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NITRIC OXIDE FORMATION IN SPARK-IGNITION ENGINES

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ABSTRACT

The automobile is the largest single source of nitric oxide—one of the major air pollutants which react in the atmosphere to form photochemical smog. Yet, the process by which nitric oxide is formed within the engine cylinder is not well understood. This paper describes the essential features of this formation process, develops a model for predicting nitric oxide concentrations and compares results calculated using the model with measurements of nitric oxide concentrations in a single cylinder CFR engine.

Nitric oxide formation is a nonequilibrium process; to follow this formation process, therefore, a thermodynamic model of the combustion process and a chemical rate equation for nitric oxide are required. We have developed a model for the combustion process which calculates the mass fraction burned and the temperatures of the burnt and unburnt gases as functions of time from a measured pressure-time curve and engine parameters. A rate equation has also been derived from the set of

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reactions thought to be important in nitric oxide production at temperatures and pressures typical of spark-ignition engines. By integrating the rate equation through the pressure-time and temperature-time sequence obtained from the combustion model, nitric oxide concentrations as a function of time in the burnt gases inside the cylinder have been computed.

These calculated concentrations have been compared with nitric oxide concentration measurements made on a CFR engine. Spectroscopic measurements of continuum radiation from the post-flame gases show that the nitric oxide concentration within the cylinder follows closely the predicted concentration-time behaviour. Nitric oxide forms slowly in the gases behind the flame front and may not reach the local equilibrium concentration depending on the temperature-time history and the portion of the charge observed. The concentration then freezes as the gas cools during the expansion stroke. The quantitative agreement between theory and experiment is good. By integrating the frozen nitric oxide concentration in each portion of the burnt gas over the whole charge, the exhaust concentration can be predicted. These computed exhaust concentrations are then compared with concentrations measured in engine exhausts.

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## 1. INTRODUCTION

Air pollution is now recognized as a major problem in the industrialized urban areas throughout the world. Most of this pollution has its origin in the combustion process, and the automobile is a prime offender—for example, the spark-ignition engine is the source of 60 percent of the pollutants emitted in the United States.

In 1952, the pioneer work of Haagen-Smit [1] showed how Los Angeles smog was formed from two pollutants--unburned hydrocarbons and nitric oxide--which originate primarily from the automobile. This smog, formed as a result of photochemical reactions in the atmosphere, is now found in many other cities around the world. It is characterized by reduced visibility, eye irritation, and shortness of breath, and high oxidant concentrations which result in extensive plant and material damage.

Since the spark-ignition engine is responsible for about half the hydrocarbon and nitric oxide emissions which enter the atmosphere, the processes by which these pollutants are formed within the engine are obviously an important subject for research.

The hydrocarbon emissions been significantly reduced. Sources outside the engine are evaporation from the gas tank and carburetor, and controls intended to eliminate these losses are now being introduced. Sources inside the cylinder are the quench zones on the cylinder walls and the crankcase blowby gases. The latter are now recycled to the intake manifold, and the former have been reduced by careful design of the cylinder head. The behaviour of the quench layers on the cylinder walls during the expansion and exhaust strokes is still a subject for conjecture, however, and our group at M.I.T. is carrying out research to obtain a better understanding of the processes involved. [2]

Nitric oxide, in contrast, is formed in the bulk of the burnt gases. Early experiments (e.g., Wimmer and McReynolds, [3] Hazen and Holiday, [4] Huls and Nickol [5]) investigated the relation between exhaust concentrations and engine-operating parameters, and from such studies a qualitative understanding of the process has been built up. For example, modifications in engine-operating conditions which increase the peak cycle temperature, or the oxygen concentration in the burnt gases, increase the nitric oxide concentration in the exhaust.

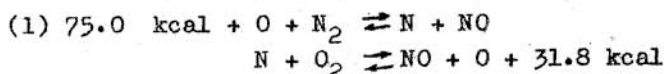
The exhaust concentration of nitric oxide, however, is determined by rate-limited processes occurring within the engine cylinder. A comparison of equilibrium nitric oxide concentrations with measured exhaust concentrations illustrates this point. Typical peak conditions within the engine are  $T = 2800$  °K at  $p = 30$  atm. For these conditions equilibrium nitric oxide concentrations vary between  $1.2 \times 10^4$  ppm for an equivalence ratio of 0.9 to  $2.6 \times 10^3$  ppm for an equivalence ratio of 1.2. Actual engine exhaust concentrations for these equivalence ratios are about 4000 ppm and 1200 ppm, respectively. We will show that this discrepancy arises first because nitric oxide formation may be too slow to reach equilibrium concentrations at peak conditions and second because during the expansion stroke, as the temperature falls, nitric oxide concentrations freeze. To date, no nitric oxide emissions controls are in service.

Our research over the last two years has been directed at understanding the rate-limiting processes which determine the nitric oxide concentration within the engine cylinder and exhaust. An important part of this work has been the development of models for predicting these concentrations. In this paper, we will describe the essential features of the model we have developed and compare it with some experimental results.

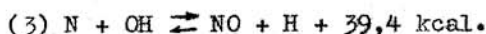
There are two parts to this model. Firstly, we need to know the chemical reactions, and their reaction rates, which are important in the nitric oxide formation process. Secondly, we must know the temperature and pressure of the combustion gases as a function of time. We can then integrate the rate equation for nitric oxide, obtained from the important reactions, through the sequence of thermodynamic states which the burnt gases follow.

## 2. KINETIC CONSIDERATIONS

Several kinetic schemes have been proposed for the formation or decomposition of nitric oxide (e.g., by Newhall and Starkman, [6] Newhall, [7] Eyzat and Guibet, [8] Lavoie, Heywood and Keck [9] . The appropriate basis for these schemes is the Zeldovich chain mechanism:



which is known to be the rate-controlling process at high temperatures (above about 2200 °K) under excess air conditions. For fuel-rich conditions additional reactions may be important, and we have added the reaction



Further reactions become important below 2200 °K, but these have little effect on nitric oxide concentrations in the temperature-pressure-residence time regime typical of spark-ignition engines.

Since at high pressures, the hydrocarbon oxidation reactions go rapidly to completion, we assume equilibrium concentrations for  $[\text{O}]$ ,  $[\text{O}_2]$ ,  $[\text{OH}]$ ,  $[\text{H}]$ , and  $[\text{N}_2]$ ; we also make the steady-state approximation for  $[\text{N}]$ . A rate equation for  $[\text{NO}]$  can then be derived [9]

$$\frac{1}{V} \frac{d[\text{NO}]}{dt} = \frac{2(1-\alpha^2)R_1}{1+\alpha K} \quad (1)$$

where  $V$  is the volume of a gas element of fixed mass,  $\alpha = [\text{NO}] / [\text{NO}]_e$ ,  $[ ]$  denoting concentration in  $\text{mol cm}^{-3}$  and subscript  $e$  equilibrium concentration;  $R_1 = k_1 [\text{O}]_e [\text{N}_2]_e$  with  $k_1$  the forward reaction rate of reaction (1);  $K = R_1 / (R_2 + R_3)$  with  $R_2$  and  $R_3$  defined similarly to  $R_1$ , but for reactions 2 and 3.  $K$  varies with fuel/air ratio and is of order 0.2.

$R_1$  and  $K$  are functions of temperature, pressure, and fuel/air ratio; thus to proceed further we need a model which predicts gas properties

during the combustion process.

#### 4. THERMODYNAMIC CONSIDERATIONS

We have developed a model for the combustion process inside the engine cylinder which predicts the temperature and density of the burnt and unburnt gases and the mass fraction burned as a function of time. The input for this calculation is a measured pressure-time curve and the engine-operating parameters. The derivation of the model has been described in detail elsewhere ; [9] here we will report only on the essential features.

The significant advance over earlier models (e.g., that of Eyzat and Guibet [8] ) is that we take account of the temperature gradient in the burnt gases which results from the different state-time histories of fuel-air elements which burn at different times. Temperature differences of about 200 °K across the charge have been measured, [10] the first parts of the charge to burn being the hottest.

The importance of this temperature gradient has been underlined by the gas sampling experiments of Alperstein and Bradow [11] and Starkman et al [12] which showed that significant gradients in nitric oxide concentration exist in the burnt gases.

We assume the following : (1) The unburnt mixture is compressed isentropically and can be treated as a perfect gas. (2) The volume of the reaction zone is negligible. (3) Each element of the mixture, after isenthalpic combustion at say time  $t_b$ , is then compressed and expanded isentropically for  $t > t_b$ . (4) Equilibrium thermodynamic properties and composition can be used for the burnt gases.

We therefore assume that mixing and heat transfer between gas elements which burn at different times are negligible. It is important to realize that this assumption need only be valid during the early part of the expansion stroke. We will show that at about 60° ATC, the

temperature has fallen sufficiently to effectively freeze all the nitric oxide decomposing reactions. Thus subsequent mixing of the gases during the major part of the expansion and all the exhaust strokes do not affect the nitric oxide concentration in the exhaust.

The four assumptions listed above enable us to calculate the temperature-time and pressure-time histories of gas elements which burn at specified times. Thus, with equation (1), we can obtain the nitric oxide concentration as a function of time in each gas element. To obtain the exhaust concentration, however, we must then integrate over the charge, and for this we need the mass fraction burned as a function of time.

An analysis based on perfect gas laws and constant specific heats for both burnt and unburnt gases [9] yields an analytic expression for the mass fraction burned ( $x$ ) as a function of cylinder pressure and volume, work done by the gas, initial energy of the charge, specific heat ratios of the gases, equivalence ratio, and the calorific value of the fuel. Typical curves for  $p$  and  $x$  as a function of time are shown in Figure 1. The maximum mass fraction burned is slightly less than unity because the cylinder head was designed for ease of optical measurements and not high combustion efficiency.

#### 4. THEORETICAL AND EXPERIMENTAL RESULTS

Figure 2 shows predicted and measured temperatures for a single cylinder Cooperative Fuel Research (CFR) engine. The calculated temperatures were obtained with the equilibrium thermodynamic model described in the previous section, and they show clearly the expected temperature gradient in the burnt gases in the limit of no mixing and heat transfer. Each line corresponds to a specific gas element. Experimental measurements using spectroscopic techniques gave temperatures comparable to these calculated values and confirmed the existence of a temperature gradient. [13]

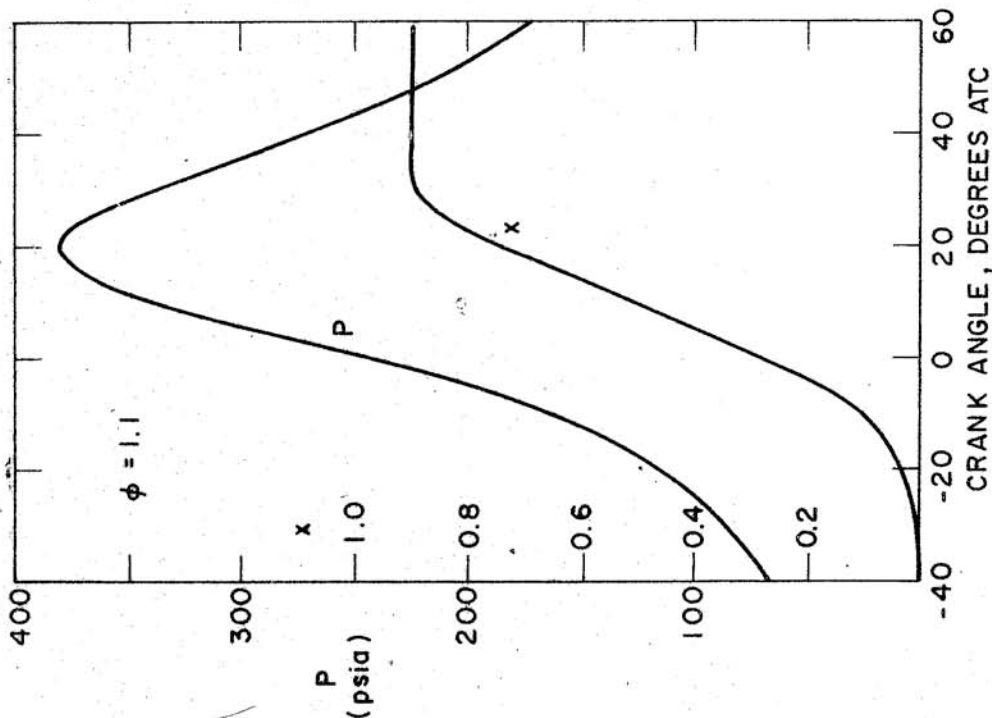


Fig. 1 - Measured pressure  $p$ , and calculated mass fraction burned  $x$ , as functions of time. Engine conditions: Equivalence ratio  $\phi = 1.1$ , 1200 rpm, compression ratio 4.9, spark advance  $40^\circ$ .

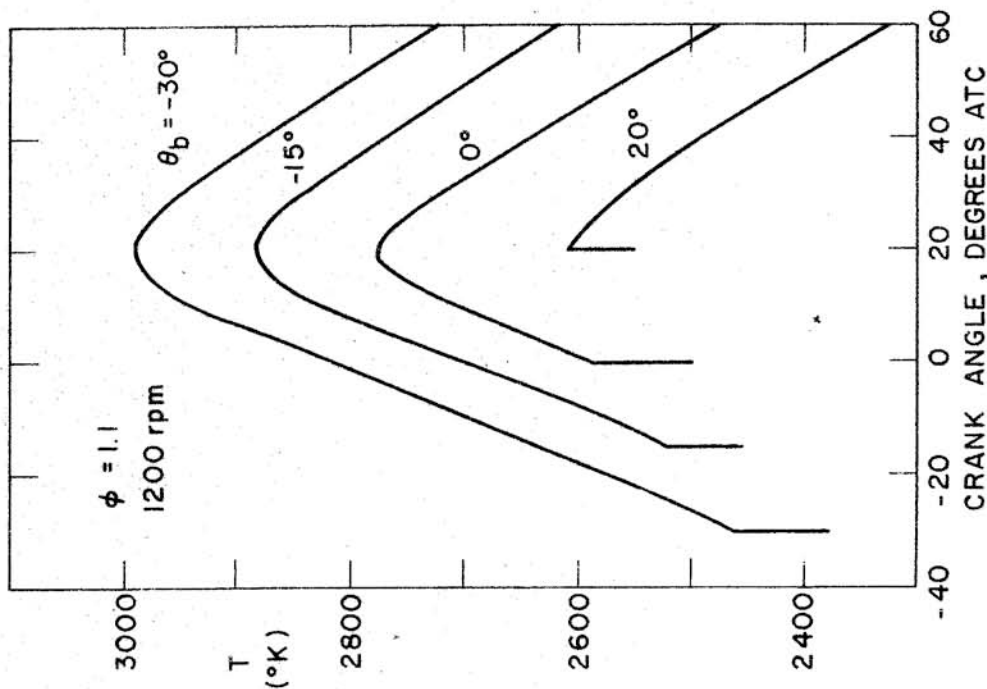


Fig. 2 - Calculated temperature distribution in the burnt gases as a function of time.  $\theta_b$  is crank angle at which element shown burnt. Engine conditions same as for Fig. 1.



Figure 3 compares our rate-limited calculations of nitric oxide concentrations with equilibrium concentrations as a function of time, for gas elements which burn at  $-30^{\circ}$  and  $10^{\circ}$ . Note that the formation process is predicted to be rate-limited, and whether the nitric oxide concentration reaches approximate equilibrium at the peak conditions will depend on the temperature-time history. The model predicts freezing of nitric oxide concentrations early in the expansion stroke; it also predicts a substantial gradient in nitric oxide concentration across the burnt gas.

Figure 4 compares the rate-limited solutions with data taken by Lavoie [13]. Nitric oxide concentrations were obtained by monitoring the radiation from the CO-O and NO-O recombination continua through quartz windows in the engine cylinder head. The arrows show the arrival times of the flame front at two different windows. The data confirm the existence of a gradient in nitric oxide concentration across the burnt gases and are in reasonable agreement with the theory. Note that there is gas movement beneath the windows as the pressure rises, and the burnt gas is compressed. Thus for increasing time, up to peak pressure, the data points represent gas elements which burned at successively later times.

To obtain the exhaust concentration, we integrate the final frozen nitric oxide concentration in each element over the whole charge. The integral required is

$$\{NO\} = \int_0^1 \{NO\}_f dx$$

where  $\{ \}$  denotes mass fraction, and  $\{NO\}_f$  is the frozen nitric oxide mass fraction of the element which burned when the mass fraction burned was  $x$ .

Plots of  $\{NO\}$  against  $x$  are shown in Figure 5 for three equivalence ratios 0.9, 1.1, and 1.2 for the same engine speed 1200 rpm, spark advance  $40^{\circ}$ , and compression ratio 4.9. Note the order of

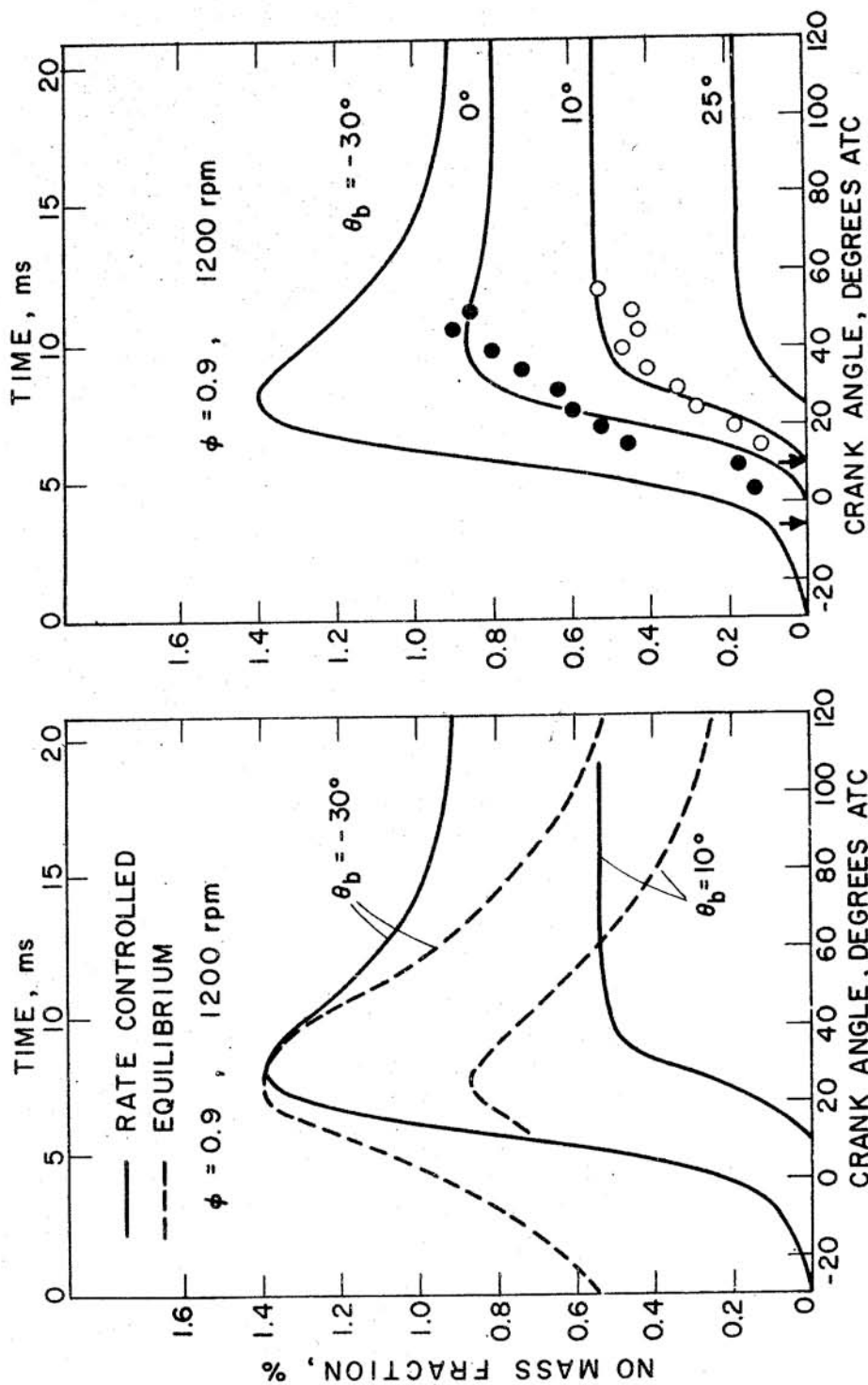


Fig. 3 - Comparison of calculated rate-limited and equilibrium nitric oxide concentrations in the first gas for first element to burn ( $\theta_b = -30^\circ$ ) and element which burns at  $x = 1/3$  ( $\theta_b = 10^\circ$ ).

Fig. 4 - Comparison of measured nitric oxide concentrations with rate-limited calculations. Arrows denote flame arrival times at the two cylinder-head windows.

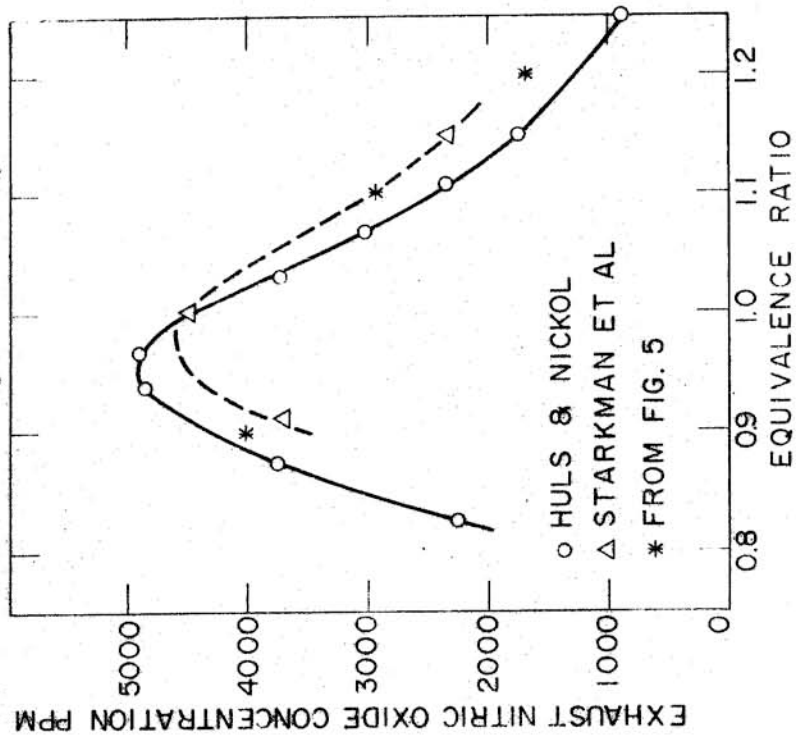


Fig. 6 - Calculated exhaust concentrations (asterisks) as a function of equivalence ratio obtained from Fig. 5 compared with exhaust measurements of Huls and Nickol (5) and Starkman et al (12).

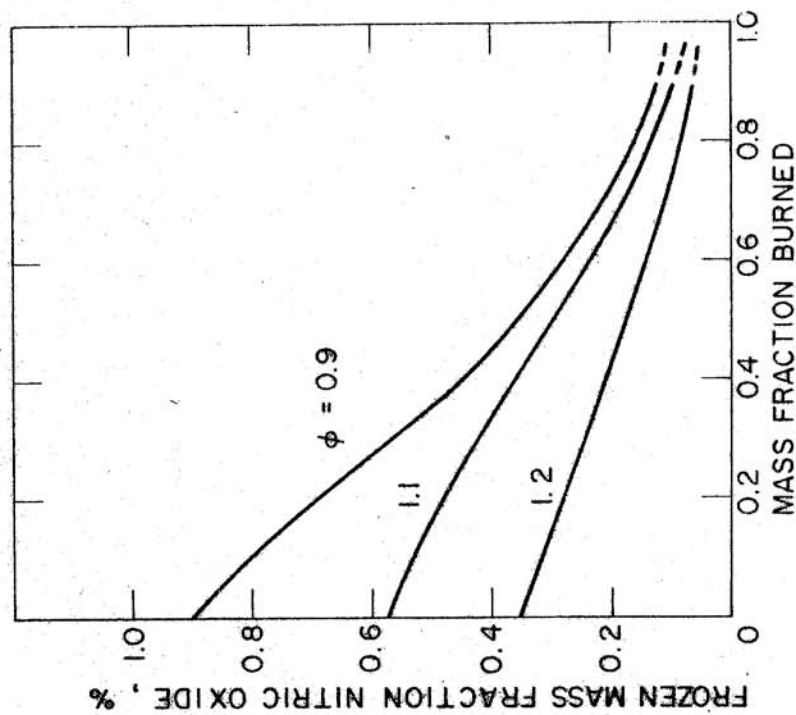


Fig. 5 - Frozen nitric oxide mass fraction as a function of  $x$ , the mass fraction burned at time at which each gas element burnt. Integrated value gives exhaust concentration.

magnitude difference in {NO} between first and last parts of the charge to burn.

The area under each curve gives the exhaust concentration, and this is shown in Figure 6. For comparison measured exhaust data from references [5] and [12] are also shown. Points on each curve are for constant spark advance, engine speed, and compression ratio. While the calculations in Figure 5 are for different engines and, presumably, different pressure-time curves, the magnitude of the theoretical predictions, and variation with equivalence ratio, are in surprisingly good agreement with the exhaust data. The conditions for Figure 6 are: calculations 1200 rpm, compression ratio 4.9, spark advance 40°; Huls and Nickol [5] 2500 rpm, compression ratio ~9, spark advance 40°; Starkman et al [12] 1275 rpm, compression ratio 7, spark advance 45°. All experiments were at full or near full throttle.

We are completing a comparison of calculated exhaust concentrations with our own experimental measurements, and the latest results will be reported at the meeting.

#### ACKNOWLEDGMENT

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