RATE-CONTROLLED CONSTRAINED-EQUILIBRIUM CALCULATIONS OF CO AND NO FREEZING IN INTERNAL COMBUSTION ENGINES

By

Mary Delichatsios and James Keck
Mechanical Engineering Department, Massachusetts Institute of Technology
Cambridge, Massachusetts

INTRODUCTION

The kinetics of carbon monoxide, CO, and nitric oxide, NO, formation in automobile engines has been the subject of extensive investigation during the past decade in connection with the problem of carbon air pollution. Measurements have shown that the level of CO and NO found in the exhaust of automobile engines is very much greater than the equilibrium value at the exhaust temperature and it has been predicted theoretically that this is due to the "freezing" of certain chemical reactions controlling the recombination of these species to form carbon dioxide, CO_2, and molecular nitrogen, N_2.

Previous theoretical studies of chemical reactions in automobile engines have involved either numerical integration of a large set of rate equations or the use of the "steady state approximation" to simplify the problem. The former technique has been used by Newhall (1) to study the freezing of CO during the power cycle of an automobile engine, while the latter has been used by Lavoie et al (2) to study the formation and freezing of NO.

In the present work the "rate controlled partial (constrained) equilibrium method" developed by Keck and Gillespie (3) has been used to investigate a wider range of operating conditions and to extend the calculation to include the "blowdown" phase of the cycle. The method is based on the assumption that the composition of a chemically reacting system can be approximated at any time by minimizing the Gibbs free energy subject to the constraints imposed by a set of previously specified rate controlling reactions. The method has the advantage over those previously used that only the rate constants for the controlling reactions are required and the number of rate equations which need to be considered is reduced by a large factor.

In applying the method to the study of CO and NO freezing in automobile engines, we have assumed as a first approximation that the expansion and blowdown processes are adiabatic and that the pressure time history for each element of gas is known. The rate-controlling reactions are then specified and the rate equations integrated to determine the temperature and composition of the burned gases as a function of time. Finally the results are compared with experimental measurements.

THERMODYNAMIC MODEL

Schematic diagrams of the cylinder and exhaust systems of a CFR engine are shown in Figure 1. It is assumed that prior to blowdown the pressure throughout the cylinder is uniform in space and known from measurements as a function of time. It is also assumed that mixing of the burned gases is negligible and that each element of burned gas expands adiabatically as the pressure falls. The burned gas elements are identified by two parameters x and z, where x is the mass fraction of burned gas in the cylinder at the time the element burned and z is the fraction of gas which has left the cylinder by the time the element arrives at the exhaust valve.

The pressure history of a gas element during blowdown is determined by assuming that the flow through the valve may be approximated as quasi-steady and isentropic. The quasi-steady assumption is justified because the opening time of the valve is large compared to the flow time through the valve; the isentropic assumption is justified because the thermodynamically important species are very close to equilibrium.

CHEMICAL KINETIC MODEL

The calculations were carried out for lean, stoichiometric, and rich fuel air mixtures. The fuel was iso-octane, C_8H_{18}, and the combustion products included the 32 species: N_2, H_2O, CO_2, CO, O_2, NO, H_2, OH, H, O, NO_2, H_2O, HO_2, H_2O_2, HNO_2, HNO, NH_3, NH_2, HCO, HNCO,

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NH, N, CH_2O, O_3, HCN, HNO_3, NO_3, H_2N_2, N_2O_3, CN, CH_3, CH_4.

The rate controlling reactions were assumed to be the threebody recombination and dissociation reactions which control the total number of moles of gas, and the molecular nitrogen bond breaking and making reactions which control the amount of "fixed nitrogen" in the burned gas. The two corresponding rate equations were integrated numerically on an IBM 650-60 computer for each gas element considered using a program developed by Warga (4) to determine the "constrained composition" and temperature at each integration step. Finally the results were averaged to obtain the concentrations of CO and NO in the exhaust gases.

Threebody Reactions

The threebody reactions considered and the rate constants used are shown in Table I.

TABLE I

THREEBODY REACTIONS AND RATE CONSTANTS FOR X = N_2*

Equation	Reaction	Rate Constant	References
1,1)	$OH + OH + X \rightleftarrows H_2O_2 + X + 52$	$k_{111}^{+} = 4 \times 10^{14} \exp (5300/RT)$	(9)
1,2)	$H + OH + X \rightleftarrows H_2O + X + 123$	$k_{121}^{+} = 2.34 \times 10^{16}$ (±50%)	(7)
1,3)	$NO + O + X \rightleftarrows NO_2 + X + 177$	$k_{131}^{+} = 1.5 \times 10^{15} \exp (1870/RT)$	(7)
1,4)	$NO + H + X \rightleftarrows HNO + X + 53$	$k_{141}^{+} = 1.3 \times 10^{16} (T/273)^{-0.9}$	(6)
1,5)	$O_2 + O + X \rightleftarrows O_3 + X + 26$	$k_{151}^{+} = 7.6 \times 10^{12} \exp (+2005/RT)$	(6)
1,6)	$O_2 + H + X \rightleftarrows HO_2 + X + 50$	$k_{161}^{+} = 3.2 \times 10^{15} \exp (1000/RT)$	(7)
1,7)	$CO + O + X \rightleftarrows CO_2 + X + 127$	$k_{171}^{+} = 10^{14}$	(7)
1,8)	$CO + H + X \rightleftarrows HCO + X + 21$	$k_{181}^{+} = 10^{15}$	estimated
1,9)	$N_2O + X \rightleftarrows N_2 + O + X + 115$	$k_{191}^{-} = 5 \times 10^{4} \exp (-58000/RT)$	(8)

Reverse rate constants were obtained by detailed balancing using equilibrium constants taken from the JANAF Tables (5). Reaction 1, 2) is in general the fastest and most important. Reactions 1, 4), 1, 6), and 1, 8) are important in stoichiometric and rich mixtures during the late period of expansion in the cylinder, when they become comparable to reaction 1, 2). For fuel lean mixtures, reactions 1, 3), 1, 5), and 1, 9) are comparable to reaction 1, 2) at temperatures below 2200°K. The third bodies considered were the three major species N_2, CO_2, and H_2O. The relative catalytic efficiencies for these third bodies are summarized in Table II.

The total number of moles of gas which is the constrained quantity in this case is given by

$$M = V \sum_{i=1}^{32} [i] = V \{[N_2] + [H_2O] + ... \}$$
1)

where [i] is the concentration of the ith species and V is the volume of a gas element of fixed mass. The corresponding rate equation is

$$\frac{1}{V} \frac{dM}{dt} = \sum_{k=1}^{9} \sum_{j=1}^{3} (R_{1kj}^{-} - R_{1kj}^{+}) = k_{111}^{-} [H_2O_2][N_2] - k_{111}^{+} [OH]^2 [N_2]$$

$$+ k_{112}^{-} [H_2O_2][CO_2] - k_{112}^{+} [OH]^2 [CO_2] + ...$$
2)

where R_{1kj}^{+} and R_{1kj}^{-} are the forward and reverse rates of reaction 1, k) for the third body j. It may be observed that although 27 possible threebody reactions have been included in the model, only one rate equation is required to determine the total number of moles of gas.

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* The recombination rate constants for reactions 1, 1) to 1, 8) are in $cm^6 mole^{-2} sec^{-1}$, the dissociation rate constant for the reaction 1, 9) is in $cm^3 mole^{-1} sec^{-1}$, and the activation energies are in kcal/mole.

TABLE II

$$A + B + X \rightarrow AB + X$$
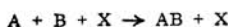
Reactions	N_2	Ar	H_2	O_2	CO_2	H_2O	References
$OH + OH + M \rightarrow H_2O_2 + M$	1	0.29		1.55	1.25	5.53	(6),(7)
$H + OH + M \rightarrow H_2O + M$	1	0.30	1.25	1.25	2.25	5	(7)
$NO + O + M \rightarrow NO_2 + M$	1	0.71		0.71	1.5	4.4	(7)
$NO + H + M \rightarrow HNO + M$	1	0.67	1.2		3	10	(6)
$CO + O + M \rightarrow CO_2 + M$	1				2	5	(7)
$CO + H + M \rightarrow HCO + M$	1				3	10	
$O_2 + O + M \rightarrow O_3 + M$	1	0.67		1.1	2.5		(6)
	1	0.71		1	2.9	10.7	(8)
$O_2 + H + M \rightarrow HO_2 + M$	1	0.5	2.5	1	3.7	16	(7)
$N_2 + O + M \rightarrow N_2O + M$	1				2	5	(8)

Underlined numbers were estimated.

Nitrogen Fixing Reactions

The "total moles" constraint governed by the threebody reactions does not give satisfactory results for the nitric oxide concentration. It predicts almost equilibrium concentration for NO during the expansion of the burned gases in the cylinder, whereas measurements (10), and kinetic models (1, 2) show freezing of NO at high values early in the expansion. The reason is that the two-body reactions associated with the nitric oxide formation or removal are rate limited. The reactions breaking the N_2 bond, for instance, are not very likely to occur (especially at low temperatures) because of the high activation energy needed, and they are the second group of rate-controlling reactions of our system. The reactions included and their rate constants are shown in Table III; the reverse rate constants were obtained by detailed balancing.

TABLE III

NITROGEN FIXING REACTIONS AND RATE CONSTANTS

Equation	Reaction	Rate Constant	References
2,1)	$NO + N \rightleftarrows N_2 + O + 75.3$	$k_{21}^+ = 3.1 \times 10^{13} \exp(-334/RT)$	(7)
2,2)	$NO + NO \rightleftarrows N_2O + O - 39$	$k_{22}^- = 2.3 \times 10^{13} \exp(-24100/RT)$	(7)
2,3)	$NH + N \rightleftarrows N_2 + H + 140$	$k_{23}^+ = 3 \times 10^{13}$	estimated
2,4)	$NH + NO \rightleftarrows N_2O + H + 25$	$k_{24}^+ = 3 \times 10^{13}$	estimated
2,5)	$2NO + N_2 \rightleftarrows 2N_2O + 0.5$	$k_{25}^+ = 0.9 \times 10^{10}$	estimated

Rate constants are in $cm^3 mole^{-1} sec^{-1}$; activation energies in kcal/mole.

The fastest and most important reaction is 2,1). Reaction 2,4) becomes important in stoichiometric and fuel-rich mixtures late in the expansion cycle, when it is comparable to 2,1); its rate has been estimated from similar reactions. Reactions 2,2) and 2,5) are important in lean mixtures, but they still are about one order of magnitude slower than 2,1). Reaction 2,3) turned out to be very slow, and thus unimportant in the present problems. It is, however, an important reaction for NO removal in the atmosphere.
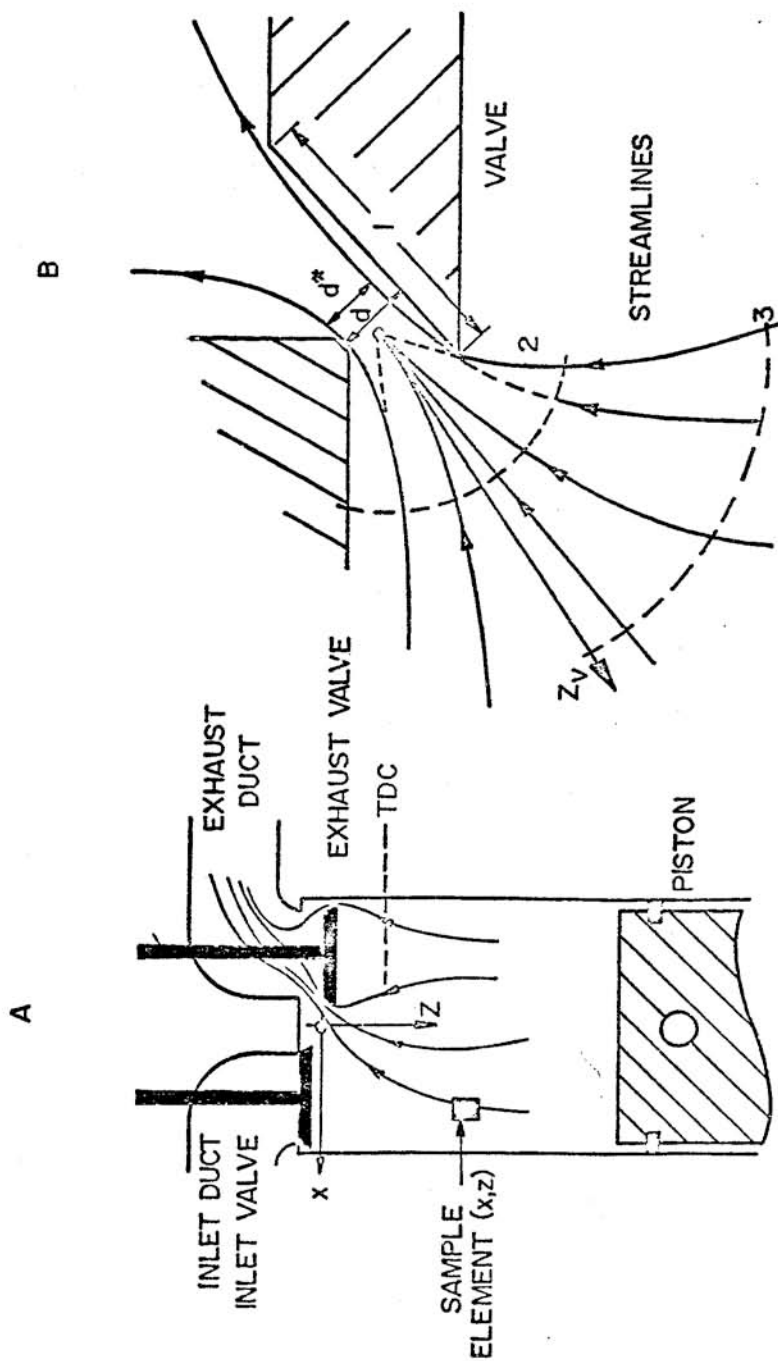
Figure 1. A. Schematic of the cylinder with exhaust valve and exhaust manifold.
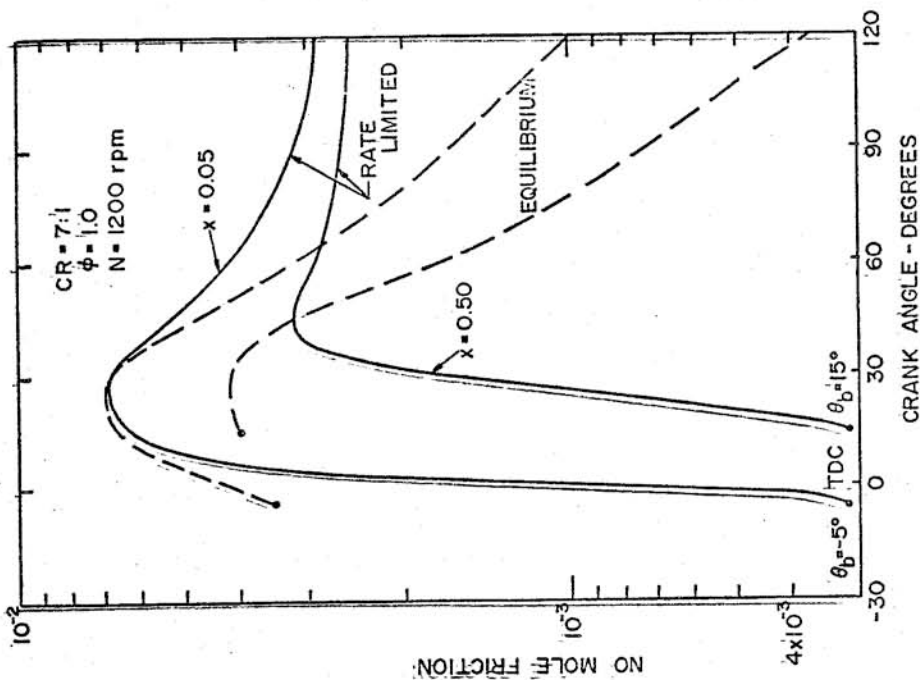   B. Schematic of flow through the exhaust valve.

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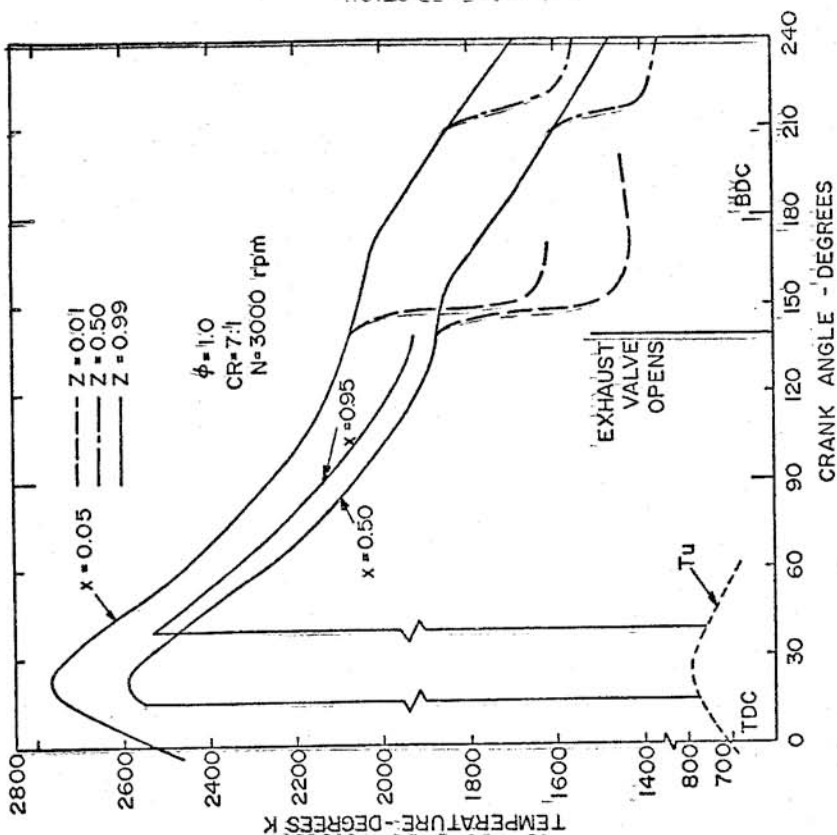Figure 3. Nitric oxide concentration versus crank angle for mass fractions burned, x = .05, x = .50.

Figure 2. Temperature versus crank angle during combustion, expansion and blow down for x = .05, .50, .99; and z = .01, .50, .99; equivalence ratio, 1.0.

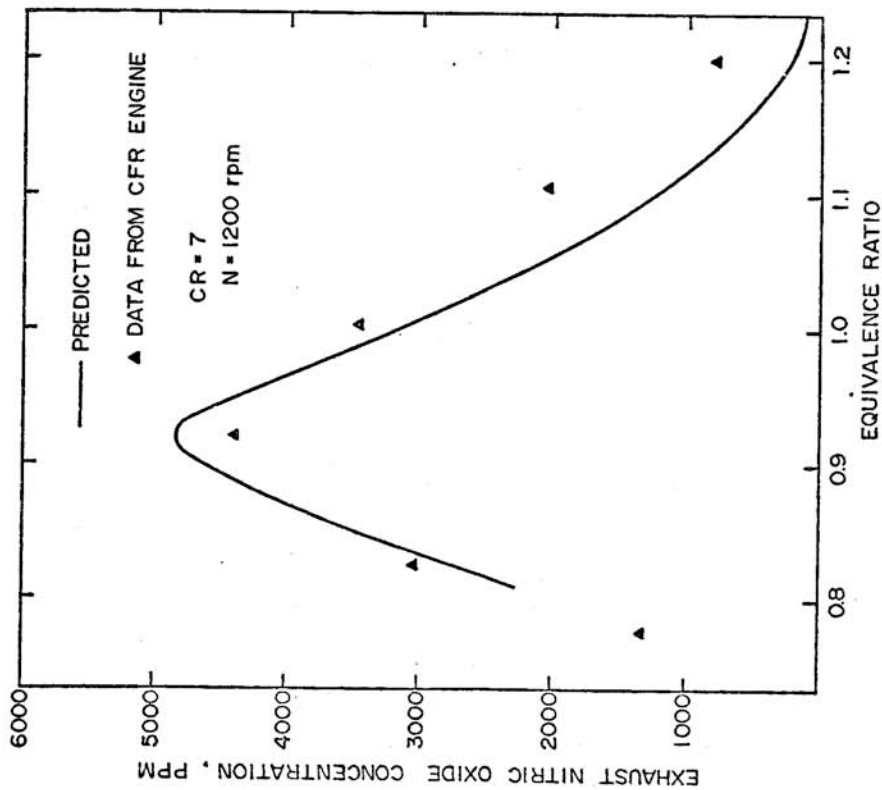Figure 5. Fractional excess in total number of particles versus time

Figure 4. Exhaust average nitric oxide concentration versus equivalence ratio.

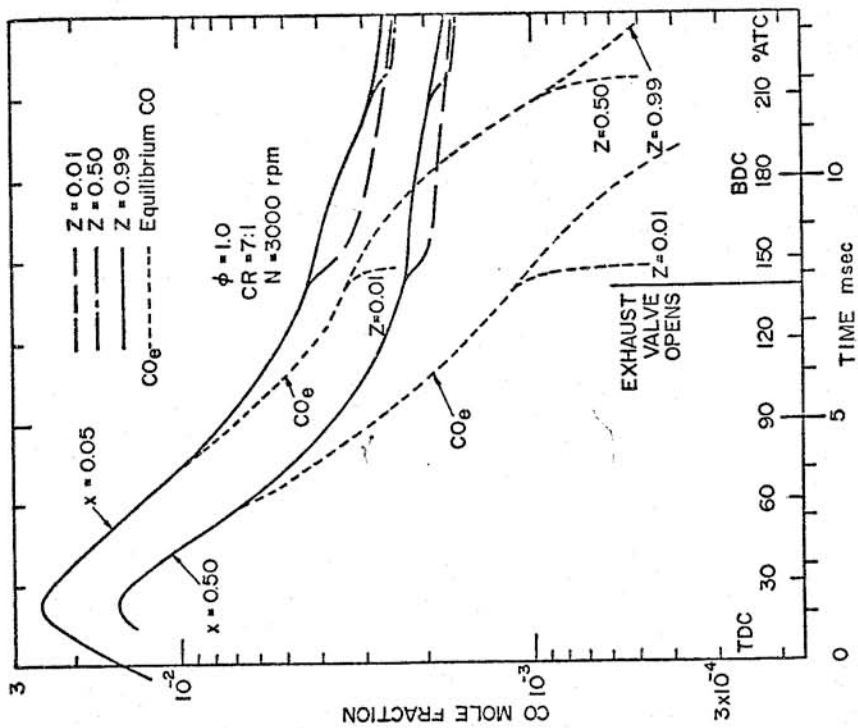Figure 7. Exhaust average CO concentration versus equivalence ratio.

Figure 6. Carbon monoxide concentration versus time during expansion and blow-down for $x = .05$ and $z = .01$, $.50$, $.99$; equivalence ratio, 1.0; engine speed, 3000 RPM.
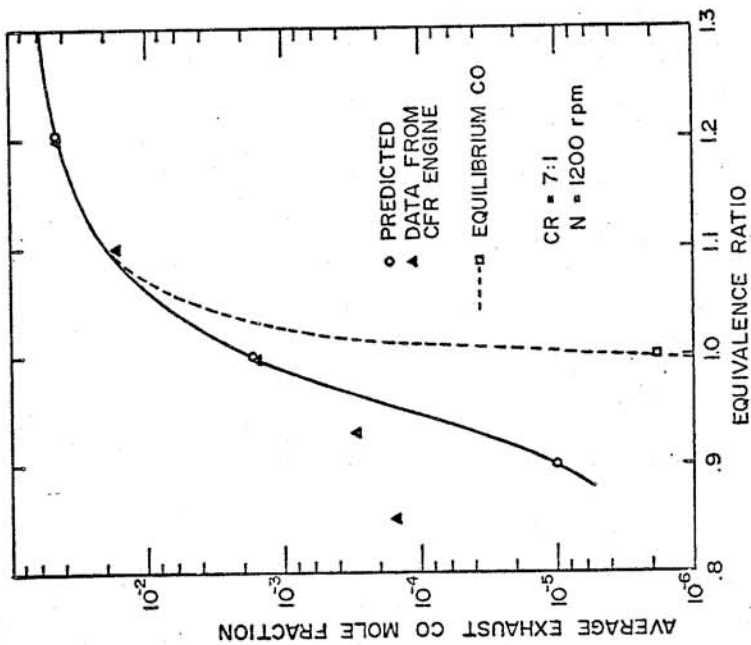
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The constrained quantity in this case is the number of moles of species containing "fixed nitrogen" which is given by

$$N_F = V \{ [NO] + [NO_2] + [HNO_2] + [HNO] + [NH_3] + [NH_2] + [HNCO] + [NH]$$

$$+ [N] + [HCN] + [HNO_3] + [NO_3] + 2[H_2N_2] + [CN] \} \qquad 3)$$

and the corresponding rate equation is:

$$\frac{1}{V}\frac{dN_F}{dt} = 2 \sum_{k=1}^{5} (R_{2k}^- - R_{2k}^+) = 2k_{21}^- [N_2][O] - 2k_{21}^+ [NO][N]$$

$$+ 2k_{22}^- [N_2O][O] - 2k_{22}^+ [NO]^2 + \ldots \qquad 4)$$

It is tacitly assumed that the reactions between the above mentioned "N fixed molecules" themselves are fast enough to be equilibrated. Among those species NO is the most abundant by two orders of magnitude. Therefore, the results should be similar to those from previous analyses (2, 11).

RESULTS AND CONCLUSIONS

The calculations were carried out for an unthrottled CFR engine operating under the conditions shown in Table IV.

TABLE IV

TYPICAL CFR ENGINE OPERATING CONDITIONS

Speed	Equivalence Ratio	Air-Flow lbm/sec	Fuel-Flow lbm/sec	Spark Advance	Inlet-Pressure psia
1200	0.9	1.1×10^{-2}	6.64×10^{-4}	30° BTC	14.31
	1.0	"	7.36	"	"
	1.2	"	8.84	"	"

The initial number of moles of gas was assumed equal to the equilibrium value in the burned gas and the initial number of moles of "fixed nitrogen" was assumed equal to that in the residual gas in the cylinder after exhaust. Some typical results are shown in Figures 2 to 7.

Figure 2 shows the temperature crank angle history of several gas elements which burn at various values of x and leave the cylinder at various values of z for a fuel-air equivalence ratio $\phi = 1$ and an engine speed of 3000 rpm. It can be seen that there is a significant temperature difference between gas elements which burn at different times and that the temperature falls sharply as each element leaves the cylinder. Note that it has been tacitly assumed in the model that the shape of the flame front during combustion is independent of axial position and that the axial flow during expansion and blowdown is quasi-one-dimensional.

The effect of the slow nitrogen fixing reactions on the NO concentrations in the engine cylinder is shown as a function of crank angle in Figure 3 for a fuel-air equivalence ratio $\phi = 1$ and an engine speed of 1200 rpm. Both equilibrium and rate limited values are given for two values of the burned mass fraction x, and it can be seen that frozen levels are well above equilibrium levels at exhaust temperatures. The predicted average exhaust concentrations of NO are compared with measured values as a function of equivalence ratio for the same engine speed in Figure 4, and the agreement is quite good except in rich mixtures where NO formation in the flame front is expected to be important. These results are in full agreement with those previously obtained by Lavoie et al (2) and Heywood et al (11) using the conventional steady state approximation to integrate the rate equations associated with the extended Zel'dovich mechanism of NO formation.

The effect of freezing of threebody reactions on the total number of moles of gas and the mole fraction of CO is shown in Figures 5 and 6 as a function of crank angle and time for an equivalence ratio $\phi = 1$ and an engine speed of 3000 rpm.

It can be seen in Figure 5 that the percentage excess in the total number of moles of gas over the final equilibrium value at low temperatures is quite small and that the departure from the local equilibrium values is even smaller. This implies a negligible effect on the temperature and pressure of the burned gases. On the other hand, it can be seen from Figure 6 that freezing of threebody reactions has a large effect on the CO concentrations. The upper curve (corresponding

to higher temperatures) shows that, although the deviation of the CO concentration from its equilibrium value is small during the expansion in the cylinder, it becomes important during the sudden expansion through the exhaust valve, when the carbon monoxide freezes at nearly the value it had before flowing through the valve. In the exhaust manifold a slow relaxation continues to take place, but the equilibrium value is never reached. The lower curve is similar in general shape to the upper one, but the deviation of the CO concentration from its equilibrium value starts earlier during expansion in the cylinder because the temperatures are lower here. The exhaust average CO concentrations are plotted as a function of equivalence ratio in Figure 7 and compared with experimental results from a typical CFR engine (12). The agreement is satisfactory for stoichiometric mixtures and, naturally, for rich mixtures, where CO is a major species. For lean mixtures the measurements are about one order of magnitude higher than the predictions.

Several reasons may be given to explain the discrepancies for lean mixtures:

1. Freezing of the two body reaction $CO + OH \rightarrow CO_2 + H$: In our analysis it was tacitly assumed that this reaction was in local equilibrium. In lean mixtures, where H and OH concentrations are small, this may not be the case. A preliminary calculation with this reaction as an additional rate controlling reaction suggests that it may account for half the observed discrepancy at $\phi = 0.9$.

2. Quench-layers on the cylinder walls rich in CO: During the burning process, carbon monoxide is formed in the flame. When the flame reaches the cylinder walls, it is quenched due to the heat losses, and there is a thin region at the wall where the gases (because of the low temperatures) do not burn, or burn partially. One may expect, then, that there should be a region of partial burning, rich in carbon monoxide, next to the quench layer of unburnt hydrocarbons. A preliminary analysis suggests that a considerable part of the CO observed in lean mixtures originates in the wall quench layers.

3. Oxidation to CO of part of the unburned hydrocarbons on the cylinder head: When the exhaust valve opens, and the exhaust gases pass through, they mix with the head wall quench layer and part of the unburned hydrocarbons contained therein become oxidized to CO.

4. Nonuniformities in equivalence ratio: The carbon monoxide has a strongly non-linear dependence on equivalence ratio, and consequently a calculation based on the mean equivalence ratio underestimates the amount of CO formed especially in mixtures which are just slightly lean. In automobile engines where the charge is well mixed this effect is expected to be quite small.

Although further work is clearly needed to explore the mechanism to CO freezing in lean mixtures, it is felt that the present rate-controlled partial-equilibrium calculations employing just two constraints give a generally satisfactory description of the non-equilibrium chemistry in automobile engines. The method is considerably simpler than those previously used to investigate this problem and can be improved as required by adding additional constraints.

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