan and Wilber[96] reported the results of a similar series of experiments using a 35 ft^3 bell jar and a 56 ft^3 spherical vessel. This investigation differed from the previous ones in that the nitrogen tetroxide and the hydrazine, unsymmetrical dimethylhydrazine or Aerozine-50 were all admitted to the evacuated vessel as preheated vapors. This study showed that the ignition process is a function of the vessel's surface to volume ratio. Unfortunately, the pressure recording instrumentation had a very poor frequency response and was not capable of detecting any pressure spiking. In the 56 ft^3 sphere, ignitions were observed at 1.6 Torr with ignition delays of about 5 seconds. Such factors as mixture ratio, temperature, rate of pressure rise and small amounts of inert gases had no significant effect on the ignition pressure. Neither did infrared radiation nor a high voltage glow discharge, although a heated wire appeared to induce repeated ignitions, as evidenced by repeated sharp rises in the pressure record. In 1963, the Air Force Rocket Propulsion Laboratory[105] reported experiments to determine the explosivity of LO_2/LH_2, LO_2/RP-1 and NTO/A-50 combinations. These experiments were similar to those conducted by Friedman, et al.[103] except that much larger quantities of hypergolics (200 lbs) were used. In these experiments the two hypergolics were contained in tanks separated by a common wall which was ruptured by an explosive charge or a metal harpoon. The TNT equivalents were of the same order of magnitude as those previously reported by Friedman, et al. As is to be expected, the harpoon rupturing device gave significantly lower TNT equivalents than the explosive charges. All those investigations suffered from a common flaw in that the ratio of contact surface between the two propellants to the liquid volume was relatively small and the reaction rate appeared to be controlled mainly by the mixing process. This was verified by Pesante[106] who measured TNT equivalents for this propellant combination as high as 49 percent, a factor of 50 greater than those previously obtained. In Pesante's experiments, oxidizer-filled glass dewars were placed in a fuel-filled tray and the entire apparatus dropped on a steel plate. The impact shattered the glass dewars exposing the NTO to the surrounding A-50. These results demonstrated quite conclusively that the burning process in the previous investigations was mixing-controlled, although the optimum ratio of contact surface to bulk volume was not obtained. In 1964, Martinkovic published a two-volume report on space vehicle compartment fire hazards associated with hypergolic propellants[107,108] similar to the previous efforts of Wasko[104] and Corbett, et al.[32] Martinkovic studied the effect on the combustion process of the confinement offered by a Plexiglas container and of the ambient pressure. When hydrazine and NTO were emitted into a closed container only fires were observed for pressures corresponding to altitudes below 200,000 feet, whereas the majority of the experiments conducted with A-50/N_2O_4 under the same conditions resulted in violent explosions. Explosions occurred for the hydrazine/NTO combination only when the liquid streams impinged on a radiating source. Above 200,000 feet the hydrazine/NTO combination failed to ignite under any of the conditions examined. For A-50/NTO, the severity of the explosions appeared to increase with altitude becoming most severe at 200,000 feet. The use of a partially open container eliminated the fire and explosion hazard for both propellant combinations below 200,000 feet. Unfortunately, these experiments were instrumented with relatively low frequency pressure transducers and consequently the quantitative value of the pressure records are somewhat limited. In the later study, Martinkovic[108/] extended the A-50/NTO experiments to altitudes up to 325,000 feet. Not only did he observe continued occurrence of explosions but also a continued increase in the intensity with altitude.

In 1964, Corbett, Seamans, Dawson, and Cheetham[109/] investigated the ignition characteristics of unconfined impinging liquid streams of hydrazine-type fuels and nitrogen tetroxide in a 1,000 ft^3 low-pressure chamber. They were primarily interested in the effect of impingement length, impingement angle, manifold geometry, propellant temperature, injection velocity and ambient pressure on the ignition delay. In over 400 experiments, no ignition was observed at environmental pressures below 60 Torr within the normal 250 millisec duration of each experiment. However, in similar experiments conducted with premixed gases, ignition and stable flames were obtained for environmental pressures as low as 3 Torr. They concluded that of all the factors included in the study only the environmental pressure significantly affected the ignition characteristics. All other parameters had little effect on ignition delay although second-order effects were obscured to some degree by the scatter of ignition delays at the lower pressure. The injector designs and modifications examined included several splash plate configurations, concentric tubes, porous plugs, and various spray nozzle injectors; none of these materially improved ignition at low pressures.

Irwin and Waddell,[110/] in 1965, studied the shock sensitivity of A-50/NTO systems by explosively shattering glass containers of A-50 placed in a glass container of nitrogen tetroxide. An additional booster charge consisting of approximately 45 lbs TNT was juxtaposed to the propellant assembly and initiated at various intervals following debouchment. The TNT equivalent of the A-50/NTO combination depended on the time delay between debouchment and the initiation of the booster. A delay of 0.6 millisecond gave the largest TNT equivalent of 45 percent, whereas only a 15 percent value was obtained for an infinite delay (no booster). It is interesting to note that the maximum percent TNT equivalent obtained with a booster (45 percent) is, within experimental error, the same as that obtained by Pesante, et al.[106/] without a booster (49 percent). In 1965, Willoughby, Mansfield, Cordale and Wilton[111/] published a summary of all the work done in the field of propellant explosive evaluation. They concluded that the experiments appear to be mixing-controlled as none of the investigators recorded TNT equivalent near their theoretical value of 125 percent.

The effect of various additives on the ignition process was also investigated. Perlee, Imhof and Zabetakis[112/] studied the effect of water vapor on the hypergolic ignition characteristics of Aerozine-50, hydrazine, and unsymmetrical dimethylhydrazine in an atmosphere of nitrogen tetroxide. Chuan, Everton, Merrigan and Wilber[96/] found that small amounts of nitrogen gas had very little effect on the ignition characteristics of A-50/nitrogen tetroxide systems in the 56 ft^3 sphere. According to Corbett, Seamans, Dawson and Cheetham,[109/] additives such as hydrazine nitrate, ammonium perchlorate, hydrazine diperchlorate and nitric oxide failed to improve the ignition delay of the hydrazine/nitrogen tetroxide and unsymmetrical dimethylhydrazine/nitrogen tetroxide systems in unconfined experiments at low pressure. One of the most extensive studies involving the effects of additives on ignition delay was conducted by Weiss, Johnson, Fisher and Gerstein.[113/] Liquid streams of hydrazine, with one to five percent additive, and nitrogen tetroxide were injected through a swirl-type mixer into a reaction chamber initially at atmospheric pressure. Of the thirty-two additives examined, twenty-one decreased the ignition delay; triethylborane and n-phenyl-2-naphthylamine gave the shortest ignition delay (about one millisecond).

It is only very recently that ignition characteristics of frozen mixtures of hydrazine-type fuels and nitrogen tetroxide have been investigated. In 1963, Rayleigh and Mickola[114/] studied a thin layer (0.1 inch) of solid hydrazine deposited on a thin layer (0.1 inch) of previously deposited frozen nitrogen tetroxide. Although considerable reaction was observed as the combination warmed from liquid nitrogen temperature (-190°C) to room temperature, there was no apparent ignition.

In 1964, DDC released an 817-page document containing translations of 43 recent Russian publications pertaining to the theory of explosives;[115/] Chapters 31 and 34 treat the explosive characteristics of hypergolic mixtures. For the hypergolic combination, tetranitromethane and aniline, which has an ignition delay of tens of seconds, evidence is given to show that ignition first occurs in the gas phase above the mixed liquids and then transits to the liquid. Willoughby, Mansfield, Goodale and Wilton[111/] in 1965 reported experiments in which UDMH and hydrazine were frozen separately in and combined under liquid nitrogen. Ignition with 32 lbs of TNT gave a TNT equivalent of 8.8 percent. Spillage of the mixture outside the tank where they warmed up and ignited hypergolically gave a TNT equivalent of 13.7 percent. In 1965, Weiss[97/] studied frozen combinations of hydrazine and nitrogen tetroxide with a differential thermal analyzer and an infrared (IR) spectrometer. In these experiments, the two propellants were frozen in layers on the glass walls of a differential thermal analyzer at liquid nitrogen temperature and allowed to warm slowly. At liquid nitrogen temperatures, the IR spectrum of this combination consisted of essentially the superposition of the IR spectra for the individual propellants. As the temperature increased above -130°C, the IR spectrum for the individuals started to weaken and another spectrum began to take form. Weiss does not indicate the nature of the material related to this product spectrum. Perlee, Imhof and Zabetakis' study[98] of the low-pressure (2 Torr) reaction between hydrazine and NTO, showed that nitrogen, water and nitrous oxide were the gas products in addition to hydrazine nitrate and trace amounts of ammonia.

IV(b). Flame Propagation

Following ignition in a flammable environment, a flame zone moves into the unburned gas mixture. According to prevalent combustion theory, this flame can exist in one of two stable configurations - deflagration or detonation. Which configuration the flame assumes depends on the initial state of the combustible mixture and the ignition process. It is believed that a gaseous detonation normally starts as a deflagration and transits to a detonation after traveling a finite distance (induction, or run-up distance). The length of this path can be modified by changing the state of the combustible gas mixture (for example, raising its temperature) or the energy density of the ignition source. Flames normally exhibit an intrinsic instability[89] which, coupled with the gas and structural dynamics of the confining vessel, exaggerates the instability phenomena resulting in gross gas motion. Under these conditions, flames either extinguish themselves or transit to a detonation, neither of which is usually desirable in rocket engines.

It is processes such as these that, directly or indirectly, currently occupy the majority of researchers in the combustion field. However, in view of the enormous effort of the past forty years one cannot hope to adequately survey this field in a monograph such as this. Consequently, it becomes necessary to confine attention to reports of immediate interest. Moreover, as the references mentioned at the beginning of this section contain excellent discussions of all aspects of combustion research prior to 1958, no attempt has been made to include these studies here. Of the publications since 1958 concerned with the more general aspects of combustion phenomena, only a few are mentioned specifically; more detailed listing is given in the accompanying bibliography.

Although it is generally believed that Hirschfelder and Curtiss'[116] mathematical model of the steady state deflagration accurately describes real flames, this theory has not yet been adequately confirmed experimentally. Furthermore, as this model does not include temporal elements it cannot describe transit phenomena. Instead of solving the exact time-dependent differential equations of flame dynamics it becomes necessary to resort to quasi-steady descriptions. Essentially this amounts to imbedding the Hirschfelder-Curtiss flame model in a fluid dynamic description of the environment. This is probably applicable as long as the wave length of the acoustic perturbation is considerably greater than the thickness of the combustion zone; obviously not the case for shock-flame interactions. If it becomes necessary to include time-dependent expressions in the mathematical model to account for the interactions of the acoustic and transport phenomena, the mathematics become so complicated that a reasonably detailed quantitative study of such models becomes impractical.[89] Various ramiforms of such models will be discussed further in Section V. Because of the complexity of the exact mathematical descriptions of time-dependent flame mechanisms, most investigations of interest to this program have been experimental.

Like deflagrations, detonations have occupied the scientific community for nearly a century. A number of more recent detonation studies were presented at the Eighth, Ninth and Tenth Symposiums on Combustion. There seems to be general agreement among researchers that deflagration transits to detonation in gases through the interaction of acoustic phenomena and physicochemical flame processes. The exact nature of this transition is not yet entirely clear although there are two general theories. According to the first theory, pressure waves are generated by the change in the rate of heat release by the flame front determined by changes in the surface area of this front. These pressure waves culminate in a shock wave which eventually merges with the flame front to form a detonation. The second theory maintains that the shock wave so generated heats the unburned gas mixture behind it to the point of spontaneous ignition and that the resulting flame front coalesces with the shock to form the detonation. Oppenheim[117] contends that although the preignition condition definitely "stimulates" the development of the detonation, it is not sufficient for the establishment of a detonation. An excellent summary of gaseous detonation research up to 1960 is given in reference (118). Wave diagram analysis has been particularly useful in characterizing the processes in such systems.[119-122]

A number of investigators have been concerned with flame acceleration in heterogeneous systems, primarily sprays. One of the first studies on heterogeneous detonation was made by Loison in 1952.[123] He demonstrated that a detonation can propagate in an air-filled pipe whose walls were previously wetted with an oil film. Williams[124-125] in studies on the combustion characteristics of sprays concluded that two-phase detonations are impossible because of the extended reaction zone formed by leisurely droplet evaporation. However, he tempered his conclusions with two observations: First, that drops below 10 microns could produce gas phase detonation, and second, that drop shattering might circumvent the slow evaporation process and thus support detonation. Webber[126] and Cramer[127] observed detonation-like flame zones in a shock-driven combustion tube. In 1961, the American Rocket Society published a volume[128] containing 16 articles dealing with this subject. In 1965, Komov and Troskin[129] reported the results of their studies on detonation of sprays in pipes, but seemed unaware of previous work in the United States. In 1965 Nicholls, Dabora and Ragland,[36] using shock initiation of diethyl-cyclohexane (DECH) sprays in an oxygen atmosphere, found pressure ratios as high as 30:1 across the combustion zone. They also found that the detonation reaction was relatively insensitive to the quantity of fuel used. Like Loison, they observed that when the tube wall was coated with liquid DECH a detonation-like combustion zone could still be obtained with shock initiation in the absence of any spray.

The first work with the hydrazine-type fuels was done to measure their explosivity, limits of flammability, and spontaneous ignition temperatures in air. In 1949, Scott, Burns and Lewis[91/] confirmed that the upper limit of flammability of hydrazine corresponds to 100 percent and measured the lower limit of hydrazine vapors in various gases at approximately 100°C and atmospheric pressure. They showed that pure hydrazine vapors do not propagate a flame below 12 Torr pressure. They also determined the minimum spontaneous ignition temperature of hydrazine in air, oxygen and nitrogen in contact with materials such as glass, platinum, ferric oxide (rust), black iron and stainless steel. In 1960, Herickes, Damon and Zabetakis[90/] determined the flammability characteristics of unsymmetrical dimethylhydrazine (UDMH), temperature limits of flammability of UDMH in air at one atmosphere pressure; limits of flammability of the UDMH-air mixture at selected elevated temperatures and pressures; spontaneous ignition temperatures of UDMH in air at 0 and 200 psig pressure; and shock sensitivity of UDMH and hydrazine containing various amounts of metal catalysts at 25° and 50°C. This study was extended in 1964 by Furno, Martindill and Zabetakis[130/] when they determined the minimum concentrations of benzene, toluene, m-xylene, cumene and n-heptane required to inhibit flame propagation through vapor mixtures of hydrazine and hydrocarbon at 125°C and atmospheric pressure. They found a correlation between the effective inhibitor concentration and the heat of formation or heat capacity of the hydrocarbon.

Numerous investigators have investigated the decomposition flame of hydrazine.[131-140/] McHale, Knox and Palmer[141/] and Michel and Wagner studied the chemical kinetics of the decomposition of hydrazine. Eberstein and Glassman[143/] used an adiabatic flow reactor to study the kinetics of decomposition of hydrazine, UDMH and MMH. Most of these investigations support the postulate that the rate of propagation of the burning process is primarily controlled by a second-order reaction.

In 1965, Heinrich[144/] studied the detonability of hydrazine vapors at various pressures. Using a 2 cm diameter, one meter long tube, he found that the hydrazine vapors could not readily be detonated by a hot-wire ignition source in this short tube but that a detonating mixture of acetylene and oxygen regularly initiated detonation. Heinrich measured detonation velocities ranging from 6000 ft/sec at initial hydrazine pressures of 16 Torr to 7080 ft/sec at 760 Torr.

In 1957 and 1958, there appeared a number of articles pertaining to the combustion characteristics of monopropellant sprays.[145-147/] Since that time only a limited number of related studies have been published. Tarifa and Notario are among those that have pursued this problem in some depth.[148-151/] In their latest report[151/] they develop the mathematical expressions for monopropellant combustion, including the chemical kinetics. Their theoretical and experimental results indicate that for a given environment state there should exist a minimum drop diameter below which the drop will not support combustion. At about this same time, Dykema and Greene[152/] reported a similar study using hydrazine and UDMH drops.

Only two articles were found pertaining to the combustion of hydrazine in nitrogen tetroxide. In one, Breen and Beltran[153/] showed that a drop of hydrazine or monomethyl hydrazine burning in a nitrogen tetroxide atmosphere supports a double flame configuration, the inner flame corresponding to decomposition of the hydrazine or monomethyl vapor and the outer flame to the oxidation reaction. Similarly, a drop of nitrogen tetroxide suspended in an atmosphere containing hydrazine vapor supports a double flame zone, the inner one corresponding to the endothermic nitrogen tetroxide dissociation flame reaction and the outer to the subsequent reduction reaction. In the other, Sawyer and Glassman[154/] report the results of a chemical kinetic study of the reaction between hydrazine and nitrogen tetroxide. By diluting the constituents with an inert gas, they slowed down the reaction rate sufficiently to follow the process in the adiabatic flow reactor, previously developed and used on similar systems.

V. Gas Dynamics and Transport

Hypergolic rocket engines exhibit three successive stages in their operation: (1) The preignition or pressurization period during which the propellants injected into the combustion chamber are dispersed, vaporized and accelerated through the chamber; (2) the unilateral combustion stage during which a flame front starting at the ignition site initially traverses the combustible mixture; and (3) the steady-state combustion process. Only the first two stages are of concern to the spiking problem, although most of the work reported in the literature concerns the third stage. References to this last stage are given in the bibliography, but are not discussed in this report.

Due to the large number of simultaneous processes occurring in rocket engine combustion chambers, a complete mathematical description of such a chamber has not yet been formulated. However, a number of liquid bipropellant rocket combustor models have been developed that have proven to be of considerable value in understanding the quantitative features of the engine's various processes. As these models are based on plausible conjecture, they do not account for processes which the author is unfamiliar. Furthermore, interaction of the included processes usually consists only of first-order effects and, in addition, generally represent an extreme oversimplification of the realistic situation. Consequently, until a more accurate description of such systems becomes available, one can never be sure that an observed anomaly is not the result of the loose mathematical description.

One of the first theoretical studies of the preignition and ignition periods of rocket engine thrust was published by Agosta and Krause.[155/] They developed a model for the bipropellant hypergolic engine using the A-50/NTO propellant combination. This model takes into account drop evaporation, drop freezing, vapor condensation on the walls, vapor flow through the nozzle and vapor-drop thermal exchange. Although the authors considered a chemical kinetic description of the preignition combustion process, they did not couple this to the pressurization process. They superimposed the vaporization pressure history and the pressure dependent ignition delay curves and defined their intersection as the point of engine ignition. Corbett, Dawson, Seamans, and Vanpee[28] applied a modified Agosta and Kraus model to their engine, using carbon tetrachloride as the candidate fluid because its physicochemical characteristics are well known. They found that a 50 percent change in the accommocation coefficient (from 1.0 to 0.5) lowered the pressure history curve by only 10 percent. When they included thermal exchange between the chamber walls and the vaporizing drops, they obtained theoretical chamber pressure histories that agreed with corresponding experimental results.

Although the number of theoretical studies concerned with hypergolic rocket preignition phenomena is rather meager, experimental investigations are considerably more numerous. Unfortunately, there is little mention of any anomalous ignition behavior, probably because low frequency response pressure transducers were used in the combustion chambers.

Rollbuhler and Tomazie[156] in 1959, reported a study of the sea level performance of 300-lb thrust hydrazine/nitrogen tetroxide engines using various types of injectors, propellant flow rates and initial propellant temperatures. Elverum and Staudhammer[157] made a similar study, employing a concentric tube injector in an effort to improve engine efficiency. Wanhainen, DeWitt, and Ross[158] also studied these engines, concentrating on performance at reduced chamber pressure (10 psia). They found that combustion instability increased as they lowered the propellant flow rates, for both four- and six-element triplet injectors. Wasserbauer and Tabate[159] in 1961, and Chilenski and Lee[160] in 1962, also studied the effect of various injector and propellant parameters on the performance of these rocket engines. None of these investigators reported any pressure spiking during the start sequence. The first indication of such spiking apparently came in 1963 from researchers at the Marquardt Corporation, developers of the Appolo 100-lb thrust RCS engine. It was during engine qualifying tests under simulated high altitude conditions that the first engine spike was experienced. Following this, a number of rocket engine developers conducted similar spike research programs. However, the major work in this area has been conducted at Marquardt Corporation[160,161] and the Manned Spacecraft Center. Minton and Zwich[162] presented Marquardt's first report of their studies at the Aviation Space Conference of the American Society of Mechanical Engineers in March 1965. It was these investigators that first showed that the pressure spike so often observed in their 100-lb thrust RCS engines under vacuum starts was in fact a series of pressure spikes, each about 50 microseconds wide. This, in conjunction with the pressure spike magnitudes (as large as 4000 psi) first suggested the possibility of a detonation-like phenomena. After hundreds of vacuum starts, they found that the ignition delay time was essentially independent of the fuel-oxidant lead relationship. With the exception of runs having long (17-20 milliseconds) lead arrangements, the ignition delay was rather consistently about four milliseconds. Minton and Zwick report that they have, on occasion, photographed a slow flame front transiting to a detonation-like front.

Kappl and Knox[163] developed a simple gas flow pressurization model for their engine, which included the heterogeneity and chemical reactivity of the system, and had an ignition criterion based on the Semenov thermal ignition mechanism. They find that two factors affect the pressurization rate of the thrust chamber, namely, the initial propellant temperature and the chamber wall temperature. This is in agreement with the model developed by Corbett, Dawson, Seamans and Vanpee.[28]

The effects of various additives on the ignition characteristics of these engines has also been studied at Marquardt Corporation by Lawver,[161] Callery Chemical Company selected nineteen candidate inhibitors which they combined with Aerozine-50 to make 1 percent inhibitor solutions. Lawver conducted vacuum start experiments with these mixtures in RCS engines and found "no detectable differences in the level of the ignition pressure for any of the fuels".

In addition to the work done at the Marquardt Corporation, the Manned Spacecraft Center in Houston, Texas has probably conducted the next largest experimental study specifically concerned with the vacuum starts of these engines. They have not only examined and extensively tested all the injectors currently available, but in addition a few of their own innovations. Although this evaluation program is continuing, they have not yet found an injector that does not exhibit spiking. Although the frequency of spiking appeared to vary between injectors, in no case was it sufficiently different to consider any one injector superior to the others. MSC is expending considerable effort both in house and on contract to determine the cause and a cure for vacuum start pressure spiking.

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