Concentrated Hydrogen Peroxide as a Propellant

NOAH S. DAVIS, JR., AND JOHN H. KEEFE

Becco Chemical Division, Food Machinery and Chemical Corp., Station B, Buffalo 7, N. Y.

Hydrogen peroxide (90%) has been used as a source of auxiliary power for helicopters, for propelling models, for steam turbines, for submarine propulsion, and in rocket-assisted take-off units. The chief advantages of using hydrogen peroxide for such systems are simplicity and reliability. In handling H_2O_2 solutions it is important to exclude dirt and to have an adequate water supply to dilute spills. Liquid 90% H_2O_2 and H_2O_2 vapors in equilibrium with the liquid under normal storage temperatures are not explosive. Vapors above 26 mole % H_2O_2 are explosive, but these are formed only under special conditions not encountered in use.

HYDROGEN peroxide has one of the longest histories of the liquid propellants. Before World War II considerable development work had been done on hydrogen peroxide in Germany. By 1938, the Germans were producing concentrated hydrogen peroxide which they used in a variety of weapons during the war, including the first operational piloted rocket airplane ever flown, the Messerschmidt Me 163. Similarly, they used hydrogen peroxide as the oxidant in the Walter 25-knot submarine, and we can be very thankful that this boat never became operational. An interesting review of some of the German experience was presented by Walter (*5*) in 1953. Following the war, production of concentrated hydrogen peroxide in Germany was banned as one of the provisions of the Allied Control Commission to regulate the military potential of defeated Germany. However, a great deal of this work has been carried on and expanded in England and in the United States.

Hydrogen peroxide aqueous solutions of 65 to 100 weight % H_2O_2 are of interest in propulsion applications. Most of the applications in this country use 90% H_2O_2. Recently 100% H_2O_2 has become commercially available. A summary of the more important physical properties of 90% H_2O_2 is presented in Table I. Hydrogen peroxide has a high density, high boiling point, and low viscosity—all desirable attributes for liquid propellants. The relatively high freezing point is a disadvantage in some cold weather applications. However, this is not so serious as might first appear: hydrogen peroxide solutions, being two-component systems of hydrogen peroxide and water, have no true freezing point, but rather a freezing point range as shown in Figure 1. In 90% hydrogen peroxide, under carefully controlled conditions the first minute crystals appear when the temperature reaches 12° F. As the temperature is decreased, additional crystals, higher in H_2O_2 concentration than the mother liquid, appear, and the liquid composition decreases along the liquidus line. At −20° F. the system is still quite mobile and, in fact, does not become a snowlike solid until the eutectic temperature of −65° F. is reached. On freezing, hydrogen peroxide solutions contract and do not burst storage containers the way water does. Actually, it is quite difficult to obtain crystallization at the expected temperature. Hydrogen peroxide solutions almost always supercool 20° to 40° F. below their true freezing points and, in some instances, have remained for hours at temperatures 70° to 80° F. below the freezing point with no sign of crystallization. This ability to supercool is probably associated with the extreme purity of concentrated hydrogen peroxide.

The addition of ammonium nitrate to 90% hydrogen peroxide lowers the freezing point without significantly reducing the performance of the solution as an oxidant. A solution of 55 weight % H_2O_2, 39% ammonium nitrate, and 6% water has a freezing point of −40° F.

Hydrogen peroxide solutions are strong oxidizing agents. They will react on contact with certain propellant fuels such as hydrazine. They can rust iron and steel. In some cases, hydrogen peroxide also acts as a reducing agent but only toward those materials that are themselves strong oxidizing agents. For example, in acid solutions hydrogen peroxide reduces potassium permanganate to manganese sulfate.

For the purpose of interstate commerce, the Interstate Commerce Commission classifies hydrogen peroxide solutions above 52 weight % as "Corrosive Materials." Actually, hydrogen peroxide is an extremely weak acid. The apparent pH readings, as determined by means of a glass electrode, are given in Table II. These values are the neutral points for hydrogen peroxide solutions and can be varied by the addition of alkali or acid. The solutions are adjusted by the manufacturer to near or slightly below the neutral point and are neutral or only slightly acid.

Hydrogen peroxide is a high energy material and requires intelligent care in handling. However, given this care, hydrogen peroxide can be used in safety. Most operators prefer to handle hydrogen peroxide rather than other rocket oxidants. Some prefer to use hydrogen peroxide to aviation gasoline because of the absence of danger from a possible spark.

What are the possible dangers from concentrated hydrogen

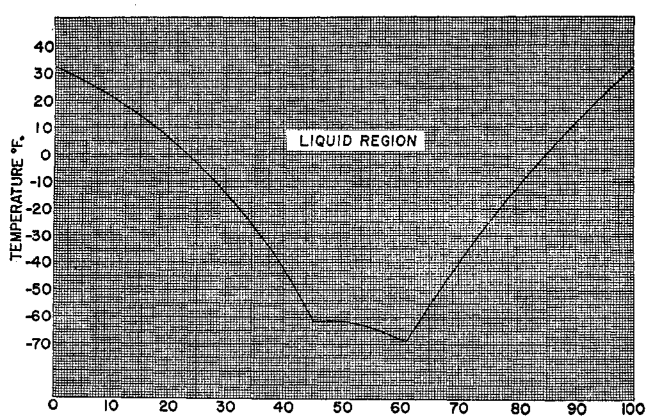


Figure 1. Freezing points of aqueous H_2O_2 solutions

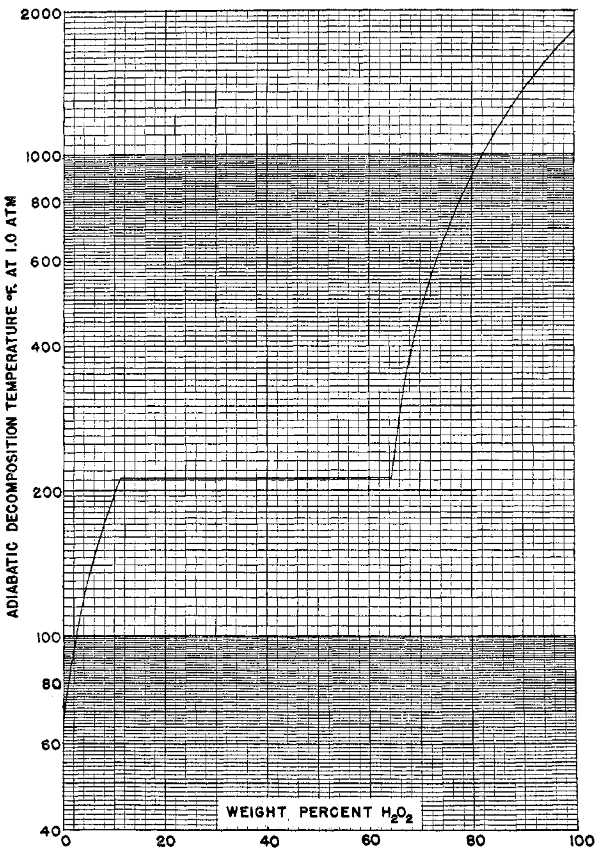


Figure 2. Adiabatic decomposition temperature for aqueous H_2O_2 solutions at 1-atm. pressure

peroxide and how can they be combatted? First, there is the danger of fire if the hydrogen peroxide is spilled on clothing or on combustible material. However, neither dynel nor Dacron fabrics will be ignited. Therefore, the operators should use this type of clothing and protective goggles or a face shield, rubber gloves, and boots. Several types of impervious compatible clothing are available and can be worn for emergency use. Such clothing is relatively hot and uncomfortable. Its use for normal handling is not required. The "buddy" system is advocated so that there is always a man standing by to aid the operator in case of an accident. It should be remembered that water will not only put out any fire if one has started, but also will dilute the hydrogen peroxide so that fire cannot result from a spill on combustible material. Therefore, it is desirable to have a large supply of water available in case of an accidental spill. Storing hydrogen peroxide containers on a stone or concrete floor and in a noncombustible type of shed is recommended.

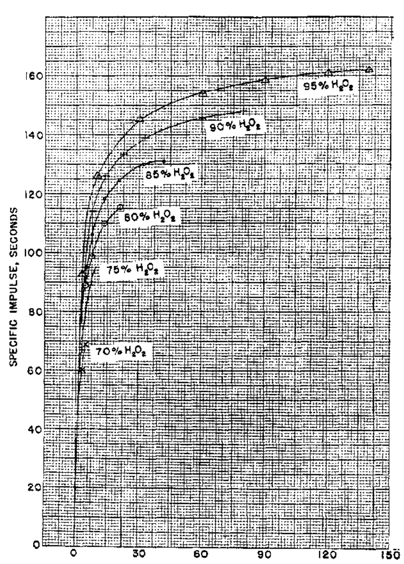
Secondly, there is the danger of skin burns. If hydrogen peroxide contacts the skin, it should be flushed away with water. Very shortly, or in a few minutes after contact, the skin will turn white. This is due to a slight diffusion of hydrogen peroxide into the skin and the formation of tiny gas bubbles. The white spot on the skin will disappear in a few hours and will not leave any permanent injury or scar. In a few cases where hydrogen peroxide was in continuous contact with tender places on the skin, such as behind the knee or under a fingernail, a minor burn has resulted, but this has cleared up in a couple of days. Such a burn is aseptic. Hydrogen peroxide is not like an acid that is corrosive to the skin, causing a painful and long-lasting injury.

Thirdly, there is the danger from excessive decomposition due to contamination. If proper materials are used and if they are cleaned properly, the hydrogen peroxide is compatible with them and can be stored for years. In drums, the average decrease in concentration is 1 to 2% per year, while in larger containers it is even less. If hydrogen peroxide becomes contaminated, the decomposition rate will increase resulting in an increase in the oxygen gas evolution rate and heat release. The increase in gas evolution rate can be used to operate warning devices so that the drum or tank can be flooded with water and the hydrogen peroxide discarded. A whistle is now available which can be put on drums or other storage containers and, if the rate of gas evolution is more than the very slight amount expected from ordinary decomposition, the whistle will blow and a red signal will appear. If electricity is available, it can be

Table I. Physical Properties of 90% H_2O_2

Density, 68° F.	
Grams/cc.	1.39
Lb./gal.	11.62
Viscosity, 64.4° F., cp.	1.30
Vapor pressure, 86° F., mm. Hg	5
Heat of formation, kcal./g.-mole	
Liquid	45.16
Vapor (100% H_2O_2)	33.29
Freezing point, ° F.[a]	12
Normal boiling point, ° F.	284
Heat of vaporization, B.t.u./lb.	590
Heat capacity (0–18.5° C.), Cal./g.-° C.	0.58
Surface tension, 64.4° F., dynes/cm.	75.53
Dielectric constant, 68° F.	77
Conductivity, 77° F., ohm/cm.	
Pure	2×10^{-6}
Commercial	10×10^{-6}
Refractive index, 68° F.	1.398
Nonvolatile residue, p.p.m.	
Commercial, specified	50
Actual	20

[a] When frozen solid, contracts by 11% of liquid volume.



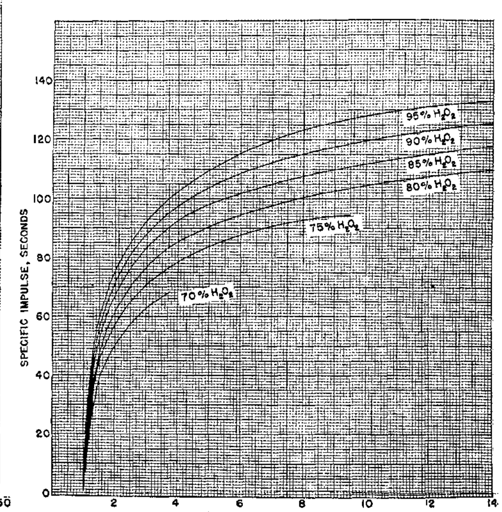
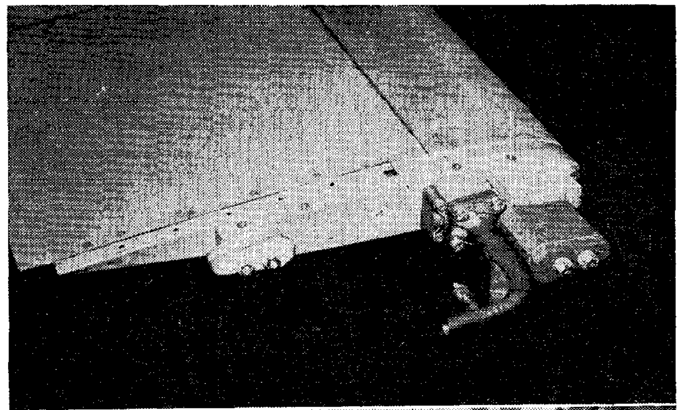
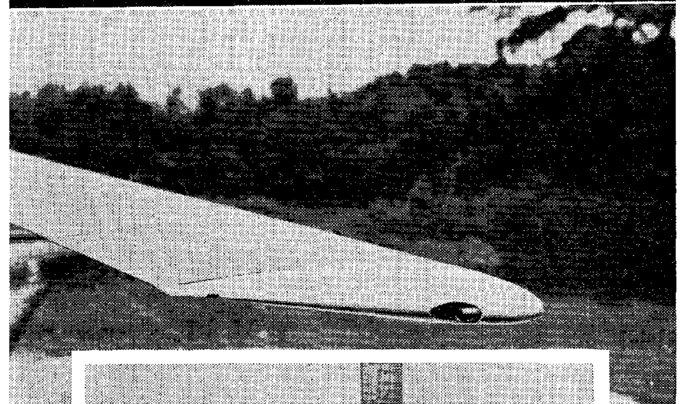


Figure 3 (Left). Specific impulse *vs.* expansion ratio for 70 to 90% H_2O_2 considering expansion to saturation point

Figure 4 (Right). Specific impulse *vs.* expansion ratio for 70 to 95% H_2O_2

Figure 6. Engine installed on rotor blade tip ▶





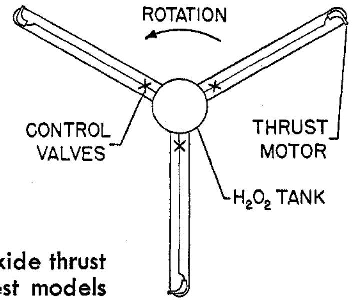
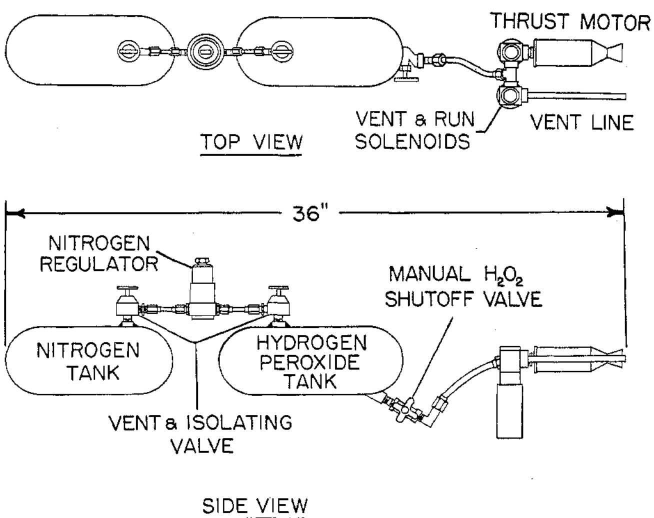


Figure 5. Hydrogen peroxide thrust engines on helicopter rotor ▶

Figure 7. Hydrogen peroxide thrust system for propulsion of test models ▼



connected to give an alarm in a guardhouse. This gas evolution alarm is more sensitive than the temperature rise alarms which have been used for years.

Concentrated hydrogen peroxide solutions have been tested by many laboratories for sensitivity to detonation and have appeared markedly insensitive for high energy materials. Only under conditions of substantial confinement and powerful initiation will partial explosion of 90% hydrogen peroxide occur. However, if hydrogen peroxide is mixed with a soluble organic in certain proportions, an explosion can occur just as with mixtures of gasoline and air, but there is no reason for making this type of mixture unintentionally. Vapors containing more than 26 mole % of hydrogen peroxide are explosive. However, vapors of this concentration are formed above 90% hydrogen peroxide only when the liquid is heated above 230° F. There is only a slight possibility that anyone using hydrogen peroxide will produce this high a concentration of the vapor. There is, therefore, no practical danger except to manufacturers who must know how to avoid it. The temperature at which hydrogen peroxide solutions are in equilibrium with explosive vapors are reported by Satterfield and coworkers (*2*). Additional information may be found in ACS Monograph No. 128 (*3*).

Materials and equipment for handling hydrogen peroxide have been previously described (*1*). A wide variety of commercial items is available for pumping, storing, and handling hydrogen peroxide. The solution is customarily shipped in special aluminum drums of 300-pound capacity or in railway tank cars of 4000, 6000, or 8000 gallons. Three types of special vehicles have been developed for the field transfer of hydrogen peroxide.

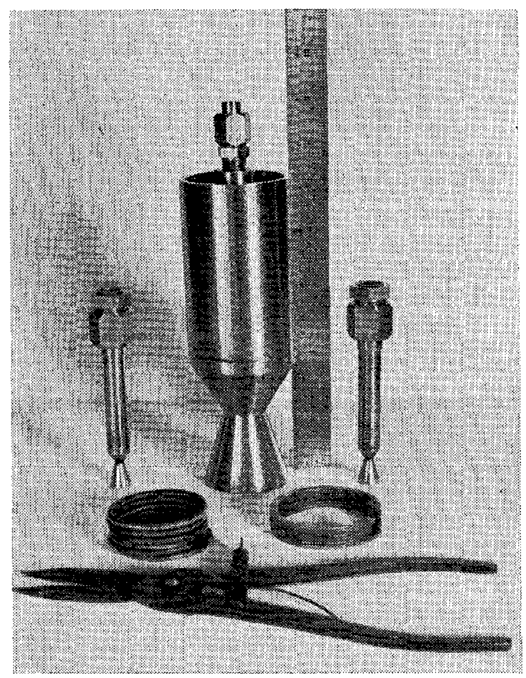


Figure 8. Hydrogen peroxide thrust motors for propulsion of free-flight models in NACA wind tunnel

Table II. Neutral Points for H_2O_2 Solutions

H_2O_2 Concn., Wt. %	Apparent pH (Glass Electrode)
50	2.4
60	2.3
70	1.7
80	1.0
90	0.1

Table III. Calculated Bipropellant Performance Characteristics (*4*)

Propellants	Ratio Oxidizer/ Fuel	Chamber Pressure, Lb./Sq. Inch	Specific Impulse[a], Sec.	Specific Gravity	Specific Impulse[b] × Specific Gravity	Chamber Temp., ° F.	Gas Exhaust Velocity, Ft./Sec.
			H_2O_2 Fuel Systems				
Hydrogen peroxide							
–hydrazine	1.45	300	247	1.23	303	4450	7950
–ANF-58 fuel	5.75	300	233	1.28	298	4680	7510
–ethyl alcohol (92.5)	3.4	300	229	1.22	279	4440	7380
–nitromethane	0.67	300	227	1.27	288	4890	7310
Hydrogen peroxide (87%)							
–nitromethane	1.0	300	229	1.28	293	4610	7380
Hydrogen peroxide (87%)	5.7	300	199.1	1.243	248	3520	6420
–methanol	3.7	300	225	1.19	268	4130	7250
			Other Oxidizer Fuel Systems				
Liquid oxygen	0.50	300	259	1.05	272	4500	8350
–hydrazine	0.832	300	274	1.12	307	...	...
Liquid oxygen							
–ethyl alcohol	1.5	300	243	0.966	235	5250	7810
–nitromethane	0.08	300	225.5	1.139	256	4700	7260
Nitric acid							
–hydrazine	1.6	300	243	1.28	311	...	7810

[a] Specific impulse is a measure of the effectiveness of a propellant system; it is pounds of force developed at flow rate of 1 pound of propellant per second; specific impulse was calculated on a frozen equilibrium basis.

[b] Specific impulse times specific gravity gives a comparison of effectiveness of propellant systems on basis of propellant volume.

These provide mobile, self-contained units for servicing hydrogen peroxide–powered aircraft and missiles. Field storage installations are quite varied. Some consist of large permanent aluminum storage tanks, pumps, and piping. In other instances, the shipping drums are simply stored on the ground and, in hot weather, shaded by a tarpaulin. In any case, it is wise to keep the storage area free of combustible materials.

One of the chief advantages of hydrogen peroxide as a propellant is the ease with which it can be catalytically decomposed into oxygen and steam. The amount of heat released and, therefore, the temperature of the resulting decomposition gases is a function of the hydrogen peroxide concentration, as shown in Figure 2. This is very important in some monopropellant applications such as powering steam turbopumps. In these cases the steam temperature can be adjusted to a low temperature consistent with the design of the turbine and then reproducibly controlled by controlling the hydrogen peroxide concentration.

The energy available in expanding the hot decomposition products through a reaction nozzle is shown in Figures 3 and 4.

Hydrogen peroxide can be used either as a monopropellant or as an oxidizer in bipropellant applications. An interesting application as a monopropellant to provide auxiliary power for helicopters has been recently developed. This work was done by Reaction Motors under sponsorship of the Bureau of Aeronautics of the Navy Department. Hydrogen peroxide is carried in a tank on the rotor shaft and fed by centrifugal force to a small catalyst chamber mounted on the tip of each rotor (Figures 5 and 6). There it is decomposed, and the exhaust jet is used to provide additional driving power for the rotor. This system was applied to a Sikorsky helicopter used by the Marine Corps. The entire weight of the filled hydrogen peroxide systems is about 350 pounds, including about 280 pounds of 90% H_2O_2. With this auxiliary power, the pay load, the rate of ascent, and the hovering ceiling of the helicopter are greatly increased, and the permissible area for landing, in case of failure of the main power plant, is increased at least fourfold.

Another application of hydrogen peroxide as a monopropellant is shown in Figure 7. This system was developed for an aircraft manufacturer for propulsion of test models. It consists of a hydrogen peroxide tank pressurized by nitrogen from a second tank, remotely controlled flow and dump valves, and a catalytic thrust chamber. The total weight of the filled system is 20 pounds including $7^1/_2$ pounds of 90% H_2O_2. It will deliver 60 pounds of thrust for 15 seconds. The system can be adjusted to deliver any thrust value between 20 and 60 pounds by presetting the nitrogen regulator and thereby controlling the flow of hydrogen peroxide to the catalyst chamber.

A third example of the use of hydrogen peroxide as a monopropellant is its use for propulsion of free-flight models in the NACA 16-foot wind tunnel at Langley Field, Va. Figure 8 shows the catalytic thrust chambers fabricated for this application. The small units deliver 3-pound thrust and the large unit, 60-pound thrust.

The performance characteristics for various hydrogen peroxide–fuel bipropellant systems is shown in Table III and compared with those for a few other oxidant fuel combinations. These values were taken in part from data presented by Sutton (*4*).

An example of the use of hydrogen peroxide as an oxidant in a combustion system is in the hydrogen peroxide submarine. Two of these, the *Excalibur* and the *Explorer*, have recently been launched in England. These represent an advance over the Walter cycle submarines developed by Germany during World War II. In England the De Havilland Co. has developed the improved *Sprite* which is an assisted take-off unit using concentrated hydrogen peroxide and kerosene. In these systems, the hydrogen peroxide is first decomposed in a catalyst chamber, and the hot decomposition gases are fed to the combustion chamber where they ignite the fuel component. Such a system has the important advantage of being inherently safer than a system relying on external power or on a third fluid for ignition. Even if the fuel is accidentally cut off, flame-out will not occur if the hydrogen peroxide continues to flow. Nearly 50% of the total thrust will be maintained. On resumption of fuel flow, ignition is automatically re-established.

There are other power applications for concentrated hydrogen peroxide such as a heat generator for maintaining equipment at a controlled temperature, an oxygen source for internal combustion engines, and a component in liquid explosives.

The field for such applications is increasing and will undoubtedly increase more rapidly as the cost of hydrogen peroxide is decreased. In 1945 the price of Becco 90% hydrogen peroxide was 95 cents per pound. Today, it is 54.4 cents per pound in tank-car lots. Further decreases can be foreseen as the uses expand.

In general, the availability, safety, and wealth of amassed design data on H_2O_2 applications make hydrogen peroxide a preferred propellant for use where a concentrated form of heat and oxygen are required. The chief advantages of using hydrogen peroxide for such systems are simplicity and reliability.

Literature Cited

(1) Davis, N. S., Jr., and Keefe, J. H., *J. Am. Rocket Soc.* **22**, 3–69 (March–April 1952).

(2) Satterfield, C. N., Kavanaugh, G. M., Resnick, H., Ind. Eng. Chem. **43**, 2507 (1951).

(3) Schumb, W. C., Satterfield, C. N., Wentworth, R. L., "Hydrogen Peroxide," ACS Monograph No. 128, Reinhold, New York, 1955.

(4) Sutton, G. P., "Rocket Propulsion Elements," Wiley, New York, 1949.

(5) Walter, H., *Jet Propulsion* **24**, 166–71 (May–June 1954).

Received for review September 23, 1955. Accepted February 28, 1956.