Using these values of p_2/p_1 and $\gamma_1 M_1^2$, the following values of the remaining detonation parameters may be read from Figure 1:

$$\gamma_2 = 1.11 \qquad \frac{T_2 M_{w_1}}{T_1 M_{w_2}} = 26.7$$

$$\rho_2/\rho_1 = 1.88 \qquad \beta = 231$$

In more general applications, the generalized chart can be used to illustrate clearly how all of the detonation parameters vary with initial composition, pressure, and temperature. That is, if data such as $\gamma_1 M_1^2$ and p_2/p_1 are available for a given detonable gaseous mixture at several initial conditions, these data may be plotted directly on the generalized chart. This plot will provide a convenient means of visualizing the change of all detonation parameters under varying initial conditions. The plot may also be used to facilitate accurate interpolation of detonation data, so that values of the detonation parameters may be conveniently obtained for initial conditions where data are not available.

Other practical applications for the generalized chart will become apparent with its use. For example, if the detonation limits for a class of detonable gaseous mixtures can be represented by a single curve on the generalized chart, such information will be extremely valuable in many applications.

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The writers are grateful for the encouragement and guidance given by D. G. Samaras and also wish to express their appreciation to Amy Clemmer, who performed the calculations and prepared the graph.

NOMENCLATURE

a = velocity of sound, cm. per second
B = energy release function, dimensionless
c_v = specific heat at constant volume, cal. per gram, °K.
D = detonation velocity—velocity of detonation wave with respect to initial mixture, cm. per second
e = specific internal energy, cal. per gram
h = energy release per unit mass of mixture, cal. per gram
J = mechanical equivalent of heat, dyne-cm./cal. or ergs per cal.
M_1 = detonative Mach number—Mach number of detonation wave with respect to initial mixture, dimensionless
$\gamma_1 M_1^2$ = Mach number function, dimensionless
M_w = molecular weight, grams per gram-mole
p = pressure, atmospheres
R = universal gas constant, cal./gram-mole, °K.
T = absolute temperature, °K.
β = modified energy release function, dimensionless
γ = specific heat ratio, dimensionless
ρ = density, grams per cc.

Subscripts

1 = initial mixture at initial conditions
2 = final mixture immediately behind detonation wave at final conditions

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Explosive Systems Containing Liquid Oxygen

Liquid Oxygen–Liquid Methane Mixtures

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Although the explosive properties of combustible gas-oxygen mixtures have been investigated extensively, little or no work has been done on the explosive properties of the same mixtures in the liquid phase. Liquid systems having densities more than 1000 times as great as the corresponding gas mixture have faster reaction rates. Knowledge of the detonation properties of a mixture in both gas and liquid systems should provide data for testing and extending the classical theory of detonation. Data are being obtained on nine systems (*5,6*).

1. Methane (l)—oxygen (l)
2. Carbon monoxide (l)—oxygen (l)
3. Cyanogen (s)—oxygen (l)
4. Carbon subnitride, C_4N_2 (s)—oxygen (l)
5. Ammonia (s)—oxygen (l)
6. Hydrogen (l)—oxygen (s)
7. Carbon (s)—oxygen (l)
8. Aluminum (s)—oxygen (l)
9. Ozone (l and s)

This article deals with the first system—mixtures of liquid oxygen with liquid methane.

MISCIBILITY OF LIQUID METHANE AND LIQUID OXYGEN

Liquid methane was found to form clear homogeneous solutions with liquid oxygen at 90° K. (-183° C.) over the whole composition range from 0 to 100% oxygen. The solutions are colorless on the methane-rich side and gradually approach the color of liquid oxygen on the oxygen-rich side. Cooling to 77° K., however, caused solid methane to separate in mixtures containing over 50 weight % methane. (Matheson C.P. methane was used in these experiments.) Fastovskiĭ and Krestinskiĭ (*4*) investigated the solubility of solid methane in liquid oxygen between 69° K. (-204° C.) and 74° K. (-199° C.). They found that at 74° K. the weight % of methane in liquid oxygen was 49.35.

EXPLOSIVE RANGE AND EXPLOSIVE FORCE OF LIQUID OXYGEN-LIQUID METHANE SYSTEM

The explosive limits and brisance characteristics of the liquid methane-liquid oxygen system were determined at 90° K. for mixtures containing 6 to 80 mole % or 3 to 67 weight % liquid methane. The equipment, shown in Figure 1 consisted of a steel plate 10 X 10 X 3/16 inch thick, placed on a steel base, which was a steel pipe (4 inches in inside diameter, 4 inches high) welded to a 12 X 18 X 1½-inch thick steel plate. The cartridge, an iron can (2 inches in outside diameter, 2¼, 3¾ inches high, 0.01-inch wall thickness) filled with 100 grams of the mixture, was placed on the steel plate centered over the 4-inch pipe. A new steel plate was used for each test.

The methane used for these experiments had a composition of 96.7% methane and 3.3% ethane, and was obtained from the Matheson Co., Rutherford, N. J.

The liquid oxygen-liquid methane mixtures were prepared in the following manner: The gaseous methane, purified by passing through a trap containing silica gel at dry ice temperatures was condensed in a Pyrex brand glass trap at liquid nitrogen temperatures. The methane was then warmed to liquid oxygen temperature and mixed in a precooled Dewar flask with a given volume of liquid oxygen. The mixing accuracy was to ±2%. The required amount of the prepared mixture (measured by volume) was poured into a precooled iron can which was then placed on a steel plate for explosion. All these operations were performed by remote control.

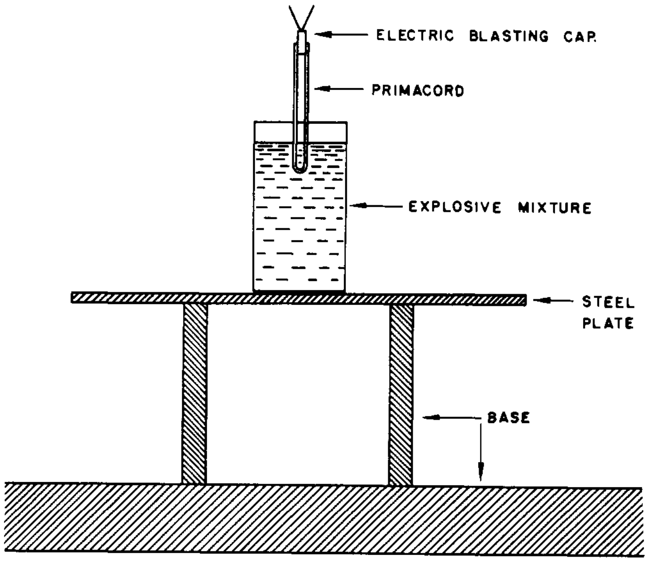

Figure 1. Brisance setup

The cartridges were initiated by means of Primacord (containing PETN, pentaerythritol tetranitrate). A 10 to 12-inch length of Primacord was folded in half and the folded end inserted into the cartridge. A No. 6 electric blasting cap was fastened to the two ends of the Primacord outside of the charge and set off electrically.

When the charge is detonated on the steel plate, a hole may be punctured in the steel plate, or the steel plate may be ruptured, bent downward, or only dented, depending on the brisance value of the explosive.

This method is a comparative one, and the results obtained are normally compared with those of TNT.

The results of these tests are presented in Table I. The lower limit of the liquid methane-liquid oxygen mixtures lies between 3 and 6 weight % (6 and 11 mole %) methane while the upper limit lies between 50 and 67 weight % (67 and 80 mole %) methane. As indicated by Table II, these explosive limits differ from the flammability limits of the gaseous mixtures.

The results also show that the most brisant mixture is the stoichiometric one [33 mole % $CH_4(l)$ + 67 mole % $O_2(l)$]. The steel test plate for this mixture is shown in Figure 2, together with the one for equimoles of liquid methane and liquid oxygen.

DETONATION VELOCITIES OF LIQUID OXYGEN-LIQUID METHANE MIXTURES

The rates of detonations of various liquid oxygen-liquid methane mixtures were determined by the rotating mirror technique. A given volume of liquid methane at 90° K. was added to a precooled steel-lined strip Dewar. The required amount of liquid oxygen was then added and the mixture stirred with a precooled stirrer by remote control. The accuracy of the mixtures was to ±2%. The total volume of mixture used was ≃300 cc. The steel liner was 25 cm. high and 46 mm. in outside

Table I. Explosive Range of Liquid CH_4–Liquid O_2 Mixtures and Effect of Varying CH_4:O_2 Ratio on Brisance

(Wt. of charge, 100 grams. Thickness of steel plate, 3/16 inch)

	Composition		Molecular CH_4:O_2 Ratio	Density of Cartridge, G./Cc.	Results
	Wt. %	Mole %			
CH_4	3	6	1:16	1.08	No detonation
O_2	97	94			
CH_4	6	11	1:8	1.05	Steel plate dented: punctured 85% of circular area of hole 10.5 cm. diam.
O_2	94	89			
CH_4	11	20	1:4	0.98	Punctured hole 10.5-cm. diam. Trace of fragment marks on plate
O_2	89	80			
CH_4	20	33	1:2 (stoichiometric)	0.88	Punctured hole 10.5-cm. diam. Fine fragment marks on plate
O_2	80	67			
CH_4	33	50	1:1	0.76	Punctured hole 10.5-cm. diam. Large fragment marks on plate. Steel plate dented
O_2	67	50			
CH_4	40	57	1:0.75	0.71	Punctured hole 10.5-cm. diam. Trace of fragment marks on steel plate
O_2	60	43			
CH_4	50	67	1:0.5	0.65	Punctured 85% of circular area of hole 10.5-cm. diam. Trace of fragment marks on plate
O_2	50	33			
CH_4	67	80	1:0.25	0.57	No detonation
O_2	33	20			
TNT				0.89	Steel plate dented and started to rupture. Dented area diam., 11-cm.; height, 2-cm.

Table II. Explosive Limits of Methane-Oxygen Mixtures

	Methane Content	
	Lower	Upper
Flammability limits of gaseous mixtures	5.4 (*9*)	59.2 (*10*)
Explosive limits of liquified mixtures	6–11	67–80

diameter, and had a wall thickness of 3 mm. It contained a row of 3-mm. holes 15 mm. apart facing the unsilvered strip of the Dewar. The Dewar was 25 cm. high and had an inside diameter of 48 mm. The blasting cap and initiator, containing a charge of plane wave booster, tetryl, and RDX (hexahydro-1,3,5-trinitro-s-triazine) composition B, respectively, with composition B being nearest the liquid mixture, were set off ½ to ¾-inch above the liquid mixture as shown in Figure 3.

Four mixtures were tested, the methane–oxygen molar ratios of these mixtures being 1:4, 1:2, 1:1.5, and 1:1. The detonation rates obtained experimentally for these mixtures are compared with the theoretically calculated values in Table III. The calculations were made using the methods described by Taylor (*11*). Cook's covolume values (*2*) and the thermodynamic data of National Bureau of Standards (*8*) were also used in these calculations.

The rotating-mirror picture of a representative liquid methane–liquid oxygen detonation is shown in Figure 4. The vertical light at the right is due to the reflection of the initiator's flash through the transparent charge. The light at the upper and left portions of the picture is due to the detonation of the initiator. The dotted, parallel diagonal straight lines in the center of the photograph show the detonation wave of the liquid methane–liquid oxygen detonation. The straight line indicates that the detonation was steady.

The experimental and calculated detonation velocities and the detonation limits of the liquid mixtures are compared graphically with the gaseous detonation velocities (*3,6*) and the gaseous flammability limits (*9,10*) in Figure 5.

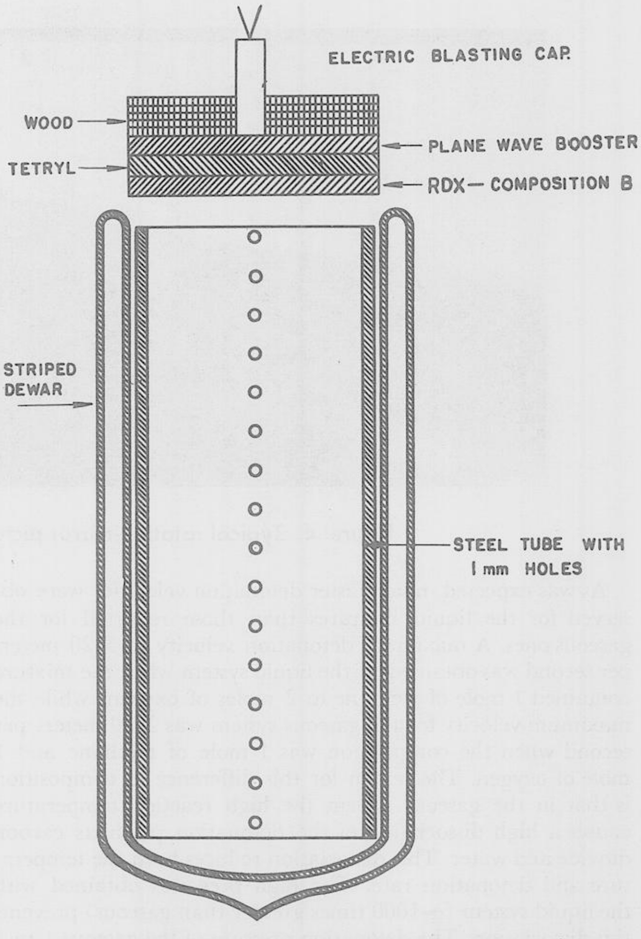

Figure 3. Explosive cell for measuring detonation velocities by rotating mirror

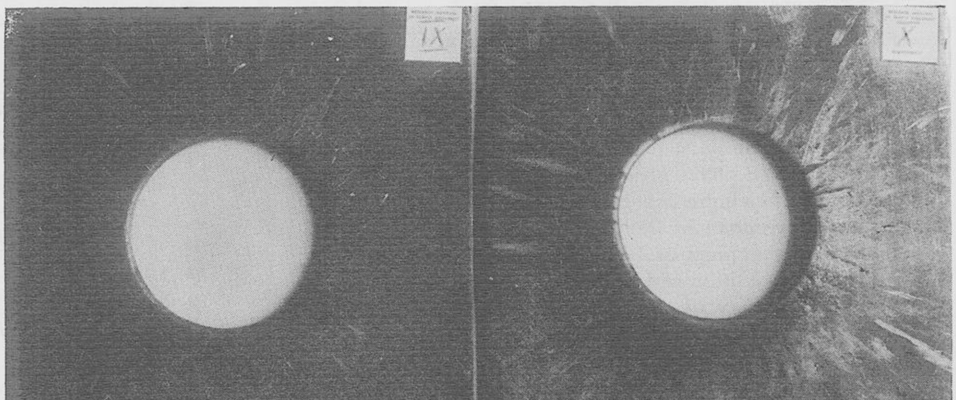

Figure 2. Steel test plates after detonation of 100-gram charges

IX. $CH_4 + 2O_2$

X. $CH_4 + O_2$

Table III. Comparison of Experimental and Theoretical Detonation Rates of Liquid Oxygen–Liquid Methane Mixtures

No.	Mixture	Density, G./Cc. (90° K.)	Detonation Velocity, M./Sec.		Calcd. Detonation Temp., °K.	Calcd. Detonation Pressure, Atm.
			Exptl.	Theor.		
1	$CH_4(l) + 4O_2(l)$	0.980	3325	4400	4150	8.1×10^4
2	$CH_4(l) + 2O_2(l)$	0.879	5110 5130	6010	5830	6.8×10^4
3	$CH_4(l) + 1.5O_2(l)$	0.830	5110	5840	4670	5.0×10^4
4	$CH_4(l) + O_2(l)$	0.765	4620 4610	5250	3040	2.9×10^4

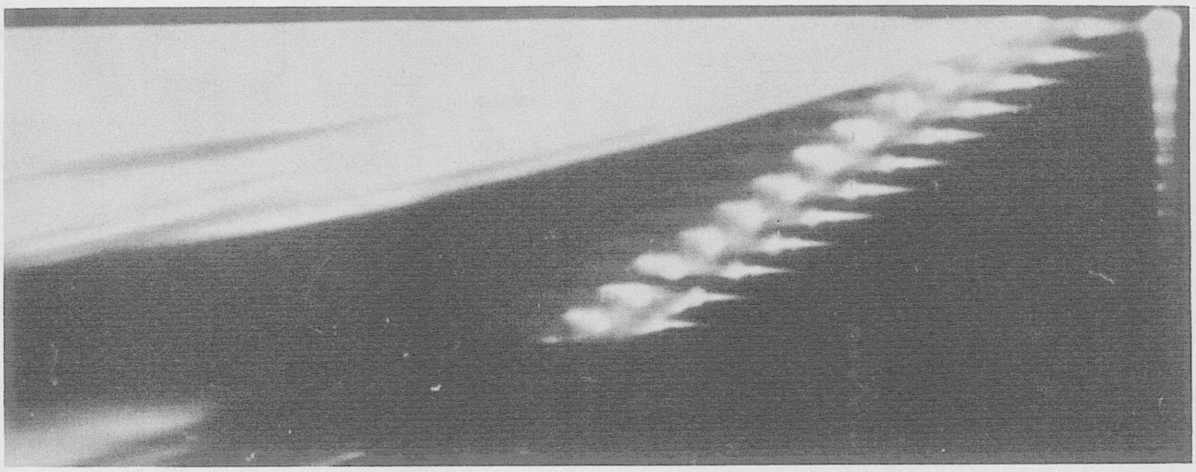

Figure 4. Typical rotating-mirror picture of liquid methane-liquid oxygen detonation

As was expected, much faster detonation velocities were observed for the liquid mixtures than those reported for the gaseous ones. A maximum detonation velocity of 5120 meters per second was obtained for the liquid system when the mixture contained 1 mole of methane to 2 moles of oxygen; while the maximum velocity for the gaseous system was 2530 meters per second when the composition was 1 mole of methane and 1 mole of oxygen. The reason for this difference in composition is that in the gaseous system the high reaction temperature causes a high dissociation of the detonation products carbon dioxide and water. This dissociation reduces both the temperature and detonation rate. The high pressures obtained with the liquid system ($\simeq$1000 times greater than gaseous) prevents this dissociation. The detonation pressure of the gaseous 1 to 1 molar mixture is 34 atm. (*1*), as compared to 29×10^3 atm. calculated for the liquid mixture with the same composition.

A large difference was observed between the calculated and experimental values, the experimental values always being lower. The two sets of values, however, fall on similar curves. These differences cannot be explained by the impurity of the methane, the presence of nitrogen in the oxygen, or the error in preparing the mixtures.

Purity of Methane. The methane contained 3.3 weight % ethane, which would tend to lower the rates. This difference, however, would be almost negligible.

Presence of Nitrogen in Oxygen. In some experiments the oxygen contained as much as 2 weight % nitrogen. Calculations showed that the addition of 4.8 weight % liquid nitrogen to a stoichiometric mixture of liquid methane and liquid oxygen ($CH_4 + 2O_2$), would lower the theoretical detonation rate by 2.7% or from 6010 to 5850 meters per second. The effect of 2 weight % nitrogen should therefore be very small.

Accuracy of Mixture Composition. The accuracy of the mixtures prepared was to $\pm 2\%$. The error caused by this deviation would be very small; in fact, at stoichiometric it would be insignificant. The only remaining explanation would be that some of the values used in the calculations, particularly the covolume values derived from conventional explosives, are not known with the accuracy required. Additional measurements with the simplest possible systems—i.e., $CO(l) + O_2(l)$—and pure ozone as well as their theoretical study, are being investigated in order to find the cause of the above discrepancy.

SENSITIVITY TESTS

The sensitivity to impact, flame, shock wave, and spark was determined only for the liquid methane–liquid oxygen mixture which had the fastest rate of detonation (33 mole % methane and 67 mole % oxygen). The impact was obtained by firing a 22-caliber, short copper bullet through a can (2 inches in diameter and 4 inches high) containing the explosive liquid mixtures, the nozzle of the gun being 40 feet from the mixtures. The sensitivity to flame was measured by a technique similar to that used in the brisance experiments except for one change—namely, the charge was set off by means of an ignited safety fuse instead of Primacord. The fuse was placed so that when its fartherest end was lit, the flame shooting out of the opposite end was 5 inches above the mixture.

The shock wave experiments were carried out with the explosive mixture in a Dewar flask (2¾ inches in inside diameter, and 4 inches high) which was buried in the ground. Tetryl pellets, 2 inches in diameter and 1 inch high, were placed and detonated 24 inches above the explosive mixture. In testing the sensitivity to sparks, a 1500-volt discharge from a 0.1-μ.f. condenser was passed through the liquid mixture, using 1 to 3-mm. gaps. The energy discharged was 113 millijoules.

Explosions were obtained in all these tests. Although they are far from complete, they show that the liquid $CH_4 + 2O_2$ mixture is very sensitive and can be easily detonated. Additional sensitivity tests to show the lower limit of stimulus needed

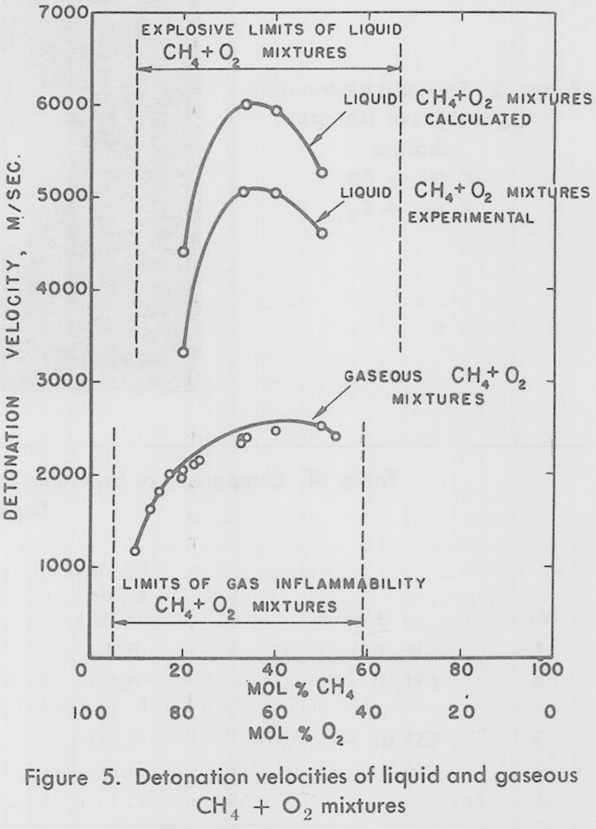

Figure 5. Detonation velocities of liquid and gaseous $CH_4 + O_2$ mixtures

for ignition would be of interest, but authors are not in a position to make them at this time.

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Ignition Limits of Hydrogen Peroxide Vapor at Pressures above Atmospheric

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Explosive characteristics of hydrogen peroxide vapor at atmospheric and subatmospheric pressures, including values for the ignition limit over this pressure range and the effect of the nature of diluent gases and method of initiation on the limit have been reported (*1, 2*). In the present study, ignition limits were determined over the pressure range of 14.7 to 95 p.s.i.a. The term "ignition limit" as used here is defined as the minimum concentration of hydrogen peroxide in a vapor mixture, under specified conditions, below which powerful external ignition cannot initiate a self-propagating reaction.

Experimental

The experimental method involved the batch distillation without rectification of a hydrogen peroxide solution and passage of the slightly superheated vapor through a borosilicate glass ignition bulb. Because water has a much higher relative volatility than hydrogen peroxide, the fraction of hydrogen peroxide present in the vapor stream increases with time, and by repeated attempts to initiate ignition in the bulb at regular time intervals, coupled with analyses of the condensed vapor, it is possible to establish closely the minimum peroxide concentration at which an explosion can be caused to occur. By placing the whole apparatus inside a pressure vessel, it was possible to establish the effect of pressure on the limit.

The apparatus used is depicted schematically in Figure 1. For a run, 125 ml. of approximately 40 mole % hydrogen peroxide solution in water was placed in the borosilicate glass boiler (200-ml. bulb capacity), and the whole system was pressurized to the desired operating pressure with nitrogen. The pressure was measured with a Bourdon-type gage calibrated by means of a dead weight gage tester. Heat for the boiler was supplied through a Glass-col heating mantle.

The vapor mixture evolved on boiling was superheated about 5° to 20° C. to prevent possible condensation and was led to a borosilicate glass ignition bulb. Boiling points for various liquid compositions were estimated by extrapolation of data on total

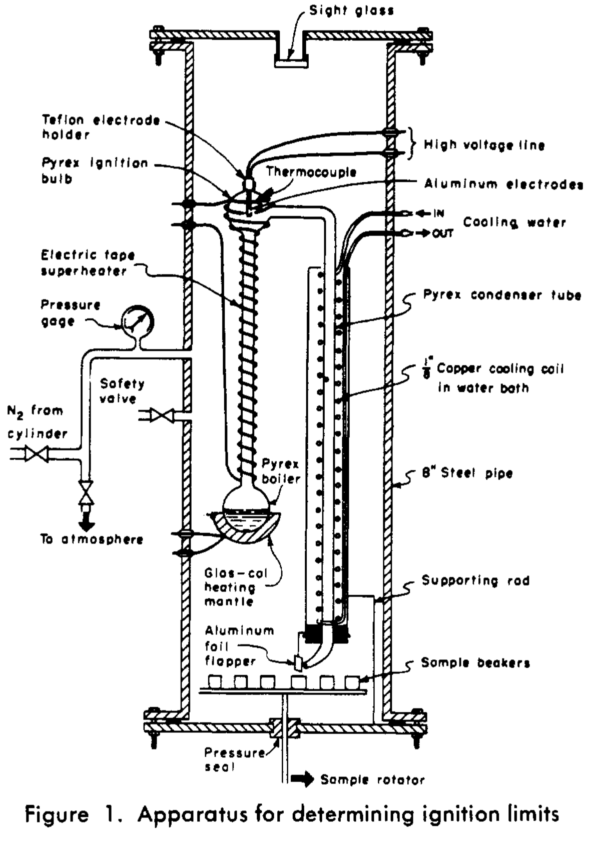

Figure 1. Apparatus for determining ignition limits

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