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**CARBON MONOXIDE OXIDATION RATES
COMPUTED FOR AUTOMOBILE EXHAUST
MANIFOLD REACTOR CONDITIONS**

by Richard S. Brokaw and David A. Bittker

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Cleveland, Ohio 44135



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CARBON MONOXIDE OXIDATION RATES COMPUTED FOR AUTOMOBILE EXHAUST MANIFOLD REACTOR CONDITIONS

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SUMMARY

Carbon monoxide oxidation rates have been computed by integrating differential equations for a system of 29 reversible chemical reactions. At temperatures above about 1030 K (1400^o F) oxidation is rapid and is complete in times short in comparison to the residence times in exhaust manifold reactors. This suggests that such reactors are mixing rate limited, not reaction rate limited. At temperatures below 1030 K rates may be considerably slower. At these lower temperatures the reaction is catalyzed by nitric oxide. Thus, elimination of nitric oxide from automotive exhausts might degrade the low temperature performance of exhaust manifold reactors.

INTRODUCTION

The thermal reactor is a candidate system for reducing the carbon monoxide and hydrocarbon content of automobile engine exhausts. In this scheme the exhaust manifold is replaced by a large, well-insulated volume. Secondary air is injected at the cylinder exhaust ports and reacts with the pollutants in this thermal reactor. Such reactors are effective in reducing carbon monoxide and hydrocarbons in the exhaust; however, questions as to cost and durability remain (ref. 1).

The thermal reactor provides volume both for mixing of the exhaust gas with added air and also for subsequent reaction. It is appropriate to inquire as to what extent the cleanup of pollutants is limited by mixing rate and to what extent chemical reaction rates are limiting. With the rate limiting process identified, a more rational design of the thermal reactor should be possible.

Carbon monoxide and hydrogen are the major combustibles in the untreated exhaust gas and may amount to several percent by volume. (Hydrogen is of no concern as a pollutant.) Hydrocarbon concentrations are considerably smaller, amounting to several

hundredths of a percent, or several hundred parts per million. While the kinetics of hydrocarbon oxidation is not known in detail, the kinetics of the oxidation of mixtures of carbon monoxide and hydrogen is well established. Thus, calculations of the rate of carbon monoxide oxidation can be made for conditions appropriate to the automotive thermal reactor. Since the concentration of hydrocarbons is small, their presence should have little or no effect on the overall behavior of the combustion process.

Conditions which are conducive to rapid carbon monoxide and hydrogen oxidation - namely large concentrations of hydrogen atoms, oxygen atoms, and hydroxyl radicals - will also bring about rapid oxidation of the hydrocarbons. Thus, the residence times that are estimated for the cleanup of carbon monoxide should also apply for the cleanup of hydrocarbons in exhaust manifold reactors.

This report presents calculated carbon monoxide oxidation rates for conditions believed appropriate to the automotive thermal reactor. The calculations suggest that temperatures in excess of 1030 K, or about 1400^o F, are required for rapid cleanup of pollutants and that present reactors may be mixing rather than reaction rate limited.

COMPUTATIONAL DETAILS

Chemical Kinetics

Calculations were carried out assuming a system of 29 reversible chemical reactions involving compounds of hydrogen, oxygen, carbon, and nitrogen. In general, rate constants were taken from as few sources as possible in hopes that some internal self-consistency might be maintained. A critical review of the literature was not attempted; rather, we have tried to draw on the reviews of others insofar as possible.

We list in appendix A the individual reactions included in our scheme and indicate the values and sources of the assumed rate constants, together with comments on the importance and role of the particular step.

Numerical Computation

Concentrations of the various species as a function of time were determined by summing the extent of reaction of a large number of simultaneous and competing chemical reactions. In these, the individual rates are dependent on concentration and temperature and the temperature, in turn, depends on changes in composition. This requires the integration, by machine, of a set of first order, nonlinear differential equations. The system was assumed to be adiabatic and to obey the ideal gas law.

The solution is part of a general chemical kinetics computer program which solves many types of complex chemical reaction problems in flowing and static systems. The integration technique is particularly suited to handle efficiently the extremes of both slow and fast chemical reaction. A brief discussion of the computer program is given in reference 2.

Input Conditions

The assumed exhaust gas compositions were appropriate for a typical hydrocarbon fuel with a H/C ratio of 1.9 burned in an engine to two air-fuel ratios - A/F = 12, typical of an idling engine, and A/F = 14, a cruise condition. These compositions were estimated from Chart 8 of reference 3. Calculations were carried out for these gas mixtures diluted with additional air (21 percent O₂, 79 percent N₂) first to stoichiometric, A/F = 14.64, and then to a substantially leaner ratio, A/F = 17. Thus, four gas mixtures were considered. The undiluted and diluted compositions are presented in table I.

For each mixture kinetic calculations were run at 100^o intervals from 900 to 1300 K (1160^o to 1880^o F); in all cases the pressure in the exhaust manifold reactor was assumed to be atmospheric. Calculations were generally extended to 20 milliseconds which is typical of the shorter residence times for the thermal reactor.

RESULTS AND DISCUSSION

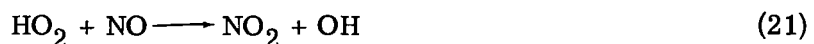
The computations contain a great deal of detailed information as to the variation of gas composition and temperature with time. This is illustrated in figures 1(a) and (b), which are semilogarithmic plots of mole fraction as a function of time. This particular calculation is for an idle condition (initial A/F = 12) diluted to stoichiometric (A/F = 14.64) with an initial temperature of 900 K. In this case, and in all but one of the others, an initial concentration of 1000 ppm of NO was assumed (10⁻³ mole fraction). The logarithm of temperature rise is shown as a dashed curve in figure 1(a).

Initially small concentrations of atoms and free radicals are produced, principally oxygen atoms by means of reaction 17 (see appendix A). Chain branching then sets in by way of reactions such as 2, 3, and 9 which involve an atom or free radical and a stable molecule:





The chain may be propagated and the identities of the chain carriers can be changed by reactions such as



These reactions cause an exponential rise in the concentrations of H, OH, NO₂, and HNO, as is apparent in figure 1(a). (The HO₂ and O concentrations also rise exponentially, but have not been plotted to prevent fig. 1(a) from becoming unduly cluttered.)

The mole fractions of NO₂ and HO₂ rise to about 10⁻⁵ and then decline; the mole fractions of HNO and H₂O₂ only rise to 10⁻⁶. These species are limited to these small concentrations because they are destroyed by rapid bimolecular processes such as



On the other hand, the mole fractions of H, OH, and O rise as high as 10⁻³ because these species are eliminated by slower termolecular reactions:





The rapid cleanup of carbon monoxide occurs by means of



When the hydroxyl radical mole fraction exceeds 10^{-4} .

All of the computations included detailed concentration histories such as figures 1(a) and (b). However, since our interest here is in carbon monoxide oxidation only, plots of carbon monoxide concentration as a function of time will be presented in figures 2(a) to 5(a) as linear plots and figures 2(b) to 5(b) as semilogarithmic plots.

In general, there is an induction period, followed by a period of more or less rapid consumption of carbon monoxide. The induction period is decreased as the initial temperature increases. This is a period of rapid buildup of the concentrations of H, OH, and O. In an actual exhaust manifold reactor it seems likely that the exhaust gases from the cylinders would have large concentrations of atoms and free radicals left over from combustion in the cylinders, which would eliminate the induction period. Indeed, it is common practice to add air as close to the exhaust valves as possible; perhaps this is because high concentrations of atoms and free radicals effectively initiate the oxidation which is later completed in the reactor.

Following the induction period there is more or less rapid oxidation. For all the calculations at 1100, 1200, and 1300 K (1520^o, 1700^o, and 1880^o F) this oxidation is invariably rapid, with carbon monoxide concentrations halved in a millisecond or less. Reaction rates are higher in the mixtures corresponding to the idle condition (figs. 2(a), 2(b), 3(a), and 3(b)), due to the higher initial carbon monoxide and hydrogen concentrations. The final cleanup of carbon monoxide is faster when there is excess air - compare figure 2(b) with 3(b) and 4(b) with 5(b). (The late stages in the oxidation are seen more clearly in the semilogarithmic plots.)

At temperatures of 900 and 1000 K (1160^o and 1340^o F) reaction may be very much slower - see especially figures 4(a), 4(b), 5(a), and 5(b). At these temperatures the rate of the chain breaking reaction



is more than twice the rate of chain branching reaction



that is, $k_4[\text{M}] > 2k_2$. Under these circumstances hydrogen atoms tend to react to form the relatively unreactive hydroperoxyl radicals, HO_2 , rather than the much more reactive oxygen atoms and hydroxyl radicals. Indeed, if there were no nitric oxide present, reaction would be very slow - undetectable within the time scale of these calculations. Thus, we would find ignition and reaction at temperatures where $2k_2 \geq k_4[\text{M}]$ and negligible reaction where $k_4[\text{M}] > 2k_2$; in other words, there is a limit temperature - a sort of chemical switch. For these mixtures this limit temperature ranges from 1016 to 1037 K, roughly 1400° F. Limit temperatures are included in table I.

However, it is well known that traces of nitric oxide sensitize the ignition of hydrogen-oxygen mixtures at temperatures below the limit. This is due to the reaction



which transforms the relatively inert perhydroxyl radical into a reactive hydroxyl radical. Nitric oxide is regenerated, largely through the reaction



The temperature history of one such low temperature mixture (initial A/F = 12, diluted to stoichiometric, initial temperature = 900 K) is shown as a dashed curve in figure 1(a). The limit condition, $2k_2 = k_4[\text{M}]$, is achieved at 1025 K after about 3.1 milliseconds. At that time the HO_2 concentration maximizes (fig. 1(b)) and the hydrogen peroxide concentration experiences a local minimum. Rapid carbon monoxide oxidation follows immediately.

The effect of nitric oxide concentration on the ignition behavior is shown as a dashed curve in figure 2(a), a calculation with 0.05 percent (500 ppm) NO, rather than the 0.1 percent (1000 ppm) assumed for the other calculations. The principal effect of reducing the NO concentration seems to be to increase the induction period by about 1 millisecond. A similar change might be expected if the rate constant for reaction (21) (which is a guess) were halved. But the nitric oxide concentration should have little effect on the course of the calculations at 1100, 1200, and 1300 K as these are above the 1025 K limit for this mixture.

It is difficult to make a definitive statement as to the extent uncertainties in other rate constants introduce uncertainty into the computed carbon monoxide oxidation rates. However, the computer printout indicates that under many circumstances reactions (1), (2), (4), and (5) are important. These rate constants are well known, with uncertainties

of 40 percent or less, and one would expect the errors in computed oxidation rates to be no larger.

CONCLUSIONS

These calculations of carbon monoxide oxidation rates for automobile exhaust manifold reactor conditions lead to the following conclusions:

1. At temperatures in excess of about 1030 K (1400^o F) oxidation is rapid and proceeds essentially to completion in 5 milliseconds or less. This is short in comparison to the residence times of 20 milliseconds or more which are typical for exhaust manifold reactors, and suggests that such reactors are limited by mixing rates, not reaction rates.

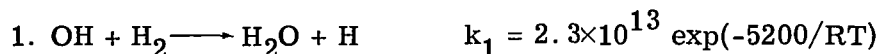
2. At temperatures below ~1030 K (1400^o F) reaction rates may be considerably slower. The reaction is catalyzed by nitric oxide and would be extremely slow in the absence of this substance. Thus reduction of nitric oxide to proposed levels of about 200 ppm might degrade the low temperature performance of exhaust manifold reactors. Low temperature oxidation rates depend crucially on the rate of the reaction $\text{HO}_2 + \text{NO} \longrightarrow \text{OH} + \text{NO}_2$; this rate has been estimated in the absence of experimental data. Thus, the low temperature calculations probably indicate only qualitative trends.

3. Calculations were carried out for exhaust gas compositions corresponding to idle and cruise conditions, with dilution air added to bring the compositions to stoichiometric, and to a leaner fuel-air ratio (A/F = 17). The mixtures diluted to stoichiometric had residual carbon monoxide concentrations of 0.2 to 0.5 percent, when the initial temperature was 1100 K or above. On the other hand, mixtures diluted to A/F = 17 had carbon monoxide concentrations of 0.05 percent in 5 milliseconds or less when initial temperatures were 1100 K or higher. Thus excess air definitely promotes the final cleanup of the last traces of carbon monoxide.

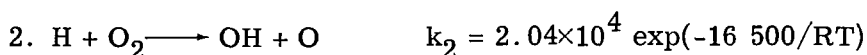
Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 21, 1970,
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APPENDIX A - SPECIFIC REACTION RATE CONSTANTS

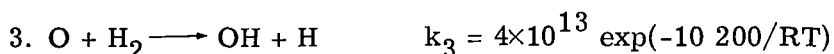
This appendix lists individual reactions included in the calculations and indicates values and sources of the assumed rate constants. Bimolecular rate constants are expressed in units of $\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}$ and termolecular rate constants are in $\text{cm}^6 \text{mole}^{-2} \text{sec}^{-1}$. Temperatures are in degrees Kelvin and activation energies are in calories.



This is an important chain propagation step in the branched-chain hydrogen-oxygen ignition scheme. The rate is very well established; the rate constant is taken from reference 4.



This rate constant, which is from reference 4, is the crucial branch in the hydrogen ignition scheme. A recent shock tube study suggests rate constants may be 35 percent smaller in the 1200 to 1400 K range (ref. 5).



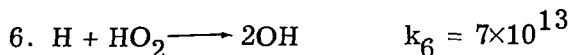
This is another branch in the $\text{H}_2\text{-O}_2$ reaction. This rate constant, from reference 4, may be 15 to 25 percent too large (refs. 5 and 6).



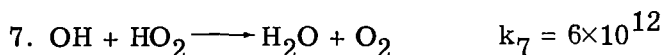
The rate constant shown is for $\text{M} = \text{argon}$. For other third bodies the rate constant was multiplied by the following factors: H_2O , 30; H_2 , 5; O_2 , 1.75; CO , 2; CO_2 , 7.35; N_2 , 2.15; and all others, 1. This important chain termination gives rise to the second limit for the $\text{H}_2\text{-O}_2$ reaction. The rate constant is from reference 4. The relative third body efficiencies are from Lewis and von Elbe (ref. 7), except for H_2O (ref. 8) and CO (a guess).



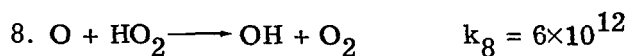
This is the principal path for the conversion of carbon monoxide to carbon dioxide. The rate constant is taken from Schofield (ref. 9). Recent shock tube results suggest a value lower by perhaps 35 percent in the range 1300 to 1900 K (ref. 5).



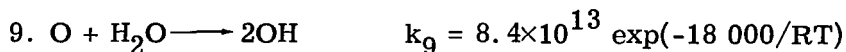
This rate constant is from reference 4. It is close to collision frequency so that the activation energy must be very small.



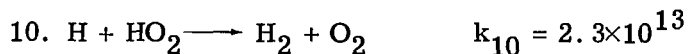
Kaufman (ref. 10) suggests that the rate constant is this large or larger.



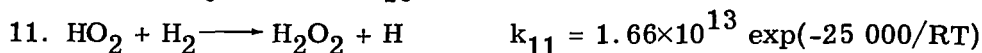
Again, a lower limit proposed by Kaufman.



Rate constant suggested by Schofield (ref. 9).



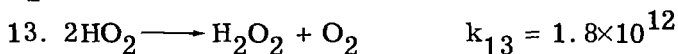
The reverse of this reaction provides a source of free radicals from H_2 and O_2 . Clyne and Thrush (ref. 11) suggest that $k_6/k_{10} \sim 3$; this combined with Baldwin's rate (ref. 4) for k_6 leads to $k_{10} \sim 2.3 \times 10^{13}$.



This is a slow reaction regenerating hydrogen atoms from the relatively inert HO_2 radicals. This rate constant is from Baldwin (ref. 4).



This rate constant is for $\text{M} = \text{nitrogen}$ from reference 4. For other third bodies the rate constant was multiplied by the following factors: H_2O , 6; O_2 , 0.78; H_2 , 2.3; H_2O_2 , 6.6; and all others, 1. These factors are from Baldwin and Brattan (ref. 12) except for H_2 (private communication from Professor R. R. Baldwin).



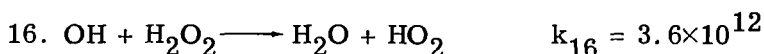
This rate constant is from reference 4.



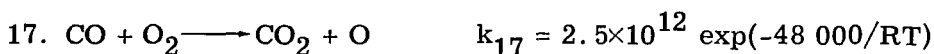
This rate constant is from reference 4.



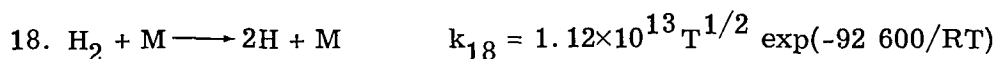
This rate constant is estimated by analogy with reaction 9. The activation energy of reaction 9 exceeds the endothermicity by 1000 calories. Since reaction 15 is exothermic, we assume an activation energy of 1000 calories with a preexponential constant similar to that for reaction 9.



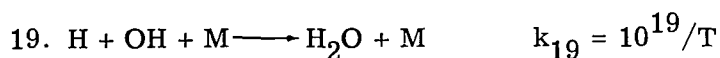
This rate constant is from reference 4. This is in reasonable agreement with more recent results (ref. 13).



This reaction between carbon monoxide and oxygen serves as an initiating source of atomic oxygen. The rate constants shown, from reference 14, may be too low, by an order of magnitude or more (ref. 5).



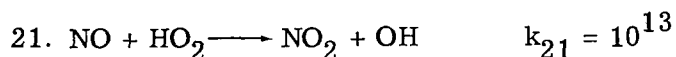
The rate constant shown is for $\text{M} = \text{H}_2$ (ref. 15). This value was used on the notion that several of the components of exhaust gas mixtures - H_2 , H_2O , CO_2 , etc. - should be considerably more effective than argon in dissociating hydrogen molecules and recombining hydrogen atoms. A perusal of recent information on relative efficiencies (ref. 16) suggests a rate lower by 40 percent might be more realistic for typical automotive exhaust gas compositions.



This rate is for $\text{M} = \text{Ar}$. The rate constant was estimated in the following manner: The rate of this recombination is about ten times as fast as the rate of hydrogen atom recombination (refs. 16 and 17), the reverse of reaction 18. And a shock tube study (ref. 18) gives $k_{-18} = 10^{18}/T$ for $\text{M} = \text{Ar}$. More recent work (ref. 19) gives $k_{19} = 7.5 \times 10^{23}/T^{2.6}$ for $\text{M} = \text{argon}$ over a wide temperature range, which gives rate constants within 40 percent of those we have used in the temperature range of interest here (900 to 1300 K). However, since nitrogen is 1.6 times as effective as argon and water is twenty times as effective (ref. 16), the rate of this reaction might be roughly four times faster in exhaust gas mixtures.



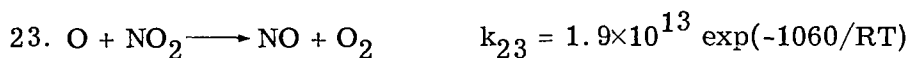
This rate, from reference 20, is for $\text{M} = \text{oxygen}$. A recent critical survey (ref. 21) suggests rates 30 to 40 percent lower in the range 900 to 1300 K.



This reaction converts the relatively unreactive hydroperoxyl radical to the reactive hydroxyl radical. It is responsible for the NO sensitized ignition at temperatures below the second limit, conditions where $k_4[\text{M}] \geq 2k_2$. We have assumed a moderately fast bimolecular rate, similar to reactions 6, 7, 8, and 10.



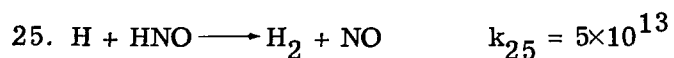
This rate constant is from reference 9.



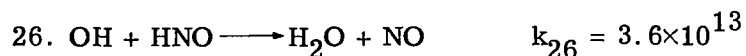
This rate constant is from reference 9.



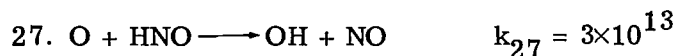
The rate constant shown is for $\text{M} = \text{argon}$. It was obtained by combining the 293 K datum of Hartley and Thrush (ref. 22) with the temperature dependence suggested by Schofield (ref. 9). For other third bodies the rate constant was multiplied by the following factors: H_2O , 6.1; H_2 , 1.87; CO_2 , 2.05; all others, 1. These factors are from reference 22.



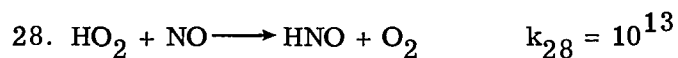
The rate constant used was inadvertently taken a factor of ten larger than the value reported in reference 23. A repeat calculation was run for a mixture at 900 K, where this reaction should be most important. There was negligible change in the concentration profiles except that the HNO concentrations were increased by as much as 40 percent. But at most, the HNO concentration barely exceeded 1 ppm.



Rate constant is from reference 23.



This estimate obtained by analogy with reaction 26.



This rate is assumed the same as reaction 21.



The rate shown for M = argon is from reference 9. For other third bodies the rate shown was multiplied by the following factors: H_2O , 6.3; O_2 , 1.0; N_2 , 1.55; CO_2 , 2.17; and all others, 1.

Rate constants for the reverse of these 29 reactions were obtained by invoking detailed balancing; in other words, the rate constant for each reverse reaction was taken as the quotient of the forward rate constant and the equilibrium constant. Thermodynamic data were taken from the JANAF thermochemical tables.

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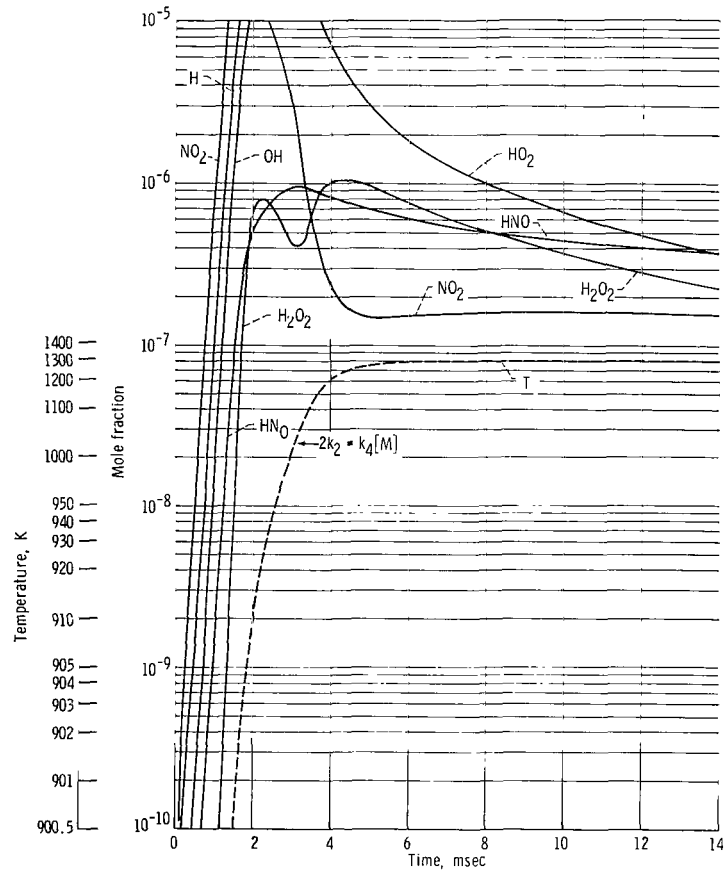
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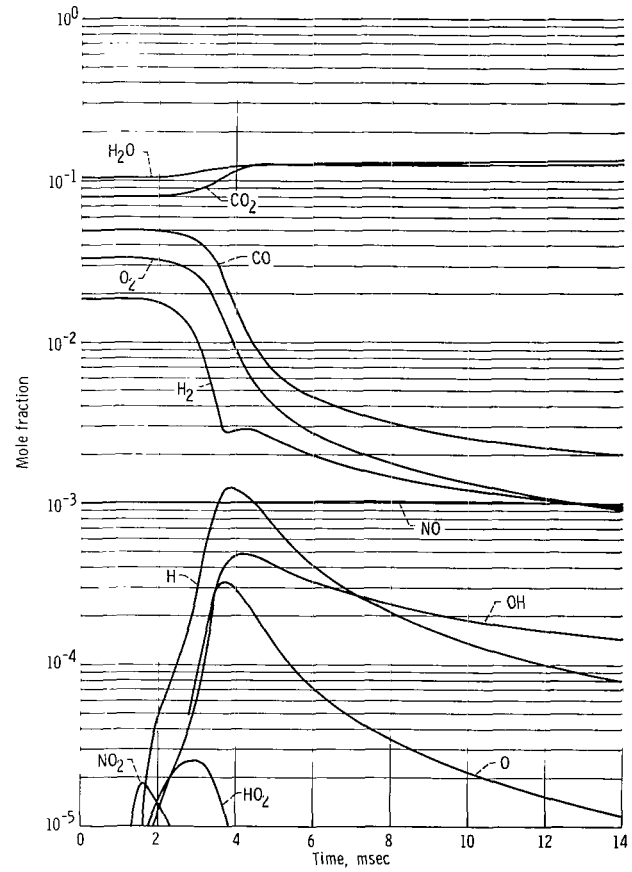
TABLE I. - ASSUMED EXHAUST GAS COMPOSITIONS^a

	H ₂	H ₂ O	CO	CO ₂	O ₂	NO	N ₂
Idle condition (engine A/F = 12)							
Undiluted	2.19	12.37	5.87	9.46	-----	0.10	70.00
Diluted to stoichiometric (overall A/F = 14.64; limit, 1025 K)	1.84	10.38	4.93	7.94	3.33	.10	71.48
Diluted lean (overall A/F = 17; limit, 1016 K)	1.61	9.06	4.30	6.93	5.57	.10	72.43
Cruise condition (engine A/F = 14)							
Undiluted	0.41	12.70	1.40	12.40	-----	0.10	73.10
Diluted to stoichiometric (overall A/F = 14.64; limit, 1037 K)	.39	12.17	1.34	11.89	0.816	.10	73.29
Diluted lean (overall A/F = 17; limit, 1028 K)	.34	10.59	1.17	10.34	3.44	.10	74.03

^aPercent by volume.

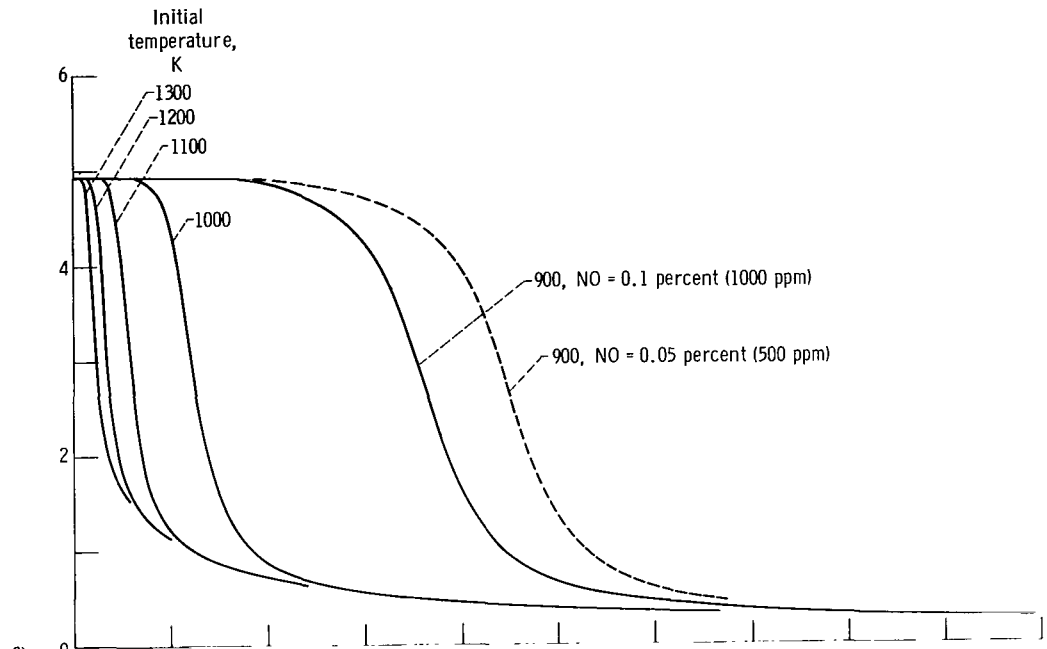


(a) Mole fraction, 10^{-10} to 10^{-5} .

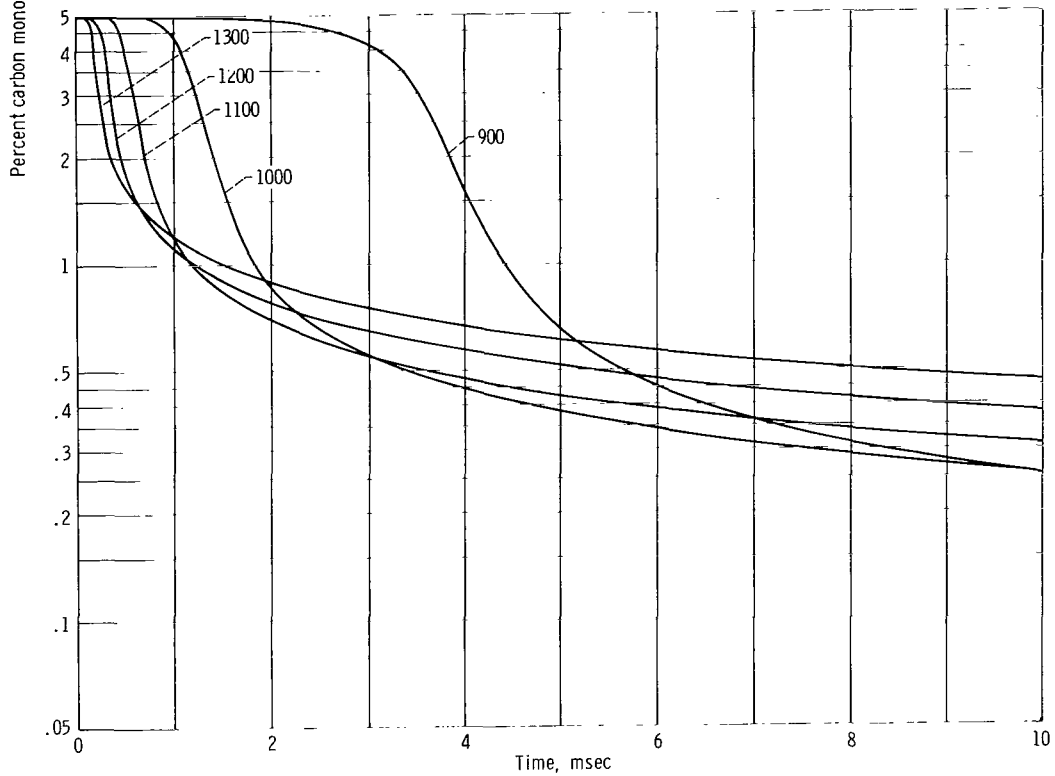


(b) Mole fraction, 10^{-5} to 10^0 .

Figure 1. - Gas composition as function of time, initial A/F = 12, diluted to Stoichiometric, $T_0 = 900$ K.



(a) Linear plot.



(b) Semilogarithmic plot.

Figure 2. - Carbon monoxide concentration as function of time. Initial A/F = 12 (idle condition), diluted to Stoichiometric.

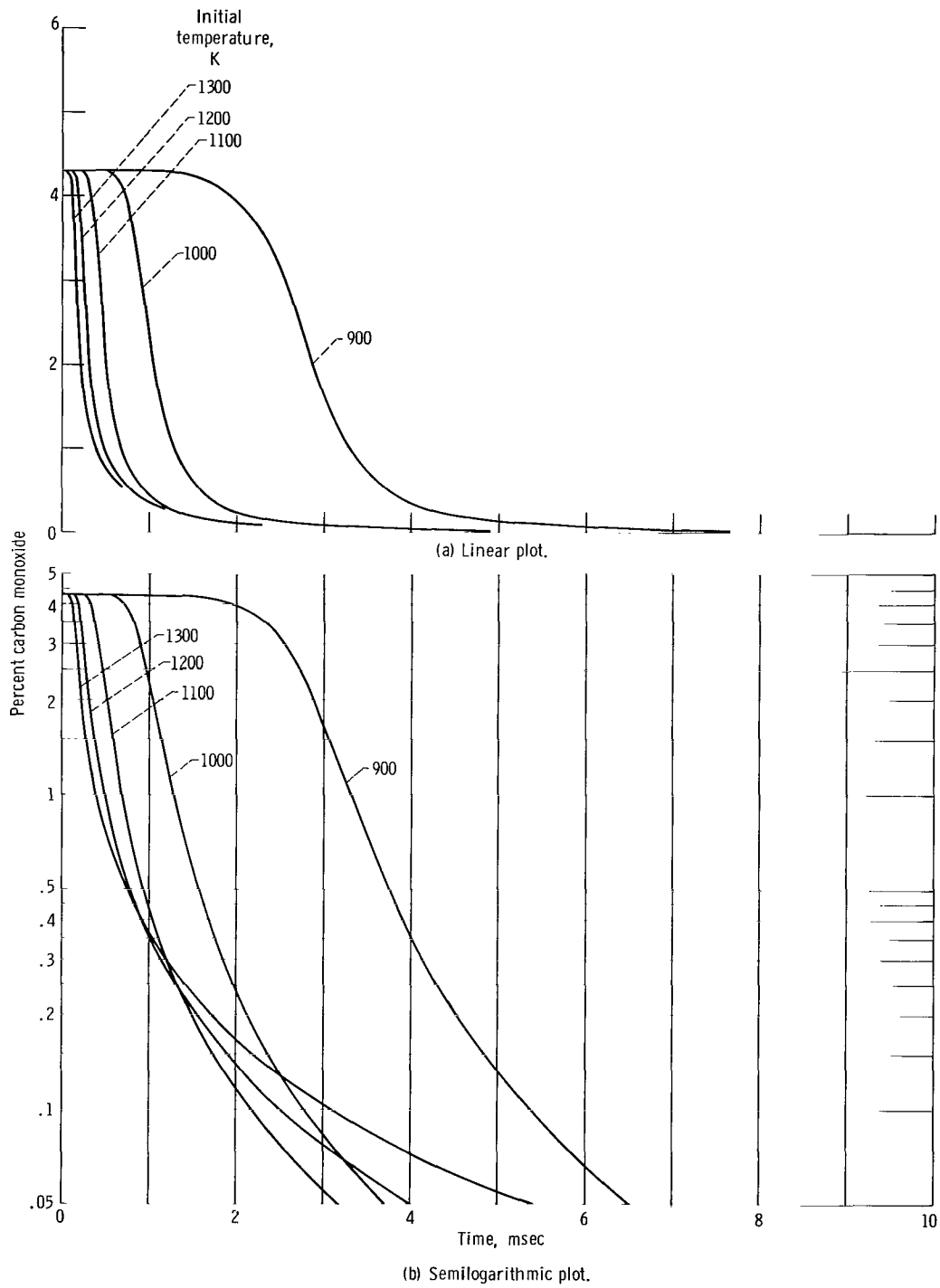
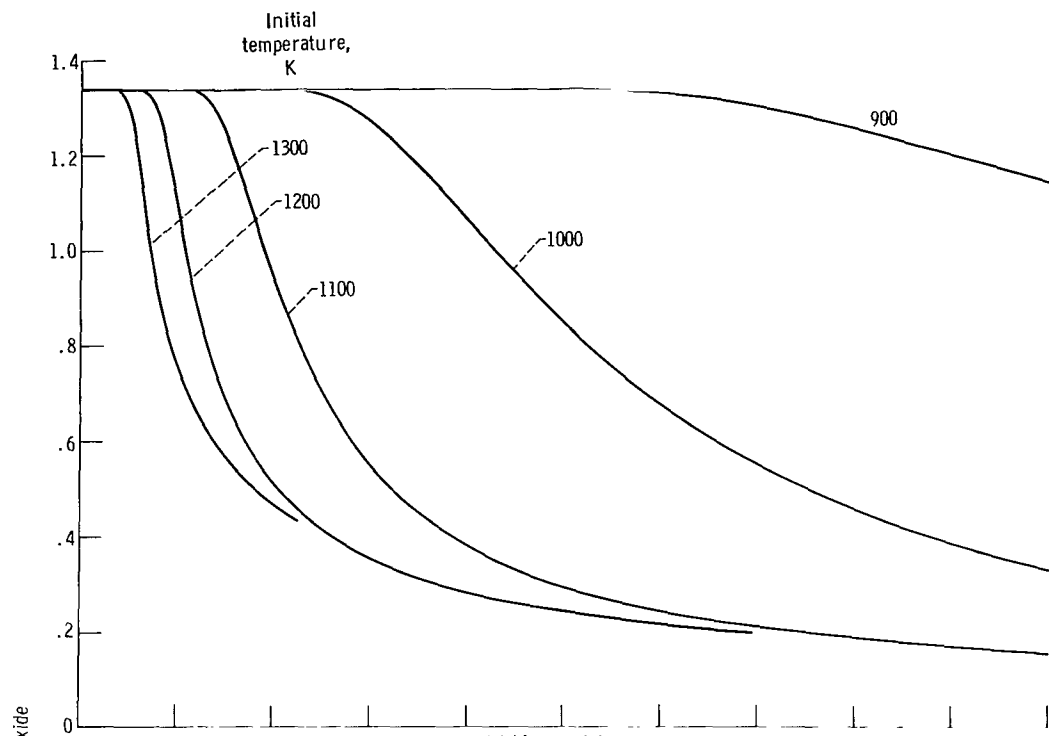
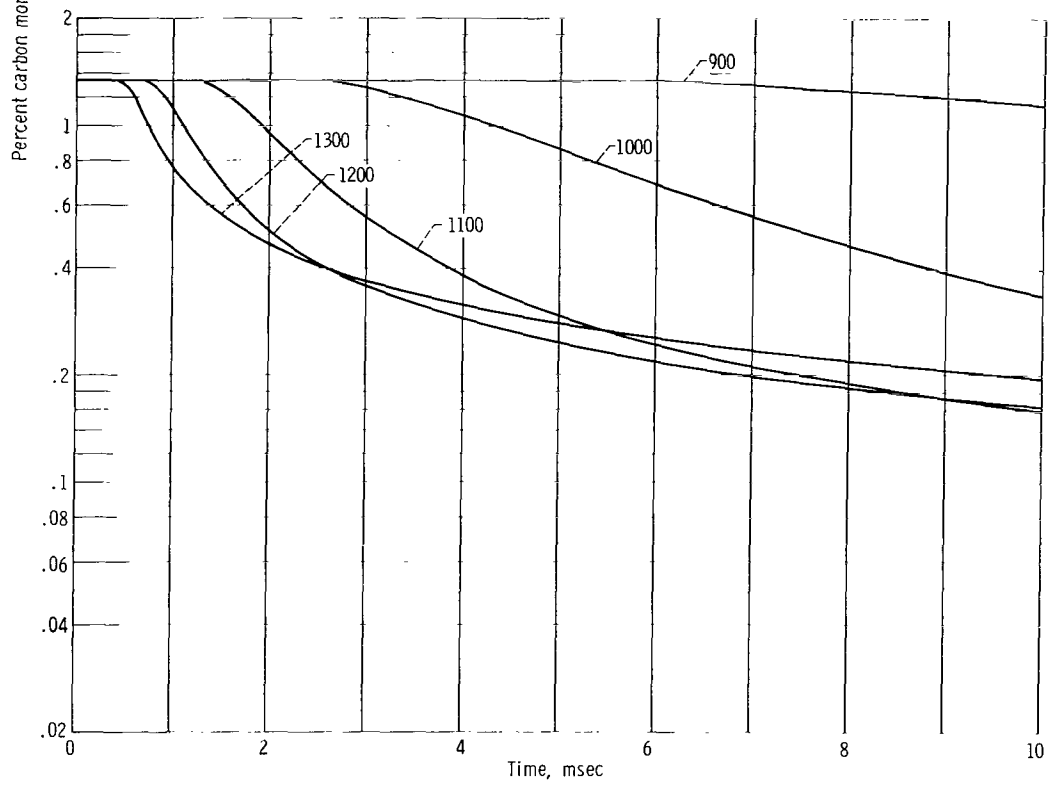


Figure 3. - Carbon monoxide concentration as function of time. Initial $A/F = 12$ (idle condition), diluted to $A/F = 17$ (lean).



(a) Linear plot.



(b) Semilogarithmic plot.

Figure 4. - Carbon monoxide concentration as function of time. Initial A/F = 14 (cruise condition), diluted to Stoichiometric.

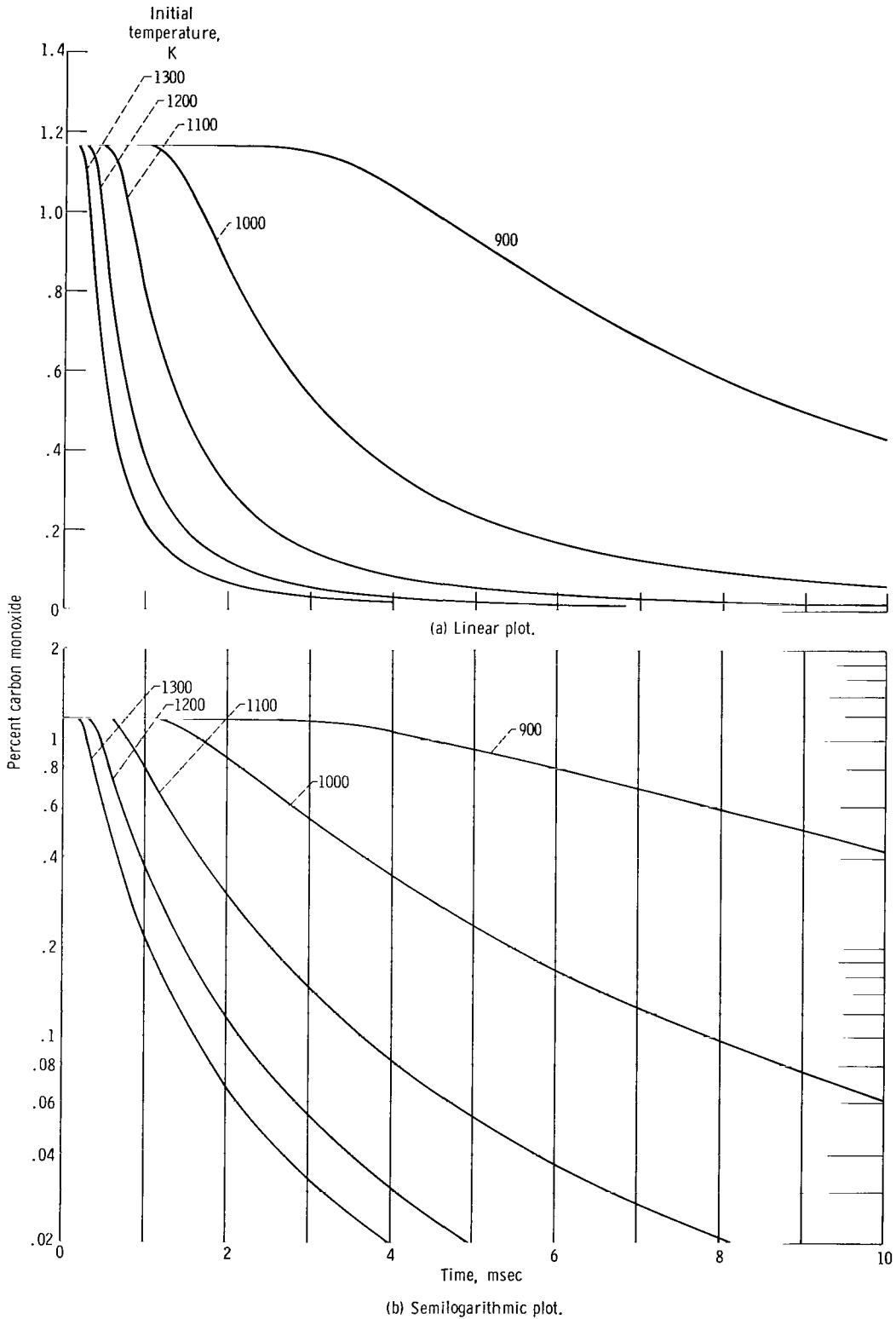


Figure 5. - Carbon monoxide concentration as function of time. Initial $A/F = 14$ (cruise condition), diluted to $A/F = 17$ (lean).

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