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STEAM BOILER TEMPERATURES

by

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Mines Branch Research Program
on Environmental Improvement

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SUMMARY

At the request of Ontario Hydro, published data were used in a computer program to predict the change that occurs in the amount of nitrogen oxide (NO) in nitrogen-oxygen mixtures at steam boiler temperatures, when the residence times at temperature, temperature and oxygen partial pressures are changed. Various projected time-temperature profiles within a firebox have been examined and it has been shown that, when the flame temperatures are maintained below 3000°F, very little NO is formed. Similarly, short excursions to very high temperatures near 3800°F may produce up to about 12,000 parts per million of NO per second of exposure.

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INTRODUCTION

In an earlier report prepared on the N-O system at the request of Ontario Hydro⁽¹⁾, the equilibria that prevail between nitrogen and oxygen at steam boiler temperatures were examined. It was shown that if equilibrium prevailed, it would be quite reasonable to expect several thousand parts per million of NO in the exit gases from a steam boiler. The nitrogen-oxygen system at high temperatures is particularly interesting because of the involvement of two opposing reactions: one to form NO from N₂ and O₂,



and the other to decompose it by the reverse reaction. After an extensive review of the data published on the kinetics of formation and decomposition of NO^(2,3,4,5,6), it was concluded that the results selected and published in the Esso report⁽⁷⁾ were probably as representative as any of the two reactions. The original equations were revised to produce an answer in parts per million of NO per second of exposure at temperature, and the net rate was calculated from the difference in the amounts of NO formed and decomposed in a one-second period. This report uses the equations to develop some recommendations

for those operating conditions that might reduce the amount of NO effluent contained in the residual gases from a steam boiler.

METHOD OF CALCULATION

In a typical 100-MW steam boiler of the type operated on the Toronto lakeshore by Ontario Hydro, about 75 tons of coal is burned each hour. About 15% excess air is used and at 500°F, about 50 million ft³ of gas is produced per hour. In the firebox, the residence time of this gas is about 0.5 second (500 millisec) as it moves through with a velocity of 40 to 50 feet per second. A variety of flame patterns are created by differences in burner placement, with the result that the profile of temperature varies with time as the gas passes upward through the firebox to the superheaters.

The general profile of temperature throughout the steam boiler is shown in Table 1.

TABLE 1

Temperatures at Various Locations Within a Typical Steam Boiler*

Location	Temperature	
	(°F)	(°C)
Firebox	>3000	(1649)
Super Heater Entry	2100	(1149)
Reheater Entry	1200	(649)
Reheater Exit	750	(399)
Air Preheater	600	(316)
Cyclones	300	(149)

*Based on the published data of Falkenberry et al(8).

Preliminary calculations indicated that the reactions for both the formation and the decomposition of NO were kinetically "frozen" at the temperature at which the gases enter the superheaters. Hence, it would be expected that the NO content of the gas emerging from the stack would be essentially the same as that leaving the firebox.

The equation used for the rate of formation (R_1) of NO, in parts per million per second, was:

$$R_1 = \text{ppm of NO formed/sec} = 3.82 \times 10^{15} e^{-68,180/T} \times P_{N_2} \times (P_{O_2})^{\frac{1}{2}} \quad [2]$$

In this equation, P_{N_2} and P_{O_2} refer to the partial pressures of the respective gases expressed as a percentage. The temperature is expressed in degrees absolute. The equation for the rate of decomposition of NO contains a term expressing its concentration. Because no more NO can decompose than has already been formed, the equation for the rate of decomposition must contain the term R_1 , modified to a percentage of NO formed during a one-second period. The relevant equation is:

$$R_2 = \text{ppm of NO decomposed/sec} = 6.964 \times 10^2 e^{-46,263/T} \times R_1^2 \times (P_{O_2})^{-\frac{1}{2}} \quad [3]$$

The net rate is then $(R_1 - R_2) = \text{ppm of NO surviving/sec}$.

RESULTS

In the first group of calculations, the net rate of NO formation was predicted over the temperature range from 3200 to 4000°F for a gas mixture containing 70% N₂, 0.5 to 4.0% oxygen, and the balance inert material. The family of curves is shown in Figure 1. It is of interest to note that, in accord with Equations 2 and 3, no NO would be expected in the absence of excess oxygen. The amount of NO formed at the peak temperature of about 3860°F increases steadily with increases in the amount of excess oxygen present. The effect of oxygen pressure on the rate of NO formation is shown in Figure 2. The temperature of maximum NO formation does not alter with changes in the amount of excess oxygen. In a coal-fired boiler it is usual to have at least 1 - 2% excess oxygen present over that required for complete combustion of the fuel. At the temperature of maximum rate of NO formation, the curve for 2% O₂ predicts that about 110,000 ppm of NO could be formed for each second the gas mixture was held at temperature. The amount is only decreased to about 80,000 ppm per second by halving the excess of oxygen or increased to 155,000 ppm per second by doubling it.

It is of particular interest to note that the equations predict that when the gas mixture is held at a temperature above 3952°F, no NO can remain in the system -- its rate of decomposition is more rapid than its rate of formation. This point is illustrated more clearly in Figure 3, where an Arrhenius-type graph is plotted for the logarithm of the rates of formation and decomposition against reciprocal temperature. To the left of the cross-over point at 3952°F, there cannot be any net recovery of NO.

Without data from a detailed probing of the flame area of a steam boiler, it is impossible to be sure of the time-temperature profile in the firebox. It is possible, however, to imagine a reasonable set of profiles and to use a computer program to calculate the net amounts of NO that would remain under various circumstances. For the purpose of this calculation, we assumed the presence of 70% N₂, 3% O₂ and 27% inert gas. All of the profiles in Figure 4 were drawn to enclose the same area, thus signifying the presence of the same amounts of nitrogen and oxygen in each projection. Profile A was drawn on the assumption that the temperature rose very rapidly during the first 20 milliseconds in the combustion zone. Thereafter it decreased slowly for the

remainder of the 500-millisecond period. Profile B assumed a gradual rise to a peak temperature and a more rapid decay of the temperature than in A. The C profile rose and fell more slowly than either A or B, while both D and E refer to essentially constant temperature operation for proportional periods of time. The residual amounts of NO are shown adjacent to their respective curves. By far the most deleterious set of circumstances is represented by curve B. In that instance the gas is exposed for a considerable period of time to temperatures between 3000 and 3800°F and the predicted amount of NO formation is 12,000 ppm. The effect of short excursions to high temperatures is shown by profile A, which resulted in only 3300 ppm of NO. Curve D shows a negligibly small amount of NO is formed when the temperature is less than 3000°F for the duration of the combustion. If a measured temperature-time profile were available it could be used for more accurate predictions, It is implied, however, that because the Ontario Hydro installations can produce up to about 700 ppm of NO, the temperature-time profiles in their boilers may approximate those of either curve C or E.

The results of the calculations were used as the basis for the following predictions.

PREDICTIONS

1. Plus or minus 1% change in the usual level of excess oxygen ($\pm 5\%$ excess air) does not appreciably alter the amount of NO produced during the combustion process. In a coal-burning operation the change would be only marginally significant. Any substantial change in the NO level would probably relate to temperature changes.
2. Probably the most significant reduction in NO levels could be achieved by spreading the flame front over a wide area to prevent local overheating above about 3000°F. This would decrease efficiency by reducing the amount of radiant heat transfer.
3. The beneficial effects of recirculating gases within a flame is probably related to maintaining a lower and flatter temperature profile rather than to reducing the oxygen level.

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FIGURES

1. Net NO production as a function of temperature.
2. Effect of oxygen pressure on the rate of NO formation.
3. Logarithm of the rates of formation and decomposition of NO plotted against reciprocal temperature.
4. Temperature-time profiles showing the net amounts of NO that remain under various circumstances.

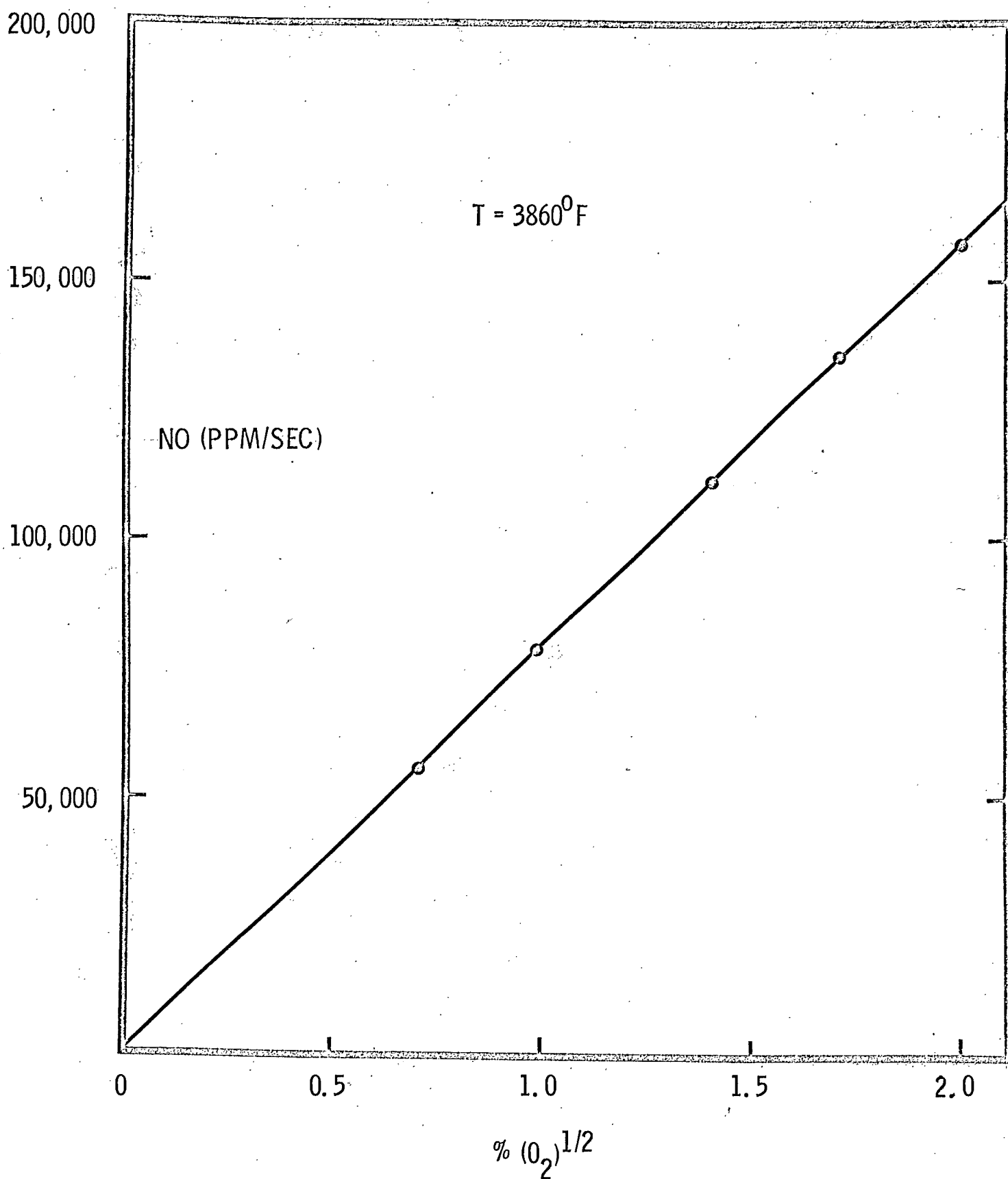


Figure 1

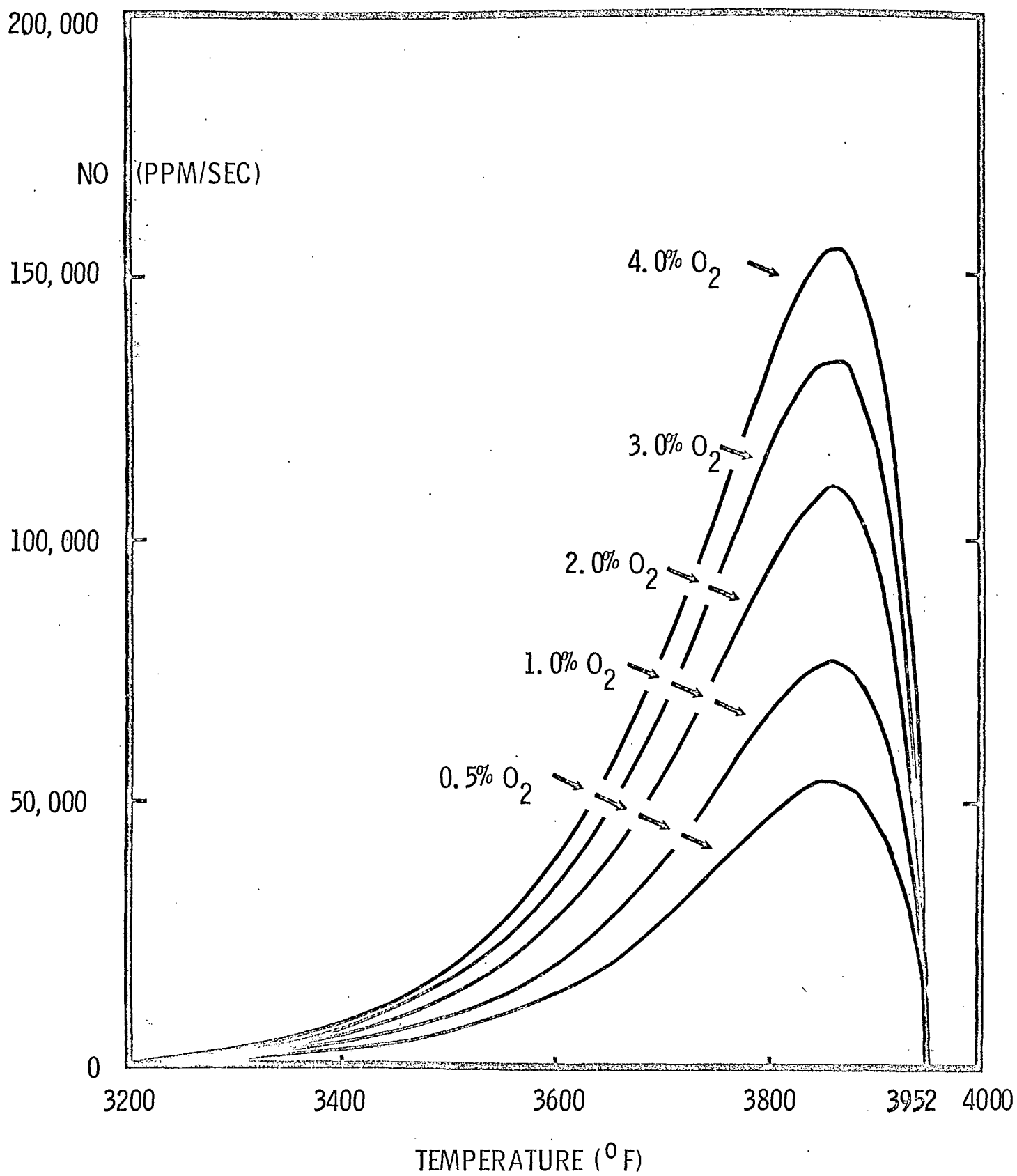


Figure 2

Figure 3

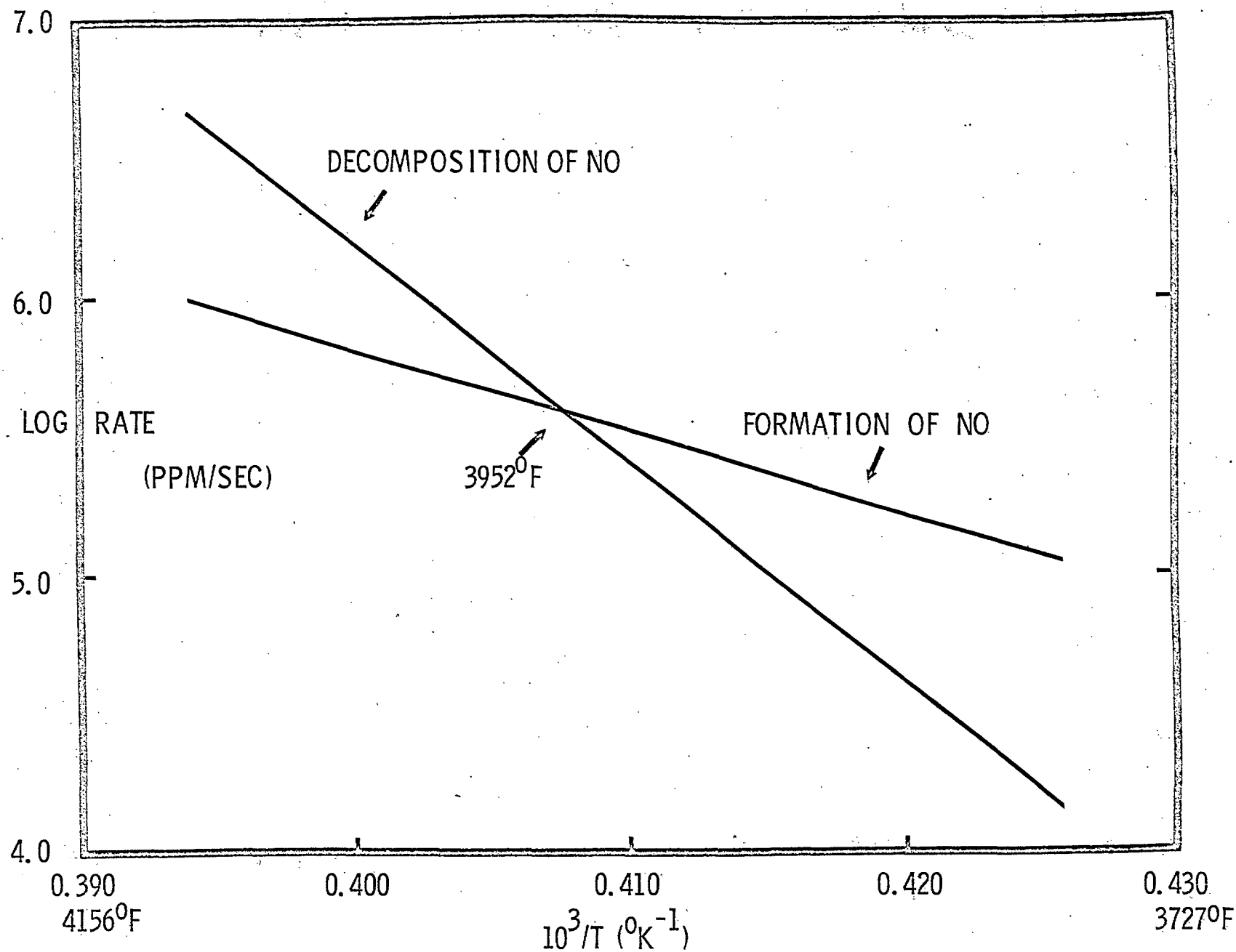


Figure 4

