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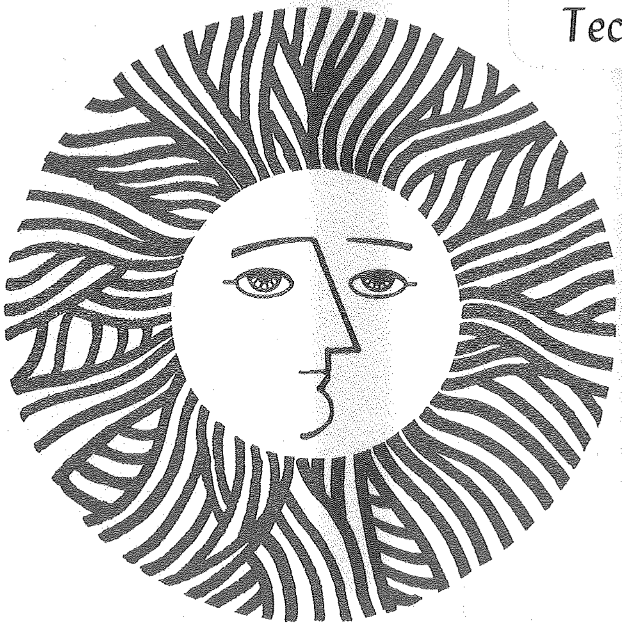

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ABSTRACT

The selective reduction of NO by NH_3 addition has been studied in a lean-burning oil fired laboratory combustion tunnel as a function of equivalence ratio, NH_3 injection temperature, concentration of NH_3 added, and the source of NO. Ammonia breakthrough was found to depend strongly on the NH_3 addition temperature. The total concentration of nitrogen containing species other than N_2, NO, and NH_3 was measured with a variety of techniques and was found to be less than 5 ppm over the range of conditions studied.

I. INTRODUCTION

More intensive regulations of the emissions of nitrogen oxides from stationary combustion sources have prompted the innovation and characterization of new control technologies suitable for applications in utilities. Previously employed technologies were largely based upon the prevention of thermal NO formation, and these are often ineffective in preventing the formation of fuel NO since the two mechanisms depend differently on experimental combustion conditions.

One of the more recent and attractive abatement technologies is the Exxon Thermal $DeNO_x$[1] described by Lyon and Longwell.[2] This process is based upon a reaction sequence between O_2, NO and NH_3. This sequence can be utilized to reduce NO selectively in the post combustion environment containing excess O_2 following NH_3 addition at a specified temperature. This process has the advantage of allowing for the destruction of NO after its formation, and thus makes no distinction between thermal and fuel NO.

Characterization of the selective reduction of NO through reaction with NH_3, added to the post combustion environment of lean mixtures has involved different types of investigations which provide complementary information. Kinetic studies have been undertaken in a quartz flow reactor by Lyon and co-workers[3-5] to elucidate mechanistic details of the $NH_3/NO/O_2$ reactions. Muzio et al.[6-7] investigated the selective reduction process for natural gas, a light oil and several types of coal, and have provided some mechanistic information and determined optimum conditions for maximizing the reduction of NO. Recent kinetic modelling studies have been undertaken by Saliman and Hanson[8] and by Miller et al.[9] to investigate whether existing kinetic data are adequate for providing explanations of the features of the selective reduction determined experimentally. Although each of these studies has increased our understanding of the chemistry associated with Thermal DeNO$_x$ and given us an appreciation of the process sensitivity to operating conditions, detailed chemical mechanistic information is still lacking.

A. Selective Reduction Studies

Four types of studies have been made, and these are: kinetic studies of reactions between $O_2/NO/NH_3$ for temperatures near 1250K, kinetic studies of the selective reduction in post combustion environments, modelling studies, and demonstration studies. A brief description of each of these and their major finding is given to provide the reader with an overview of Thermal DeNO$_x$.

Lyon[3] investigated NH_3-NO-O_2 reactions in a quartz flow reactor at 1250K and found nearly quantitative reduction of NO in 75 msec. The products of reaction were not measured directly and were inferred since it was determined that the nitrogen containing products were not oxidizable to NO over a platinum catalyst at 1270K. Lyon states that this evidence eliminates all candidates except N_2 and N_2O. The compound N_2O was eliminated from further consideration through spectroscopic measurements. The other major product besides N_2 which was consistent with atom balance considerations was postulated to be H_2O.

In a more extensive investigation of reactions of the $NH_3/NO/O_2$ system in a quartz flow reactor, Lyon and Benn[4] monitored reaction progress by measuring O_2, NO and NH_3 concentrations at different residence times. This was done as a function of initial reactant concentration and temperature. Ammonia oxidation was found to occur in competition with the selective reduction of NO such that the NO concentration tends to approach a steady state value. A first order rate for NO decomposition was found to be consistent with the data over a temperature range of 1144 to 1226K. A reaction order of one half was determined for both NH_3 and O_2. A free radical mechanism was discussed which gave a reasonable explanation of many of the features of the NO reduction.

In order to understand better the chemistry of NH_3 oxidation which occurs in competition with the selective reduction of NO, Lyon et al.[5] investigated the oxidation at temperatures between 1250 and 1350K. In agreement with high temperature (2000K) shock tube results, ammonia oxidation is preceeded by an induction time. No activation energy was given for the oxidation since the rate law describing NH_3 disappearance changed functional form between 1310 and 1350K. The compounds H_2 and NO were found to promote the NH_3 oxidation rate, and H_2 was also generated as a reaction product. Surface reactions on the quartz reactor walls were shown to be unimportant. The authors carefully reviewed reaction mechanisms previously useful in elucidating the features of high temperature NH_3 oxidation, and argue convincingly that these mechanisms are inadequate for explaining their experimental results. Significantly more information is required on reactions of NH, NH_2, HNO, and other radical species to elucidate the kinetic mechanism of NH_3 oxidation in the 1100 to 1400K temperature range.

Muzio et al.[6] studied the selective reduction of NO by NH_3 in the post combustion environment of a laboratory scale combustion tunnel using natural gas as a fuel. The temperature at the injection point was varied over the range from 950 to 1860 K. Continuous gas analyzers were used to measure O_2, NO/NO_x, CO, and SO_2, and standard electrodes were used to measure ammonia and cyano species. The reduction of NO was optimized at injector temperatures of 1230K and eighty percent NO reductions were achieved at a ratio of injected NH_3 to initial NO of unity. In a later study, Muzio et al.[7] investigated the selective reduction in the post combustion environment of a firetube boiler modified to fire pulverized coal with preheated combustion air. Several types of coal with different sulfur content were used in this study. The optimum reduction temperature varied with coal type. Reduction of NO on the order of 55% could be achieved while limiting the NH_3 breakthrough to less than 50 ppm with judicious selection of the temperature at the point of injection. The Muzio et al.[6,7] results and their relationship to our own will be discussed in detail subsequently.

Banna and Branch[10] investigated the selective reduction in the post combustion environment of lean premixed methane/oxygen/argon/ammonia flames. Secondary ammonia was introduced through injection holes distributed radially above the burner or through a secondary diffusion jet. Their experiment is unique since the product species N_2 and H_2O were measured directly via gas chromatography. Their results indicate that NH_3 oxidation is the dominant pathway at temperatures in excess of 1350K, and that optimum reduction of NO is achieved at 1220K. Both the oxidation and reduction were insignificant at temperatures less than 1100K. Reaction times on the order of .01 sec were reported.

In a combination experimental and modelling study, Lewis et al.[11] indicate that it also is possible to achieve NO reductions by injecting NH_3 in a rich first stage in the 1600-1800K temperature range. Although specific analytical techniques are not mentioned, they report that neither

NH_3 nor HCN was detected in the product stream. Reductions on the order of 95% were achieved during their experiments. It is difficult to evaluate this study since many important experimental details are not given in the paper.

Modelling studies of the selective reduction have been performed by Saliman and Hanson[8] and Miller et al.[9] Each of these groups has performed isothermal plug flow calculations and attempted to characterize the selective reduction in the fully equilibrated post combustion environment of lean methane/air mixtures. Although each group uses a somewhat different set of reactions and kinetic parameters, each concludes that reactions between NH_2 and NO are primarily responsible for NO removal and stress the significance of OH in influencing NO conversion. Each of these studies is plagued by insufficient kinetic data in the temperature range of interest.

The Thermal $DeNO_x$ process has been commercially demonstrated for gas and oil fired steam boilers and process furnaces. Two excellent reports[12,13] have been written under contract to the Environmental Protection Agency. One of these reviews the applicability of the Thermal $DeNO_x$ process to coal fired boilers and attempts to answer whether successful application of the process is related to boiler type. A cost analysis is performed on retrofit and new applications. The second report provides a technical assessment of the $DeNO_x$ process and places special emphasis on discussing the effects of temperature fluctuations and ammonia breakthrough in utility applications.

II. DESCRIPTION OF THE EXPERIMENT

A. Experimental Apparatus

The experimental apparatus used in this study consists of a laboratory scale combustion tunnel with associated control and measuring devices and the analytical instrumentation used to measure intermediate and product species concentrations. The combustion tunnel consists of a combustion section, an ammonia injection region, and a reaction and sampling section, and is illustrated in Figure 1.

Complete, stable, and reproducible burning of a fuel oil/air mixture is accomplished in the first section. All reactant flow rates are measured by rotameters calibrated with the appropriate fluid and are corrected for temperature and pressure variations. The tunnel pressure is near atmospheric, with only a slight vacuum (< 2 torr) provided by the exhaust hood fans. Air is supplied by a laboratory compressor to a 5 cm inside diameter low alloy steel tube at the upstream end of the apparatus. Air flow rates can be varied from 3.3 to 35.0 gm/sec, but are nominally 9 g/sec. The fuel used throughout is #1 diesel oil, supplied by the Shell Oil Company. It has a measured density of 0.836 gm/ml. Elemental analysis of the oil yields a hydrogen/carbon ratio of 1.85, 0.04% by weight sulfur, and < 0.1% by weight nitrogen. The fuel is delivered to a Monarch high pressure atomizing oil burner nozzle (Type R, 30° radius spray), and fuel flow can be set in the range from 15 to 42 gm/min, depending on the fuel pressure and nozzle size.

Two methods are used to achieve the NO levels typically found in the exhausts of commercial installations. Gaseous NO (Matheson CP grade) can be injected into the air supply upstream of the combustion section.

Another and somewhat more realistic method to simulate fuel-bound nitrogen compounds is accomplished by mixing pyridine (Mallinckrodt, research grade) with the fuel oil prior to addition to the fuel storage and delivery system.

In order to simulate the Thermal DeNO$_x$ process in a utility, it is important to achieve stable, complete combustion of the fuel oil under a variety of conditions with the products thoroughly mixed prior to reaching the ammonia injection region. Rapid mixing and burning of the mixture is enhanced by several fixed disks located behind the fuel nozzle. Many different designs and placements were attempted in the early stages of the research, including the addition of several swirl blades, before a successful arrangement was found. A 10 cm diameter section of steel tubing was installed immediately downstream of the fuel nozzle to increase the residence time of the reactants in the flame region. A quartz tube is located at the end of the combustion section which allows visual inspection of the flame, and aids in determining the sooting characteristics of the system. An acoustical vibration and feedback problem was mitigated by packing the air supply lines with steel wool and placing fixed and adjustable baffles in the exhaust line.

The temperature of the combustion products leaving the first section is adjusted by watercooling of the tunnel wall. Thirty meters of 0.6 cm copper tubing is wrapped around the 10 cm diameter section of the tunnel. Water flow rates up to 4 liters per minute through the tubing permits adjustment of the gas temperature to the desired values.

Ammonia injection is accomplished by the system developed previously[14]. Mixtures of NH_3 and N_2 are introduced into the product gas stream through four symmetrically oriented quartz injectors. The injectors are positioned to supply the NH_3/N_2 mixture counterflow to the combustion product stream, which aids in rapid mixing. Matheson CP grade anhydrous ammonia is used without further purification, and is mixed prior to being introduced into the injectors with gaseous nitrogen obtained from a 160 l liquid N_2 tank which is passed through a heat exchanger to warm the gas to room temperature. An excess of N_2 is injected to reduce changes in mixing due to variations in the NH_3 flow. Previous experiments showed that the ammonia/nitrogen mixture does not react when passed through the heated quartz injectors[15].

The reaction and sampling region begins immediately downstream of the ammonia injectors, and is ~ 60 cm long. This section, and parts of the ammonia injection region and exhaust lines, are insulated with layers of 2.5 cm thick Fiberfrax alumina silica insulation to reduce heat losses. Temperature or composition sampling can be performed at four different axial locations, separated by 12 cm. Each probe position has four tapped ports 90° apart to permit sampling in either the horizontal or vertical plane. Probes can also be positioned at a desired radial location by inserting machined stops in the port opposite the probe. The error in the radial probe position using this method is estimated to be ±1 mm; however, this method requires cooling of the tunnel before a probe can be repositioned. Positioning of the probes while the combustor is continuously operating can be accomplished using marked probes. This method has the advantage of allowing many measurements to be taken under identical firing conditions with only a slightly larger error (±2 mm) in the probe position.

B. Analytical Techniques

Temperatures are measured with bare wire Chromel/Alumel thermocouples. Corrections for radiation loss are made using measurements obtained from a suction pyrometer (aspirated thermocouple) using the same Chromel/Alumel junction. All temperatures reported here are corrected by adding the appropriate radiation correction to the respective bare wire measurement; the accuracy of the temperature measurements is estimated to be ±5K.

Gas samples are withdrawn from the reaction section through microprobes located at the four axial test port positions. The probes are constructed from 3.0 mm O.D., 2.0 mm I.D. quartz tubing, and are approximately 10 cm long. The tips of the probes are drawn down to an orifice diameter of 0.3 to 0.5 mm. This design is typically described as an "aerodynamically quenched" probe; however, recent evidence suggests that the primary quenching mechanism in probes of this type is convective cooling and not aerodynamic quenching[16].

C. Species Analysis

1. CO and CO_2 Measurements

Concentrations of CO and CO_2 are measured using Beckman Model 315 non-dispersive infrared continuous gas analyzers (NDIR). Metal bellows vacuum pumps, located in the analyzer housings, are used to withdraw the samples. Unheated Teflon lines are used to transport the gases to the analyzers. Water is removed through the use of two ice-bath cooled condensers in series. Calibration gases were obtained from different commercial vendors. Self-consistency of the gases and instrument linearity were checked by using several different calibration gas concentrations. Each instrument is calibrated immediately before and after measurements were taken.

2. H_2O Measurements

Water concentrations are determined by inserting a pre-weighed magnesium perchlorate drying tube between the probe and a metal bellows vacuum pump. Heated Teflon lines are used to connect the probe to the drying tube. After exiting the pump, the volume of the now dry gas is measured with a calibrated wet test meter corrected for temperature, pressure, and water vapor concentration. The drying tube is weighed immediately after the exhaust is passed through it. The relative error in the accuracy of this method is estimated to be ±3%.

3. NH_3 Measurements

A wet chemical method for ammonia analysis, based on the sodium phenolate method, has been developed in our laboratory. A sampling probe is connected by unheated Teflon lines to two pyrex U-tubes in series. The tubes are filled with 3 mm diameter pyrex spheres coated with a dilute (5×10^{-3}M) solution of phosphoric acid. The sample gases are pulled through the tubes at a rate of ~ 100 ml/min by a metal bellows pump which exhausts into a bubble flowmeter or a calibrated wet test meter. Two tubes are used in series to insure complete trapping of the ammonia.

Immediately after collection, the beads are transferred to 100 ml graduated cylinders. The tubes and adapters are rinsed several times with NH_3 free distilled water, with all of the washings added to the sample. Additional water is added to dilute the sample to a convenient volume. The dissolved ammonia is chlorinated to chloramine, NH_2Cl, which is then reacted with sodium phenolate to form an indophenol dye of unknown structure with an absorption maximum at 632 mm. The optical density of the sample is measured against a blank in a Beckman DU spectrophotometer. For a 1.0 liter gas sample and a liquid volume of 60 ml, concentrations from 35 to 315 ppm can be measured. Different sample sizes can be used to extend the measurable concentration range.

Possible interference by higher amines was examined by preparing known standards containing other amines. Ethyl amine exhibits an extinction coefficient of about 1/4 of that of ammonia. Dimethyl and higher amines show no interference. Other combustion exhaust products, with the exception of SO_2, do not alter the measurements. Absolute errors using this method are determined by measuring NH_3 concentrations under cold flow conditions, and are estimated to be less than 10% when sampling combustion products. The method yields excellent results, but suffers from a low sampling rate and long analysis time. This technique is highly advantageous since it can be used as a reliable standard to determine if other methods yield consistent results.

Perhaps the most convenient method for measuring NH_3 is to oxidize it to NO on a catalytic surface, followed by NO detection in a chemiluminescent analyzer. However, most NO analyzers are not equipped to handle the high concentrations of water vapor present in combustion exhausts. Condensation of water anywhere in the system can lead to large errors due to the high solubility of NH_3 in water. In addition, NH_3 is often adsorbed on many types of surfaces, especially metals. To avoid these problems, a ThermoElectron Model 12A chemiluminescent analyzer (CLA) was modified to prevent condensation and reduce the length of the sampling system that operates at near-atmospheric pressures. The capillary metering system has been mounted outside of the analyzer in a heated box, and is connnected to the sampling probe by a 15 cm heated Teflon line. Reduced pressure (~30 torr) Teflon lines connect the capillary box to the stainless steel converter and reaction chamber in the analyzer housing.

The efficiency of the converter was measured using NH_3/air mixtures metered through calibrated rotameters. The converter is run at an indicated temperature of ~1200 K, the highest practical temperature that can be obtained. All NH_3 values reported that are measured by this method have been corrected for the converter efficiency.

One of the major problems with the ammonia/chemiluminescent measurements is interference from other nitrogenous species, such as NO_2, that can be converted to NO under the same conditions[17]. It is thus necessary to use the phenolate method, which gives an independent measure of NH_3, to determine if the CLA method is free from interfering species. Table I lists the measured NH_3 values using both methods under a variety of combustion conditions. In all cases, agreement is within experimental error of the methods. It should be noted that little or no reaction of NH_3 and NO was measured in the catalytic converter of the chemiluminescent analyzer, even though the temperature of the converter is in the range employed in the Thermal DeNO$_x$ process.

Ammonia can also be measured with a gas-permeable specific ion electrode (Orion Model 95-10). This technique is often used for ammonia measurements, with the ammonia collected by bubbling exhaust gases through a dilute acid solution. The NH_3 can be collected quantitatively, but the CO_2 that dissolves in the solution can lead to a 20% error in the electrode potential. It was found that the collection technique developed for the sodium phenolate method also works well for the ion analysis. When the CO_2 interference is taken into account, the ion electrode works as well as the sodium phenolate method. This method has the disadvantage of suffering from a large amine interference and is also plagued by low sampling rates and long analysis times.

4. NO Measurements

The ThermoElectron Model 12A chemiluminescent analyzer, described in the NH_3 measurement section, is also used to measure NO concentrations. Calibration gases of NO in N_2 were purchased from commercial sources. Aluminum cylinders were specified for the gases, since previous experience indicated that NO can react when stored in iron tanks. Concentrations of the calibration gases were checked by mass spectrometer analysis and by comparison with NBS standards. Instrument linearity was checked by dilution of NO samples with measured amounts of nitrogen.

5. HCN Measurements

Hydrogen cyanide was measured by a variety of techniques. The first, and the simplest, employed a Matheson Kitagawa detector tube kit. Samples are withdrawn through a probe into a Kitagawa tube that is connected to the probe by a short (~ 5 cm) piece of Teflon tubing. Alternately, the probe is removed and the tube inserted into the hot gas stream that flows from the opening. The sensing limit claimed by the manufacturer is on the order of 0.2 ppm. The presence of more than 5 ppm SO_2 or 5 ppm NH_3 interferes with the HCN measurement, the former causing higher readings while the latter lowers the resulting measurement.

The second method employs an Orion Model 94-06 CN^- ion electrode. Samples are collected using the glass bead method developed for the NH_3 measurements, with either a dilute acid or base used to coat the spheres. Using reasonable sized gas samples, a concentration of HCN in the gas phase of ~ 1 ppm should be measurable. The expected combustion products should not significantly interfere with the CN^- measurement.

The third method, gas chromatography, is used to measure HCN and other nitriles. A Varian 3700 gas chromatograph is equipped with a flame ionization detector, and is interfaced to a Spectra-Physics IV B integrator. The column, 5% Carbowax 400 on Chromasorb T (TFE 6) [18], has been successfully used to measure HCN at low ppm concentrations, and higher nitriles at unknown concentrations from combustion-type mixtures. Sample gases are pulled through a heated 5 cm^3 stainless steel sample loop by a rotary vacuum pump. The probe and sample loop are connected by a heated Teflon line approximately 1 meter in length. A calibration mixture of 106 ppm HCN in N_2 was prepared and stored in a stainless steel cylinder. The gas is periodically checked by mass spectrometer analysis to insure that the concentration of HCN is unchanged. The lower limit of detection for HCN is estimated to be in the 1-5 ppm range.

6. Hydrocarbons, O_2, and N_2 Measurements

A Hewlett-Packard 5750 gas chromatograph with thermal conductivity and flame ionization detectors is used to measure a variety of compounds. The Spectra-Physics integrator is also used in this system. Two columns are used in an automatically switched configuration. One column is filled with Porapak Q, the other with MS-5A molecular sieve. Water is removed in an ice-cooled condenser before introduction into a 0.5 cm^3 sampling loop. A calibration mixture consisting of various hydrocarbons (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8), CO and CO_2, and N_2 is used. Hydrocarbons can be measured in the 0.01% range with reasonable accuracy. Air is also used to calibrate the instrument for O_2 and N_2.

III. SYSTEM CHARACTERIZATION

Prior to examining the reduction of NO by NH_3 addition, the performance of the combustion tunnel was characterized to obtain information on the uniformity and reproducibility of the experimental conditions. The combustion of the fuel oil spray, mixing of the post-combustion gases, and the injection and subsequent reaction of the NH_3 were quantified by measuring temperature and composition profiles in the apparatus in both axial and radial directions.

A significant and frequently mentioned parameter in the following paragraphs is the combustion product temperature at the point of ammonia injection. To avoid any confusion which might result from abbreviating this description to "NH_3 injection temperature" or "injection temperature", the combustion product temperature at the ammonia injection site will hereafter be referred to as T* (Figure 1).

Axial and radial temperature profiles were measured in the reaction and sampling region for a variety of equivalence ratios and flow rates. A typical axial profile is shown in Figure 2. The axial gradients were found to be essentially linear with a slope of approximately 1 K/cm. Typical radial temperature profiles are shown in Figure 3, where the radial distance is measured from the combustor wall to the centerline of the tunnel. These profiles were measured at probe position B (see Figure 1). Radial profiles normally exhibit a shape characteristic of steady-state turbulent pipe flow which demonstrates the well mixed nature of the combustion products downstream of the ammonia injection site. The magnitude of the radial temperature gradient has only a weak dependence on the centerline temperature, but exhibits a much larger dependence on the total mass flow rate. At high throughputs the radial gradient is smaller, but the residence time of molecules in the reaction section is reduced. An intermediate flow rate which results in an average velocity of about 17 m/s is used to yield reasonable radial gradients (20-25 K change from the centerline position to one ∿ 80% of the distance to the combustor wall) while allowing approximately 40 msec reaction time.

Other indications of complete combustion are the absence of large temperature fluctuations, the uniform distribution of combustion products in the reaction section, and the agreement between measured concentrations and those calculated assuming equilibrium conditions.

Concentration profiles of CO and CO_2 were measured in both axial and radial directions. The average concentration measured at $T^* = 1236$ K and $\phi = 0.68$ is 10.54%, within experimental error of the calculated equilibrium value of 10.43%. No significant axial or radial gradients were observed. Measurements of CO concentration profiles were consistent with the CO_2 results, again with no significant gradients present. At equivalence ratios less than 0.95, CO concentrations in the range of 40 to 60 ppm were measured. While these values are higher than the calculated equilibrium values, they are in good agreement with results obtained from similar combustion systems[19]. Measurements of O_2 and H_2O were not as extensive as those for CO and CO_2, but they were within experimental error of their expected equilibrium values. No unburned hydrocarbons were ever detected when combustion occurred under lean conditions.

Nitric oxide levels were also measured before adding nitrogenous compounds to the fuel. This thermal NO concentration was found to be somewhat dependent on the equivalence ratio and T* value. At a fixed temperature and equivalence ratio, however, no concentration gradients were observed in the reaction section. For lean mixtures and T* values from 1100 to 1350 K, NO measurements were in the range of 35-65 ppm. These concentrations are reasonable for the conditions employed and show the expected dependence on equivalence ratio and temperature. Measurements made in the NO_x mode of the chemiluminescent analyzer prior to the addition of NH_3 indicate that NO_2 concentrations are less than 2 ppm.

The equivalence ratio in this study varied from 0.6 to 0.95. Rich combustion was attempted but stable and reproducible burning of a fuel oil spray under rich conditions could not be achieved. Problems arise from two sources when the equivalence ratio exceeds 1.0: the visible flame length increases until it extends into the reaction and sampling region, and significant sooting occurs throughout the combustion region. This restriction is not severe, since practical combustion systems operate under lean-burning conditions.

A. NH_3 Mixing Characterization

The rapid and thorough mixing of the NH_3/N_2 mixture with the combustion exhaust is crucial in the control of the selective reduction process. Mixing characteristics were determined by flowing NO/N_2 mixtures through the NH_3 injectors. It was previously determined that less than 4% of the NO reacted when passed through the flame zone of a lean flame[14]. It can thus be expected that any NO introduced through the NH_3 injectors will remain unreacted as it passes through the sampling region. After initial adjustment of the injector positions under cold flow conditions, final adjustments are made under combustion conditions.

One set of these measurements is presented in Table II. The measured NO concentrations fluctuated randomly around an average value with the range of these fluctuations reported in the last column of the table. Injectors were adjusted until all NO readings downstream of probe position A were within 10% of each other. This method is extremely sensitive to injector malfunctions or misalignment. The ease with which NO measurements can be made allows for routine checks on the mixing performance.

B. Reduction of NO by NH_3

It is important to discuss the meaning of the term initial NO concentration since there is much confusion regarding this term in the literature. There are two NO sources in our experiments: one is the result of prototype fuel nitrogen compounds, and the other is the thermal NO formed during the combustion process. Two different prototype fuel nitrogen compounds, NO and pyridine, were used in this study. The term initial NO concentration, $[NO_i]$, will be used here to designate the total NO concentration measured in the reaction section when no NH_3 is added. This concentration can be monitored at the final probe station since measurements of NO concentrations exhibited no axial or radical gradients for the conditions studied.

The experiments were designed to determine the effects of changing experimental variables such as the equivalence ratio, the combustion product temperature (T*), the amount of NH_3 added, and the amount and type of fuel nitrogen. Product emissions were determined for the range of variables investigated. Particular emphasis was placed upon monitoring "odd nitrogen" compounds (nitrogenous species other than N_2, NO,

NO_2 and NH_3). The equivalence ratios given in the following figures were calculated from the measured flows of the reactants. Because of the uncertainties associated with the rotameters, the error in the equivalence ratio is estimated to be ±5%, or approximately ±0.05. The reproducibility in the metering system is much better, as evidenced by our ability to closely reproduce (±5K) a T* value for a given set of flow conditions. The amount of NH_3 added in these experiments is normalized to the initial NO concentration, and is defined as $\beta = [NH_3]_i/[NO]_i$. The uncertainty in a β value is estimated to be ±3%. The concentration of fuel nitrogen when pyridine is used is calculated from the physical properties of the pyridine which is added volumetrically to the fuel supply. The calculated values presented have an estimated error of ±5%. Elemental analyses were also performed on selected samples to confirm the fuel composition[20].

Experiments were performed with NH_3 injection to insure that the residence time in the reaction section was sufficient to allow complete reaction before the gases entered the exhaust line. Axial and radial NO and NH_3 concentrations were monitored in order to determine reaction progress. One set of centerline measurements, performed at $\phi = 0.83$ and T* = 1224K, is presented in Figures 4 and 5. For the range of conditions employed in this study, the reaction between NO and NH_3 is essentially complete (>95%) by the final probe station, with most (>85%) of the ultimate NO reduction occurring by probe position B, 33 cm downstream of the NH_3 injectors. Ammonia concentration profiles corroborate these results. Measurements of this type allow us to present measurements only from probe position D with confidence that the reduction reaction is complete.

IV. RESULTS

A. Fuel Nitrogen: NO

The first set of experiments on the reduction process employed NO, injected into the air supply upstream of the fuel nozzle, as the prototype fuel nitrogen compound. The NO was metered until the initial NO concentration downstream, $[NO]_i$, was measured to be 500 ± 10 ppm. The amount of NO decomposition through the combustion zone was determined by first setting the NO flow as described above, and then introducing the same flow of NO through the NH_3 injectors while monitoring the NO level at the final probe station. The amount of NO that survived through the flame zone depended markedly on the equivalence ratio, with only small variations for different T* values. Survival of NO ranged from $\sim$78% at $\phi = 0.95$ to $\sim$95% at $\phi = 0.83$.

Figure 6 shows the results of the reduction of NO by NH_3 at a fixed temperature (T* = 1120 K) and equivalence ratio ($\phi = 0.83$) as a function of β. The final NO concentration, $[NO]_f$, is defined as the measured value of NO at the centerline of the final probe station when NH_3 is added to the combustion products. Two trends are observed which are common to all experiments involving NO or pyridine addition to the fuel supply: as more ammonia is injected, more NO reduction occurs, even at β values greater than 4.0; and the ammonia breakthrough increases with increasing β.

Determination of the temperature at which maximum NO reduction occurs at a fixed equivalence ratio is shown in Figures 7, 8 and 9. The reduction process shows a dependence on both the ammonia concentration and the equivalence ratio. At a fixed equivalence ratio, the optimum reduction temperature increases with increasing β. At high ϕ values this trend is less obvious, and it becomes more apparent at more lean conditions. The range for the optimum reduction temperature varied from ∿1150 to values in excess of 1250K. The fraction of NO reduced, $[NO]_f/[NO]_i$, depends on T* and β but does not vary significantly with changes in ϕ. For example, at $\beta \simeq 2.5$, the maximum NO reductions, while occuring at different T* values, is ∿0.7 for all three equivalence ratios.

Ammonia breakthrough, the concentration of ammonia measured at the final probe station, is presented in Figure 10 for an equivalence ratio of 0.83. The results show that the temperature is the dominant factor in determining the concentration of ammonia remaining after the reduction process. The measured values were obtained using the chemiluminescent technique which were periodically compared with measurements made with the sodium phenolate techniques. For the range of conditions covered in Figure 10, the fraction of NO remaining after reduction ranges from ∿0.1 to 0.8, corresponding to concentrations of 50 to 400 ppm. The level of NO reduction appears to have no effect on the ammonia breakthrough, additional evidence that the reaction is complete by the final probe station. Figure 11 shows ammonia breakthrough for the three different equivalence ratios, measured by the CLA, sodium phenolate, and specific ion electrode methods. The agreement between the techniques is within the experimental error of the measurements, and is a strong indication that no interfering species (other nitrogenous compounds besides N_2, NO, and NH_3) are present in any measurable quantities in this system. No significant differences in the ammonia concentrations were seen at the different equivalence ratios, suggesting that the oxygen concentration is not a limiting factor for the reduction reactions in lean combustion product gases.

Numerous attempts were made to measure HCN or other "odd nitrogen" species, employing all of the methods described in the experimental section. Concentrations of HCN were found to be below 1 ppm (the lowest detectable concentration) for all conditions studied, even when β values >4.0 were used with temperature values that allowed for only slight reduction of NO concentrations. There was no evidence for any other "odd nitrogen" compound measurable on the gas chromatographic and gas chromatographic/mass spectrometric equipment. These results corroborate the ammonia measurements that show no measurable concentrations of interfering nitrogen compounds. It should be noted that no hydrocarbons or H_2 were observed in the product gases during these experiments.

Because no measurable quantities of "odd nitrogen" species were observed for the conditions, experiments were undertaken to show that nitrogenous species could be measured at low concentrations when appropriate conditions were provided. Calibration gases were detected and measured successfully, but the combustion product conditions are severely different from the cold flow calibration conditions. Rich combustion of the fuel oil to provide hydrocarbons in the product gas flow was not feasibile due to reproducibility and stability problems arising from excessive flame length and sooting. To simulate combustion where hydrocarbons or hydrocarbon fragments are present, propane gas was injected into the combustion tunnel downstream of the visible fuel oil/air flame. Under these conditions, HCN was observed in the 1 to 10 ppm range, and four resolved peaks were detected on the gas chromatograph. Retention times and peak width were recorded, but no attempt was made to identify these compounds. Under normal conditions these peaks were never observed.

B. Fuel Nitrogen: Pyridine

In order to simulate the effect of other nitrogenous species commonly found in fuels we have studied the reduction process when pyridine is added to the fuel oil as a prototype fuel nitrogen compound. The pyridine is added volumetrically and is thoroughly mixed with the oil prior to spraying the fuel into the combustion tunnel. While a constant amount of pyridine is added to the fuel, the resulting NO concentration, $[NO]_i$, changes as a function of temperature and equivalence ratio of the reacting mixture. This is due to the incomplete conversion of the fuel nitrogen to NO as it passes through the flame, and the production of NO by thermal NO reaction mechanisms. Complete conversion of the nitrogen in a 4.93% by volume pyridine in fuel oil mixture would result in an NO concentration of approximately 1200 ppm at an equivalence ratio of 0.89. Table IV lists the conversion efficiencies measured at various temperatures and equivalence ratios. The conversion percentages are corrected for the thermal NO produced when the fuel oil alone is burned under the same combustion conditions. Since pyridine itself is a fuel, the equivalence ratio should be corrected for its presence. However, at the concentrations used in this study, the change in the equivalence ratio with pyridine is well within the experimental error in the ratio introduced by the uncertainties in the flow metering. The NO concentrations when no ammonia is added range from 495 to 590 ppm. All NO reduction data are normalized to the measured initial NO concentrations.

With the pyridine-doped fuel, no visible changes were observed in the flame, or in the measured temperatures; however, low concentrations of an oxidizable nitrogen compound were observed in the NO_x mode of the chemiluminescent analyzer. Measured values were typically 5±5 ppm. Since the measured concentration is a difference between the NO concentration and the NO plus oxidizable nitrogen compounds concentration, there is large uncertainty in the measured value which is estimated to be as large as the measured value itself. No NH_3 or HCN could be detected by the other methods employed, indicating that the observed species is most probably NO_2.

The temperature dependence of the reduction process is shown in Figures 12, 13, and 14 for equivalence ratios of 0.78, 0.89, and 0.95. These measurements essentially duplicate the conditions studied when NO was used as the fuel nitrogen compound. The results of the ammonia addition on the reduction process are substantially the same as described previously. The extent of NO reduction, and optimum reaction conditions are not significantly different for the two different fuel nitrogen compounds. It is important to note, however, that the more extensive data for the pyridine doped fuel case permit greater precision in determining the optimum reduction conditions.

A portion of the ammonia breakthrough results are presented in Figure 15. These results are for the three different equivalence ratios at approximately the same β values (4.2 - 4.4). The measurements, made over a month long period of time and with the three different measurement techniques, illustrate the agreement and the estimated uncertainties in the measured quantities. These results are in good agreement with the ammonia breakthrough measurements presented in the previous section, again indicating that the type of fuel nitrogen compound used does not effect the reduction process for lean combustion, and that the NH_3 breakthrough is independent of the equivalence ratio.

Numerous attempts were again made to measure the presence of any other nitrogenous species. Apart from the small concentrations of the compound presumed to be NO_2 that were observed and discussed previously, no measurable quantities of these "odd nitrogen" species were detected for the range of experimental conditions studied. The agreement between the results using NO or pyridine as the fuel nitrogen species is strong evidence that no significant quantities of unobserved nitrogenous species are generated when pyridine is admixed with the fuel oil and then burned. Consistent with our other results, no hydrocarbons were observed in the combustion exhaust product gases.

V. DISCUSSION

The reduction of NO by NH_3 addition has been studied over a range of temperatures, equivalence ratios, amounts of NH_3 injected, and types and concentrations of fuel nitrogen. One of the most important results of this study is the absence of appreciable concentrations of nitrogenous species other than N_2, NO, NO_2, and NH_3 when the reduction occurs under lean conditions. A conservative upper limit for the total concentration of these "odd nitrogen" species is 5 ppm. We set this limit based on the absence of compounds measured directly by techniques such as GC, GC/MS, and wet chemical methods which are sensitive to nitrogenous compounds, and the agreement between the different analytical techniques used to measure NO, NO_x, and NH_3. As the different methods employed have widely different interferences, an appreciable concentration of an unobserved "odd nitrogen" compound could be detected as a difference in the measured concentration of NO_x or NH_3. Nitrogen compounds that are most certainly absent include HCN, nitriles, and amines. The carbon skeleton of nitriles or amines would have been detected by the flame ionization detector. The absence of hydrocarbons or H_2 in the exhaust gases corroborates these results. Lyon and Longwell[2] speculate that HCN is not present unless hydrocarbons are present, and our own experimental results have verified their speculation. Muzio et al.[7] found no HCN was generated when NH_3 was introduced into the exhaust gases of a coal-fired combustor. The compound N_2O is not detectable in the CLA. Nitrous oxide is separable on Poropak Q but was not detected; however, we did not establish the sensitivity of the thermal conductivity detector to N_2O. In his initial flow reactor study, Lyon[3] found that N_2O was not a product of the $O_2/NO/NH_3$ reaction, and Muzio et al.[6] never measured it as a reaction product and concluded that if it were present, it would be in concentrations less than the limit of detectability (50 ppm).

The extent of the NO reduction and the optimum conditions measured are qualitatively in agreement with results obtained previously by Muzio et al.[6] but differ somewhat quantitatively. The differences reported in the optimum temperatures (generally $< 50K$) most probably reflect differences in experimental design (temperature gradients, size of combustor, residence time in the reaction zone), method of ammonia injection, and measurement and definition of the ammonia injection temperature (T* in this study). In addition, the observed dependence of the optimum temperature on β and the equivalence ratio can also partially account for the discrepancies.

The differences in the magnitude of the NO reduction for a set of experimental conditions is more puzzling. Muzio et al.[6] and Lyon and Benn[4] report greater reductions of NO for a fixed β at the optimum temperature than we observe. It is important to note that the coal fired experiments and commercial demonstrations[12] of the Thermal $DeNO_x$ process have not achieved reductions of the magnitude of the earlier investigations.

We have examined our own results to determine if an explanation for the differences in results can be established. Experimental evidence has been given to establish that the NO and NH_3 reactions are complete in our experiment. This evidence is provided in Figures 4 and 5 which illustrate that the NO and NH_3 profiles are flat between the two terminal probe stations. The oxidation of NH_3 occurs in competition with the reduction of NO, and is enhanced over reduction at temperatures in excess of the optimum temperatures. Both competitive mechanisms are inhibited as the temperature is reduced. Reaction times are significantly influenced by the temperature field and by the progress of precursor reactions. Our temperature gradients are less than Muzio et al.[6] and we have demonstrated experimentally that NH_3 is injected without decomposition and that is mixed into the flow field uniformly before the first probe station. We have also ascertained that the extent of selective reduction is independent of radial position.

At T* values of 1300K, the final NH_3 concentration is negligible at $\beta < 2.6$ at all equivalence ratios and this provides additional information that the reaction is complete in the residence time available which is less than 40 msec. It is also true that the NH_3 oxidation mechanism is more competitive at the higher temperature. At T* of 1240K, both NO and NH_3 are present at the final probe station and the axial concentration profiles indicate complete reaction. A plausible explanation consistent with the data is that the reaction is completed through thermal quenching. If NH_3 disappearance is dominated by NH_2 formation via the reaction

$$NH_3 + OH \rightarrow NH_2 + H_2O,$$

it is important to compare the rate of NH_2 formation to the cooling rate which ensues after NH_3 addition to the combustor. Although the reaction rate for the NH_3 + OH reaction was recently measured by Silver and Kolb[21] for temperatures over the range 294-1075K, the rate of NH_3 disappearance cannot be evaluated without a knowledge of the OH concentration. The cooling rate can be estimated by assuming a linear axial gradient, and is approximately 1500K/sec. The effect of cooling rate should be ascertained experimentally. Ammonia oxidation is suppressed at 1120K. Consideration of the initial NH_3 concentration and the extent of NH reduction reveals that the ammonia breakthrough is approximately quantitative. Radical concentrations at this temperature are insufficient to quantitatively reduce the NO or allow for appreciable oxidation of the NH_3.

It is difficult to compare our results directly with the experimental studies of Lyon and his colleagues[3-5] or with the computational studies[8,9] which have modelled experimental results. Lyon and colleagues have studied the selective reduction of NO and NH_3 oxidation under isothermal conditions in a plug flow reactor. There are no products of combustion present. Modelling studies have been focused upon investigation of the competitive reactions under isothermal conditions for fully equilibrated products of combustion as initial conditions. Our own CO measurements which are in excess of equilibrium concentrations provide indirect evidence that OH concentrations prior to NH_3 addition are in excess of equilibrium values, and this could have an appreciable effect on the net rate of the selective reduction of NO.

The method of ammonia injection in our apparatus was extensively studied, with the conclusion that rapid and complete mixing was indeed occurring. Reaction of the ammonia as it passes through the injector system, yielding a lower concentration of ammonia than calculated, was also considered, but we have experimentally determined that no reaction occurred in NH_3 - N_2 mixtures when passed through hot quartz tubing similar to the injectors. Lyon and Benn[4] also demonstrated that hot quartz had no effect on the reaction rates of $O_2/NO/NH_3$ reactions. Catalytic effects due to probes, thermocouples and walls are more difficult to assess in the different experimental environments.

Additional experimental data are required to further assess the effects of residence time, temperature gradients and non-equilibrium combustion product mixtures. Modelling efforts could also be improved by well-documented experimental results. Experiments which provide kinetic data for elementary reactions important in the complex $O_2/NO/NH_3$ mechanism in the temperature range 1000-1500K are most certainly warranted and would be invaluable in improving our understanding of the selective reduction of NO by NH_3.

ACKNOWLEDGEMENT

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REFERENCES

1. Lyon, R.K., U.S. Patent No. 3,900,554, August 1975.
2. Lyon, R.K. and Longwell, J.P., EPRI NO_x Control Technology Seminar, San Francisco, CA, 1976.
3. Lyon, R.K., Int. J. Chem. Kin., 8, 315, 1976.
4. Lyon, R.K. and Benn, D.J., Seventeenth Symposium (International) on Combustion, 601-610, 1979.
5. Lyon, R.K., Hardy, J.E. and Benn, D.J., Paper No. WSS/CI 78-51, presented at the Fall Meeting of the Western States Section of The Combustion Institute, 1978.
6. Muzio, L.J., Arand, J.K. and Teixeira, D.P., Sixteenth Symposium (International) on Combustion, 199-208, 1977.
7. Muzio, L.J., Arand, J.K. and Maloney, K.L., Report No. KVB-15500-717B, 1978.
8. Saliman, S. and Hanson, R.K. Combustion Science and Technology, 23, 225, 1980.
9. Miller, J.A., Branch, M.C., Kee, R.J. To be published in Combustion and Flame, 1981.
10. Banna, S.M., and Branch, M.C., Paper No. WSS/CI 78-50, presented at the Fall Meeting of the Western States Section of The Combustion Institute, 1978.
11. Lewis, P.F., Brogan, T., Johnson, D.M., Stevens, F.M., and Kothandaraman, G. Paper presented at the Fall Meeting of the Eastern States Section of The Combustion Institute, 1980.
12. EPA/IERL-RTP Report No. EPA-600/7-79-079, March 1979.
13. EPA/IERL-RTP Report No. EPA-600/7-79-111, May 1979.
14. Brown, N.J., Sawyer, R.F., and Eitzen, T.S. Report to the California Air Resources Board, 1979.
15. Basden, K.A., private communication.
16. Colket III, M.B., Chiappetta, L.J., Zabielski, M.F., Seery, D.J., Guile, R.N., and Dodge, L.G. To be published in the Eighteenth Symposium (International) on Combustion, 1981.
17. Matthews, R.D., Sawyer, R.F., and Schefer, R.W., Environmental Science and Technology, 11, 1092, 1977.

18. Myerson, A.L. Fifteenth Symposium (International) on Combustion, 1085, 1975.

19. Starkman, E.S. Combustion Generated Air Pollution. Plenum Press, New York, 1971.

20. Analyses were performed by the Microchemical Analysis Laboratory, University of Calfornia, Berkeley.

21. Silver, J.A., and Kolb, C.E. Chem. Phys. Lett. 75, 1, 191, 1980.

LIST OF TABLES

LIST OF FIGURES

TABLE I

NH_3 MEASUREMENTS

T* (K)	ϕ	[NO] (ppm)	$[NH_3]$ (ppm) a) NO_x	$[NH_3]$ (ppm) b) PHENOLATE
1100	.83	320	677	653
1169	.95	117	318	352
1229	.78	29	340	362
1233	.74	265	27	32
		31	249	274
1235	.73	350	8	12
		49	2	1
300	0	0	810	788

a) measured by chemiluminescent method

b) measured by the sodium phenolate method

TABLE II

CO_2 Concentration Profiles

Probe Axial Position	Probe Radial Position†	$[CO_2]$ Dry, Volume %
D	CL	10.52
C	CL	10.55
B	CL	10.52
D	CL - 1/2	10.49
D	CL	10.52
D	CL + 1/2	10.56
D	CL + 3/4	10.57
D	CL - 3/4	10.55

Average $[CO_2]$ = 10.54 ± .03%

$T^* = 1236$ K $\phi = 0.68$

† Radial probe position centerline is CL; fractions indicate fraction of distance from centerline to combustor wall.

TABLE III

NH_3 Injection System Mixing Characteristics

Probe Axial Position	Probe Radial Position	[NO] ppm†
B	CL	600-620
	CL + 1/2	610-630
	CL - 1/2	620-640
	CL - 3/4	590-610
	CL + 3/4	620-650
C	CL	620-630
	CL + 1/2	600-610
	CL + 3/4	600-620
	CL - 1/2	590-610
	CL - 3/4	570-580
D	CL	600-620
	CL - 1/2	610-620
	CL + 3/8	600-610
	CL + 3/4	580-590
	CL + 1/2	590-610

† Range of values indicate concentrations measured over ~ 1 min. Fluctuations measured over the same time with calibration gases were ± 1 ppm.

Operating Conditions: $\phi = 0.89$, $T^* = 1220$ K

TABLE IV

ϕ	T*		$[NO]_i$ [a]	%
	mV	Corrected	ppm	Conversion to NO[b]
0.78	33.8	1103	545 - 555	42
	34.7	1128	560 - 565	43
	36.0	1147	570 - 575	44
	36.8	1170	580 - 585	45
	37.7	1197	580 - 585	45
	38.6	1224	585 - 590	46
0.89	37.0	1176	570 - 580	45
	37.4	1188	560 - 580	44
	37.5	1191	565 - 575	44
	37.7	1197	570 - 580	45
	38.0	1206	565 - 580	44
	38.2	1212	565 - 580	44
	38.3	1215	575 - 590	45
	39.8	1261	560 - 590	44
0.95	37.2	1182	530 - 540	41
	37.6	1194	540 - 550	42
	38.7	1227	540 - 550	42
	39.5	1252	530 - 540	41
	40.6	1289	530 - 545	41
	41.3	1315	515 - 535	40

a) measured at final probe station
b) thermal NO is subtracted when calculating conversion efficiencies

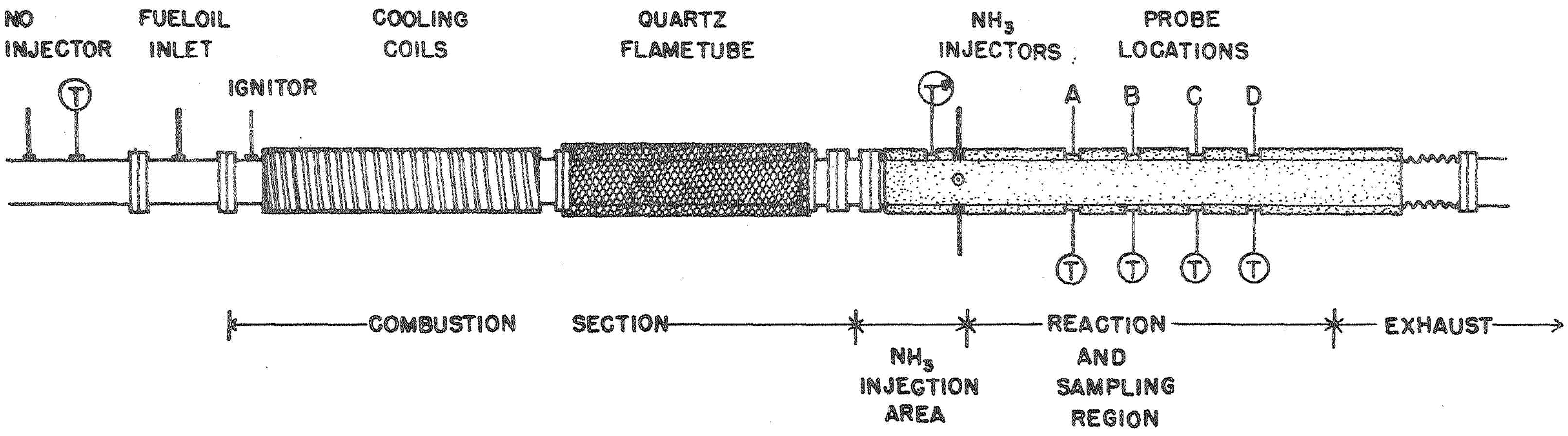
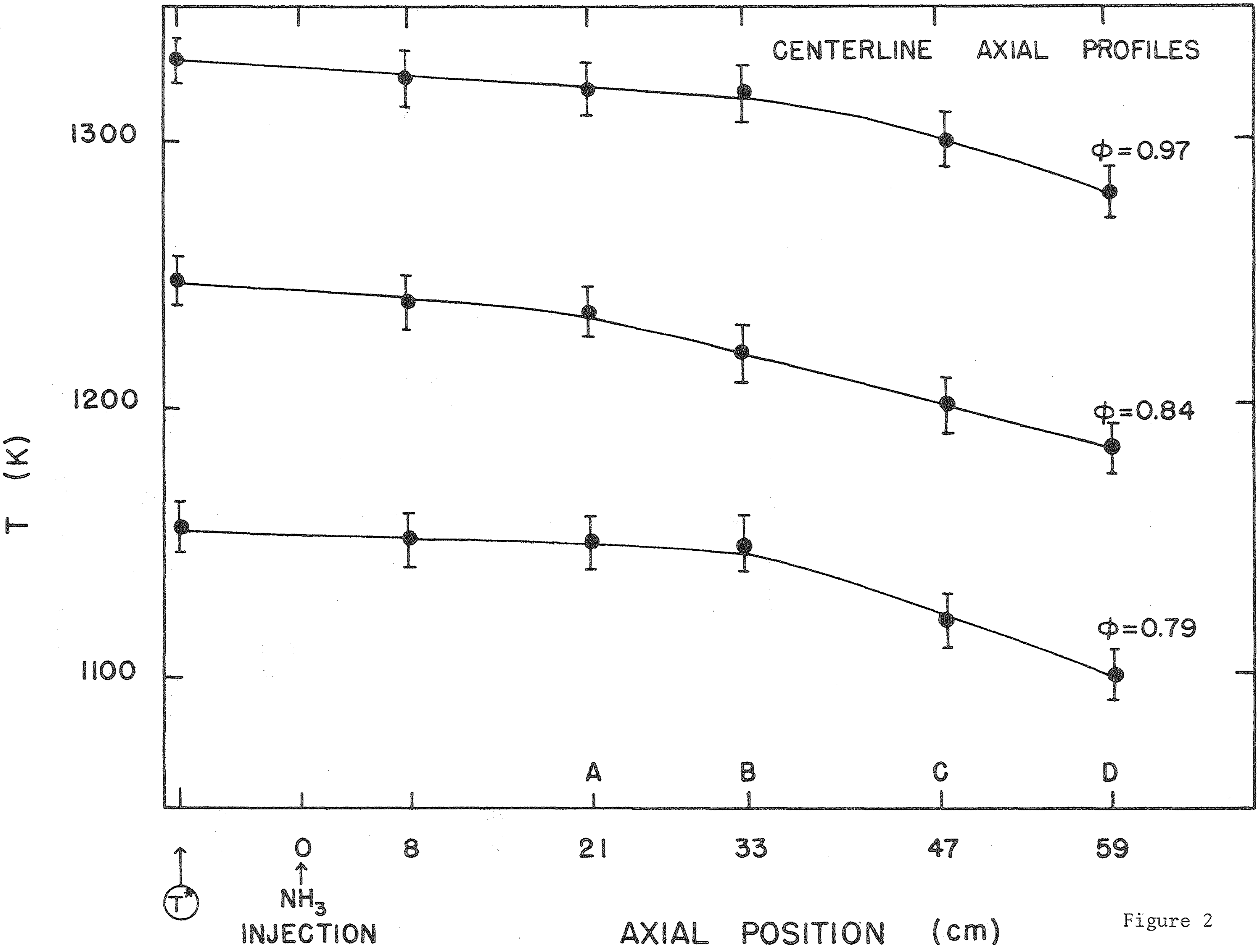

NO INJECTOR
FUELOIL INLET
IGNITOR
COOLING COILS
QUARTZ FLAMETUBE
NH_3 INJECTORS
PROBE LOCATIONS
T
A
B
C
D
T
T
T
T
T
COMBUSTION SECTION
NH_3 INJECTION AREA
REACTION AND SAMPLING REGION
EXHAUST

Figure 1



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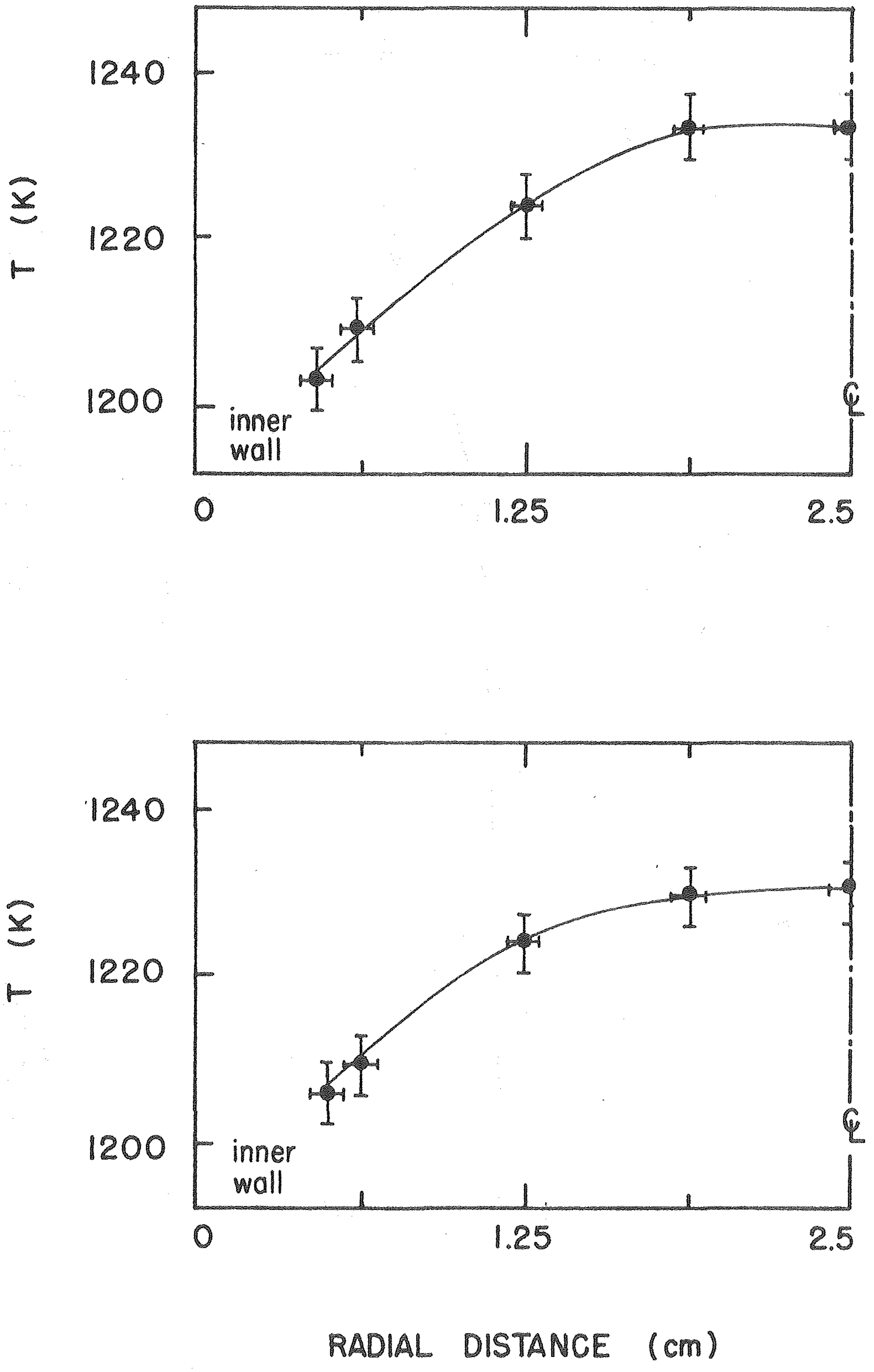

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Figure 3

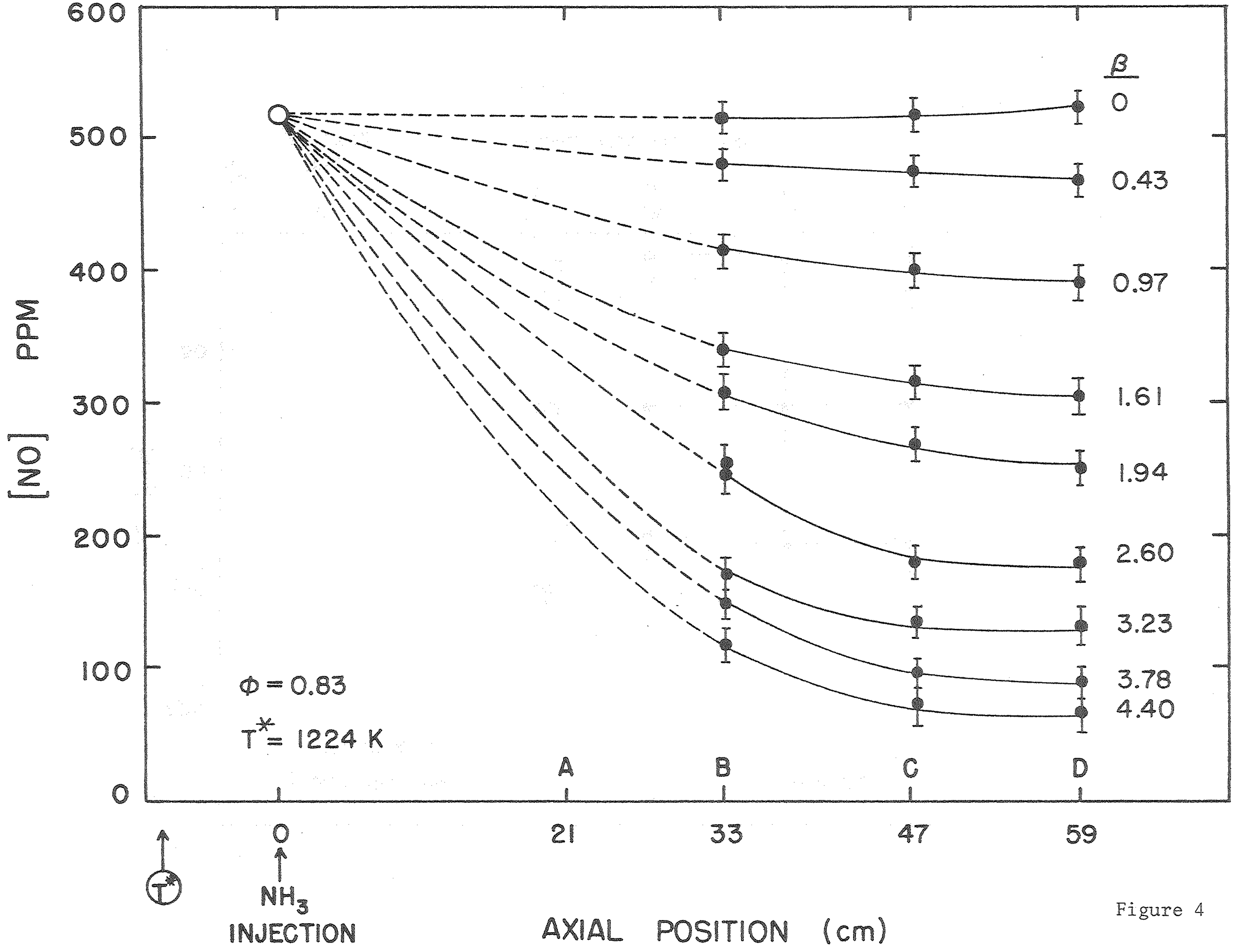

Figure 4

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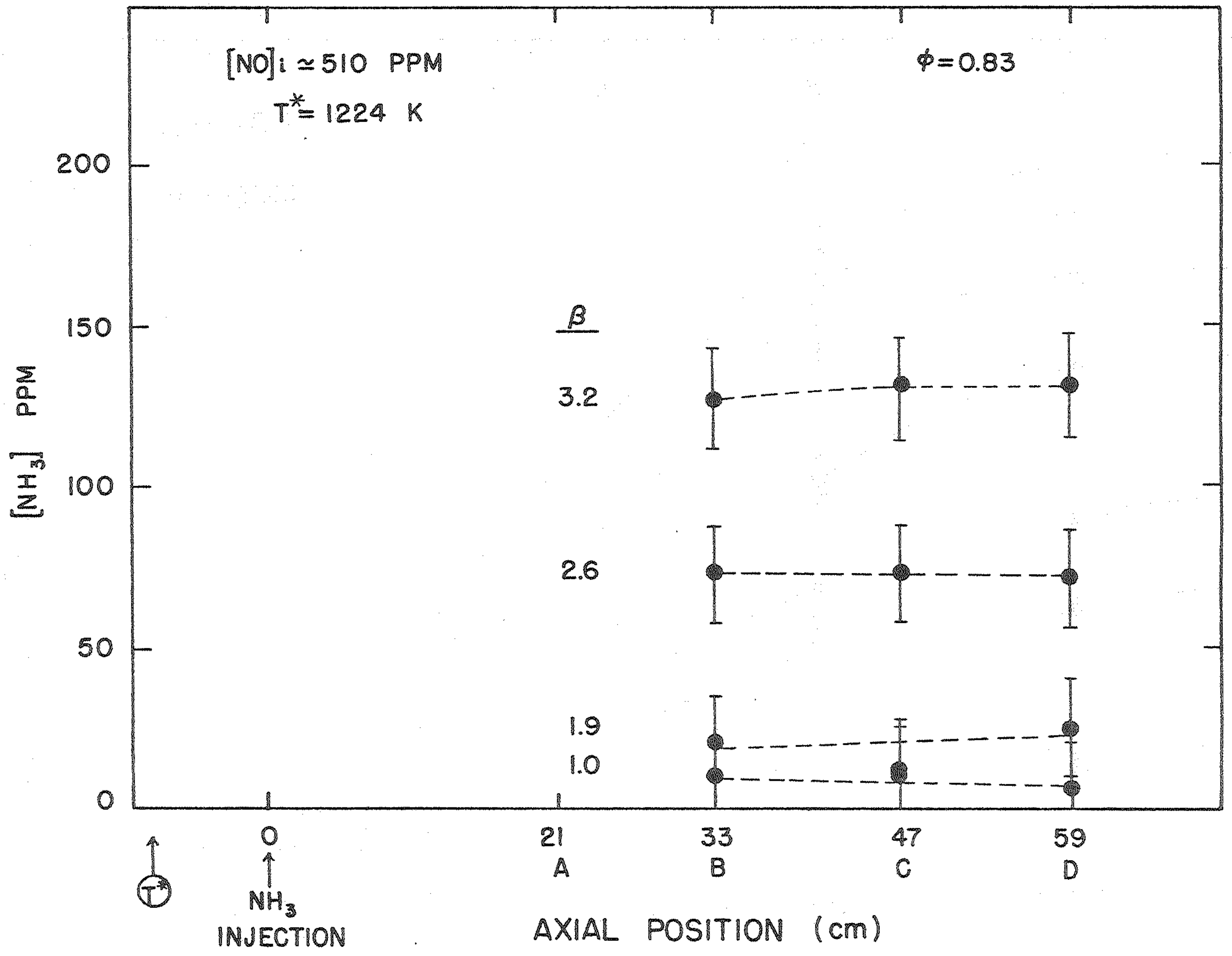

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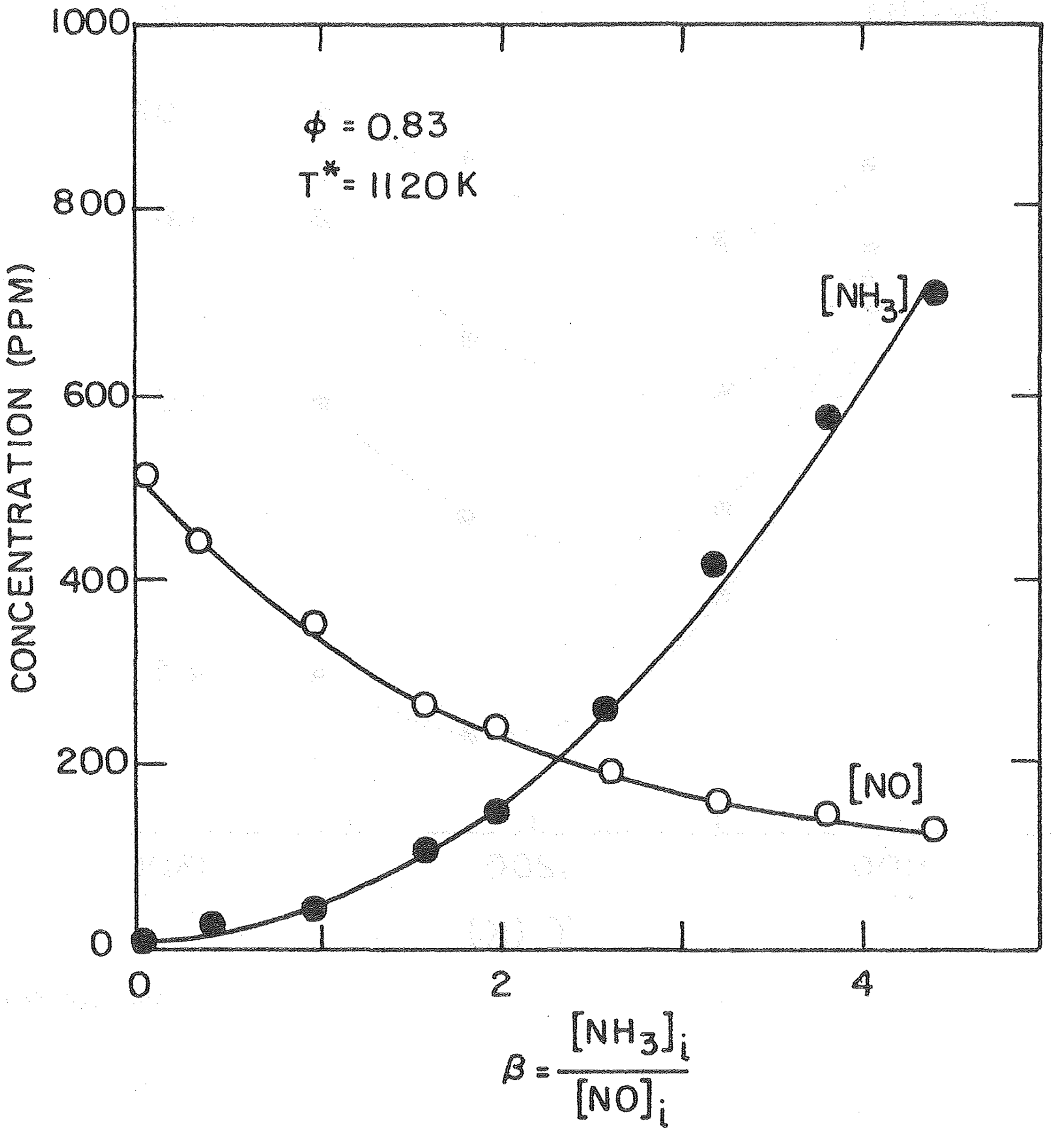

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Figure 6

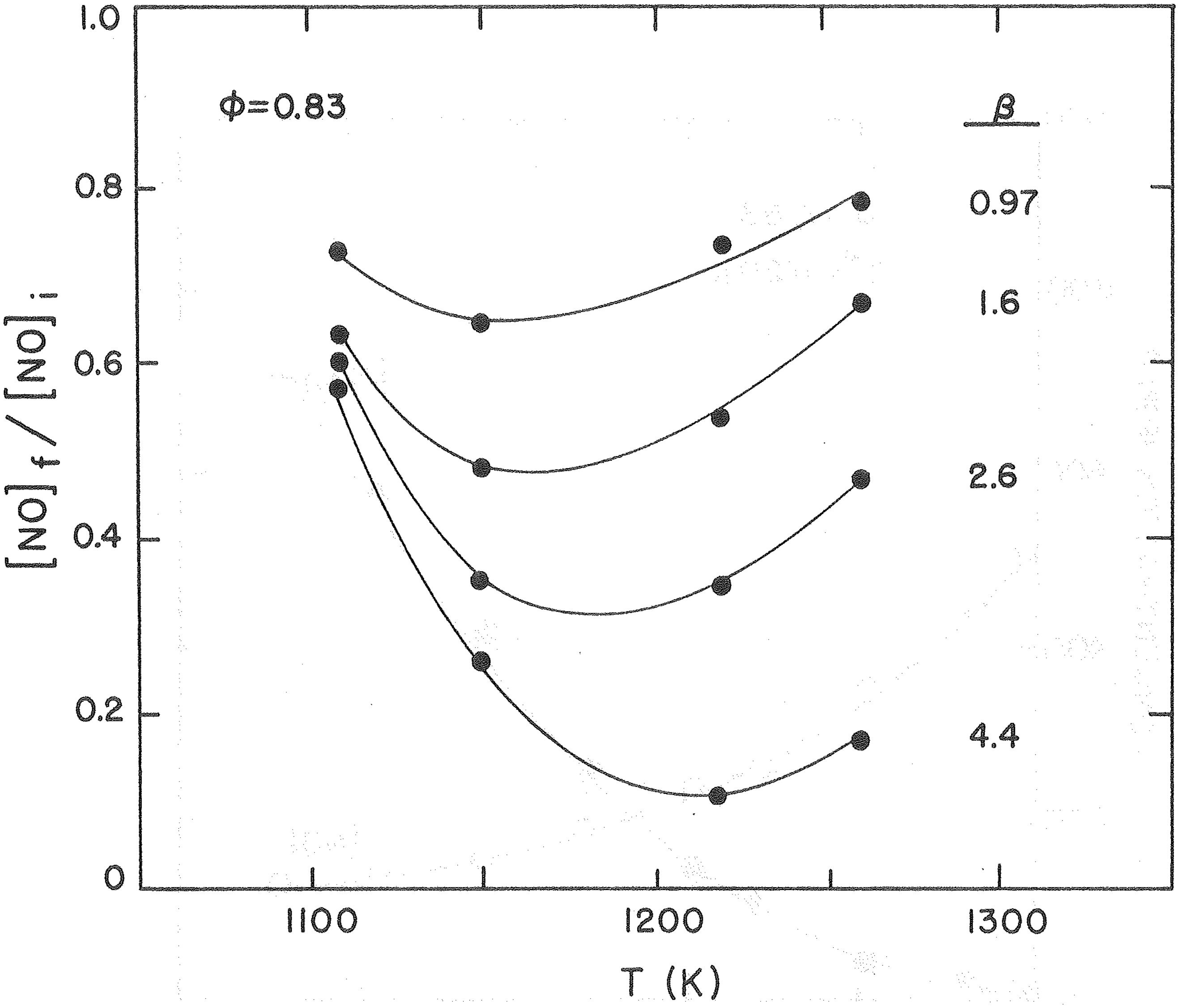

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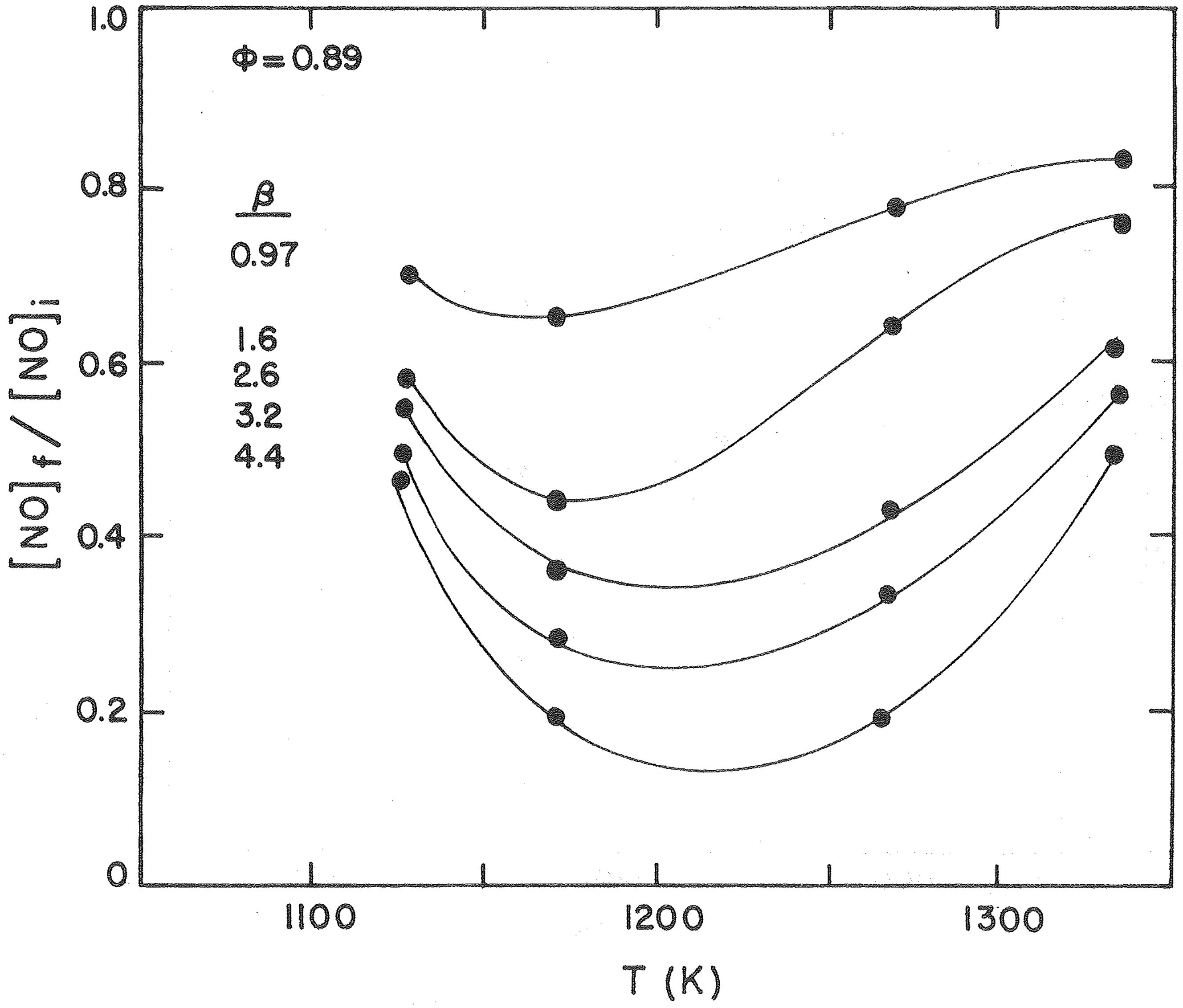
Figure 7



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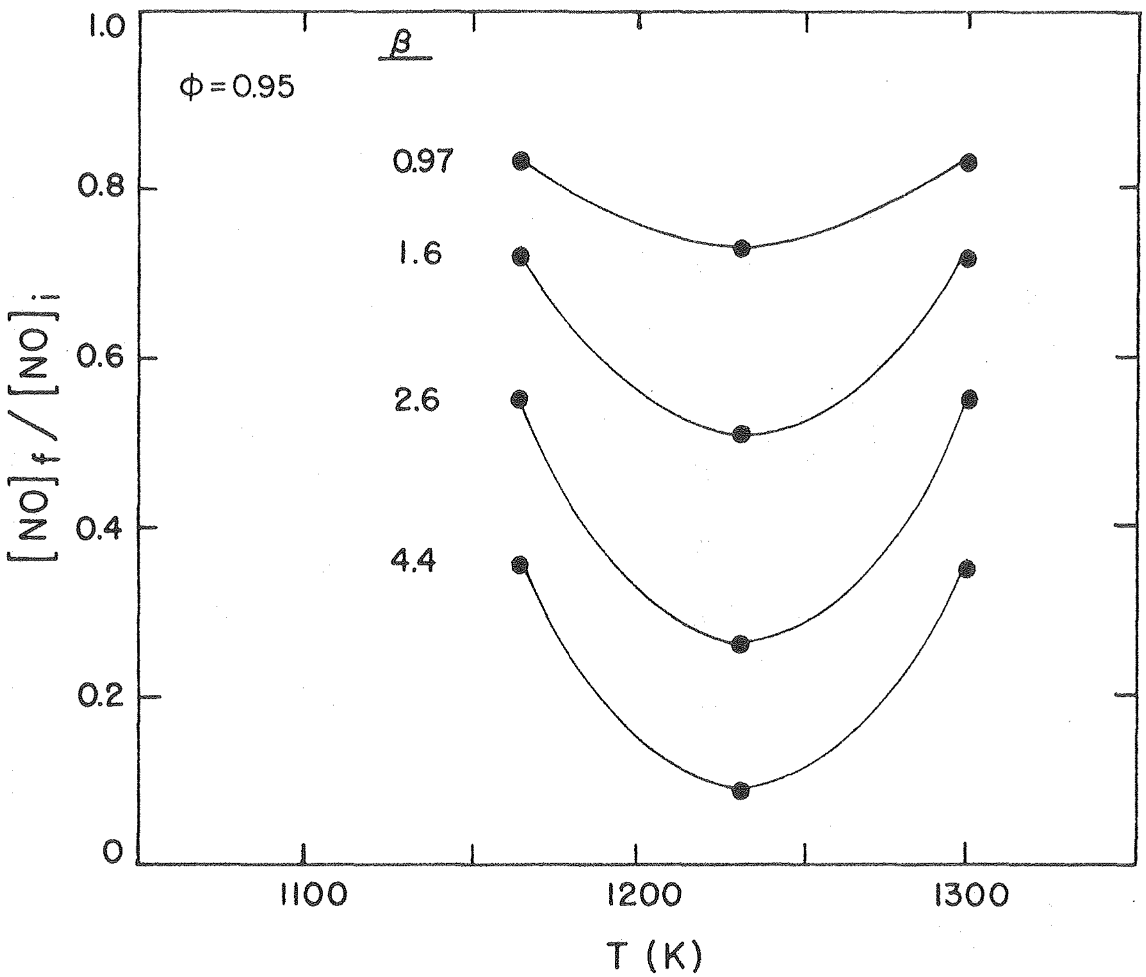

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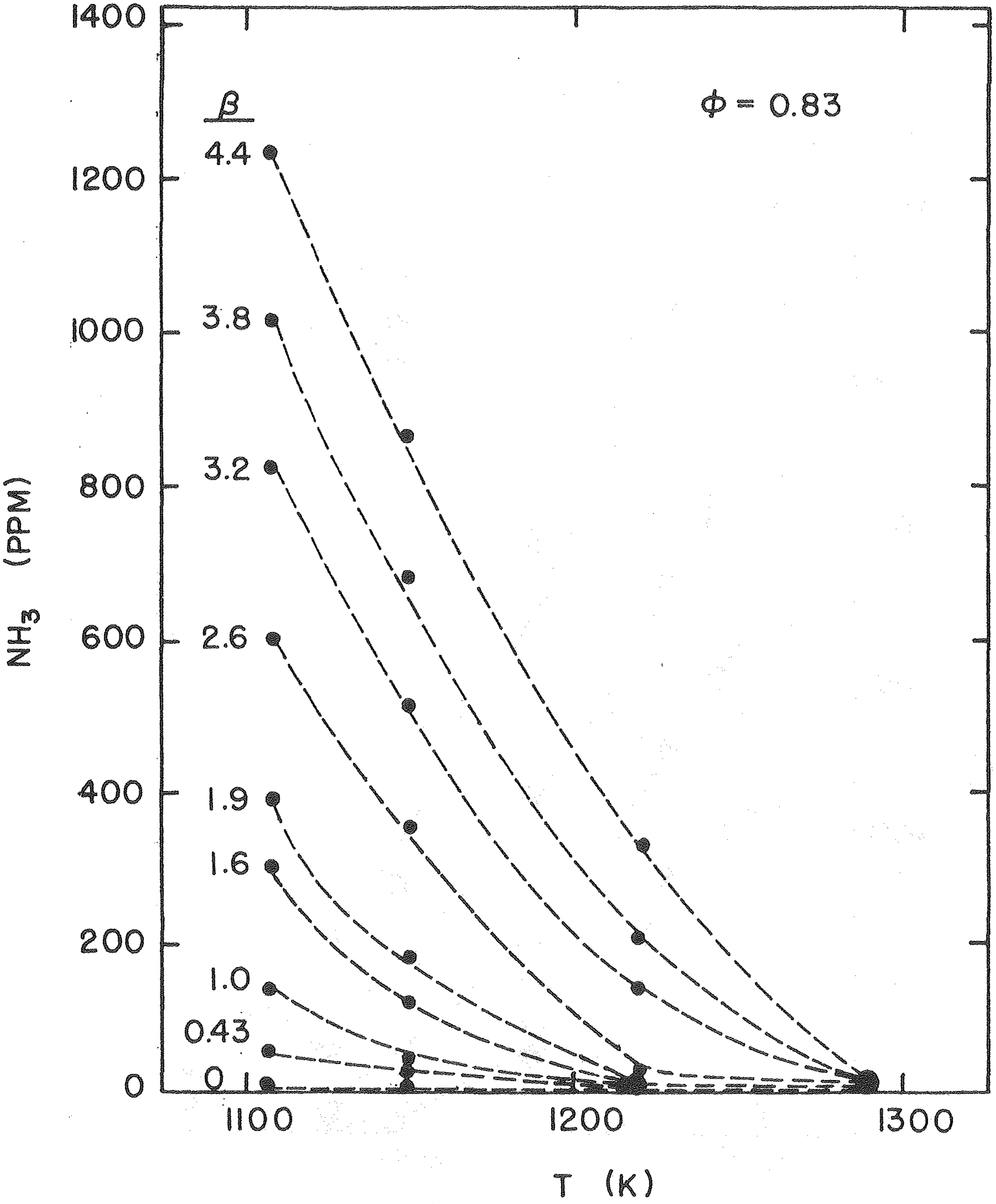
Figure 9


1400
1200
1000
800
600
400
200
0
NH₃ (PPM)
1100
1200
1300
T (K)
β
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3.8
3.2
2.6
1.9
1.6
1.0
0.43
0.1
φ = 0.83

Figure 10

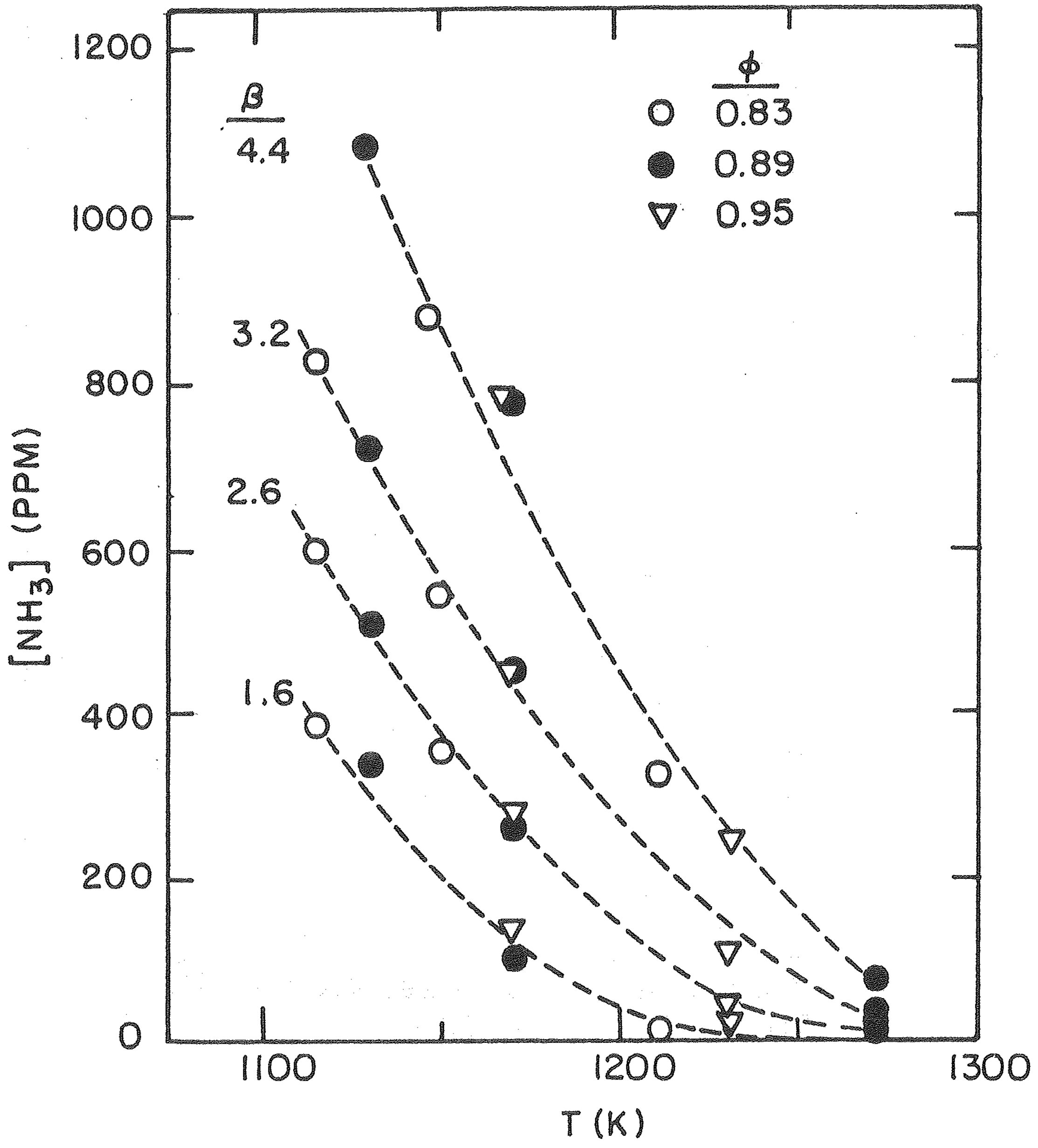

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Figure 11

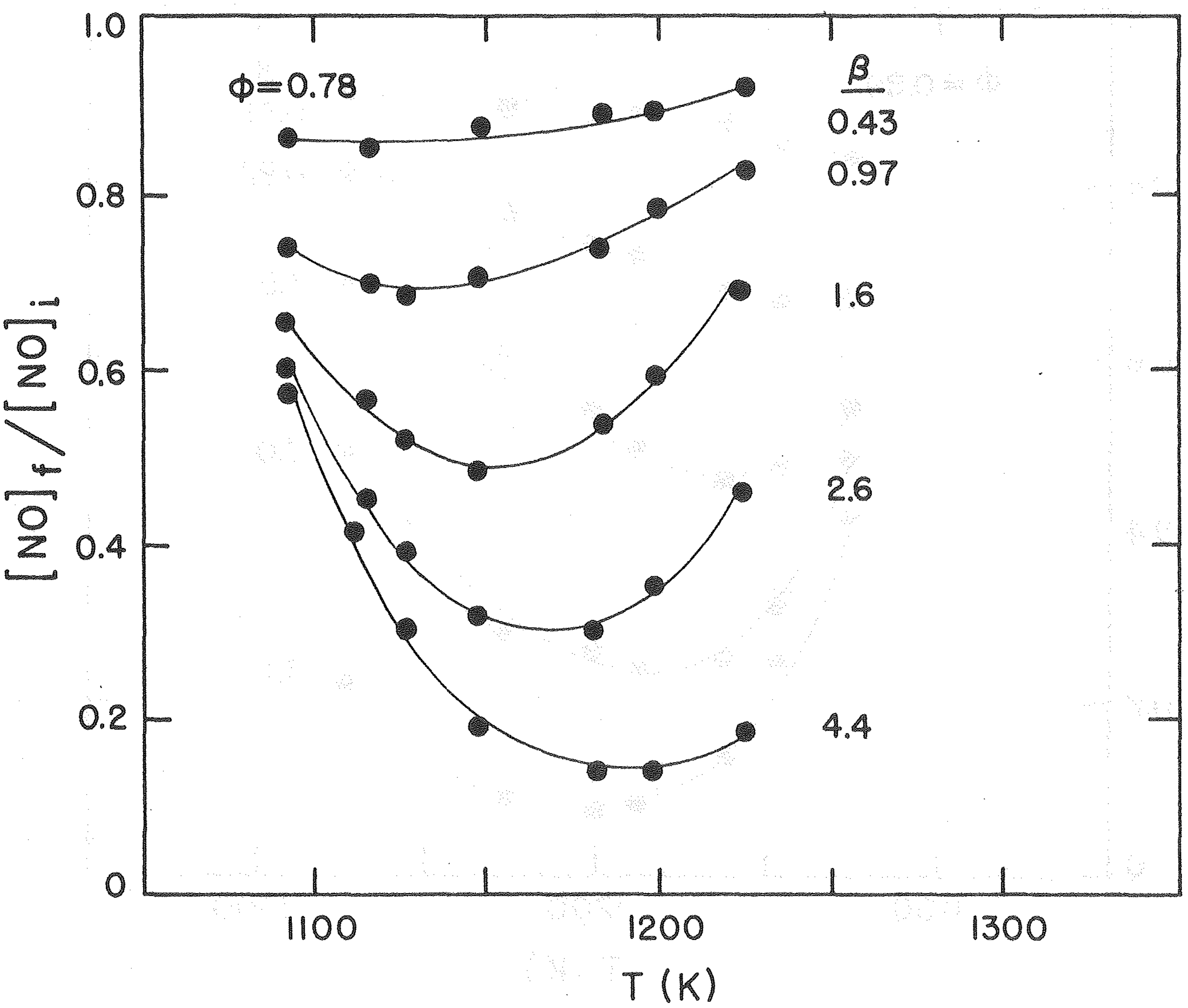

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Figure 12

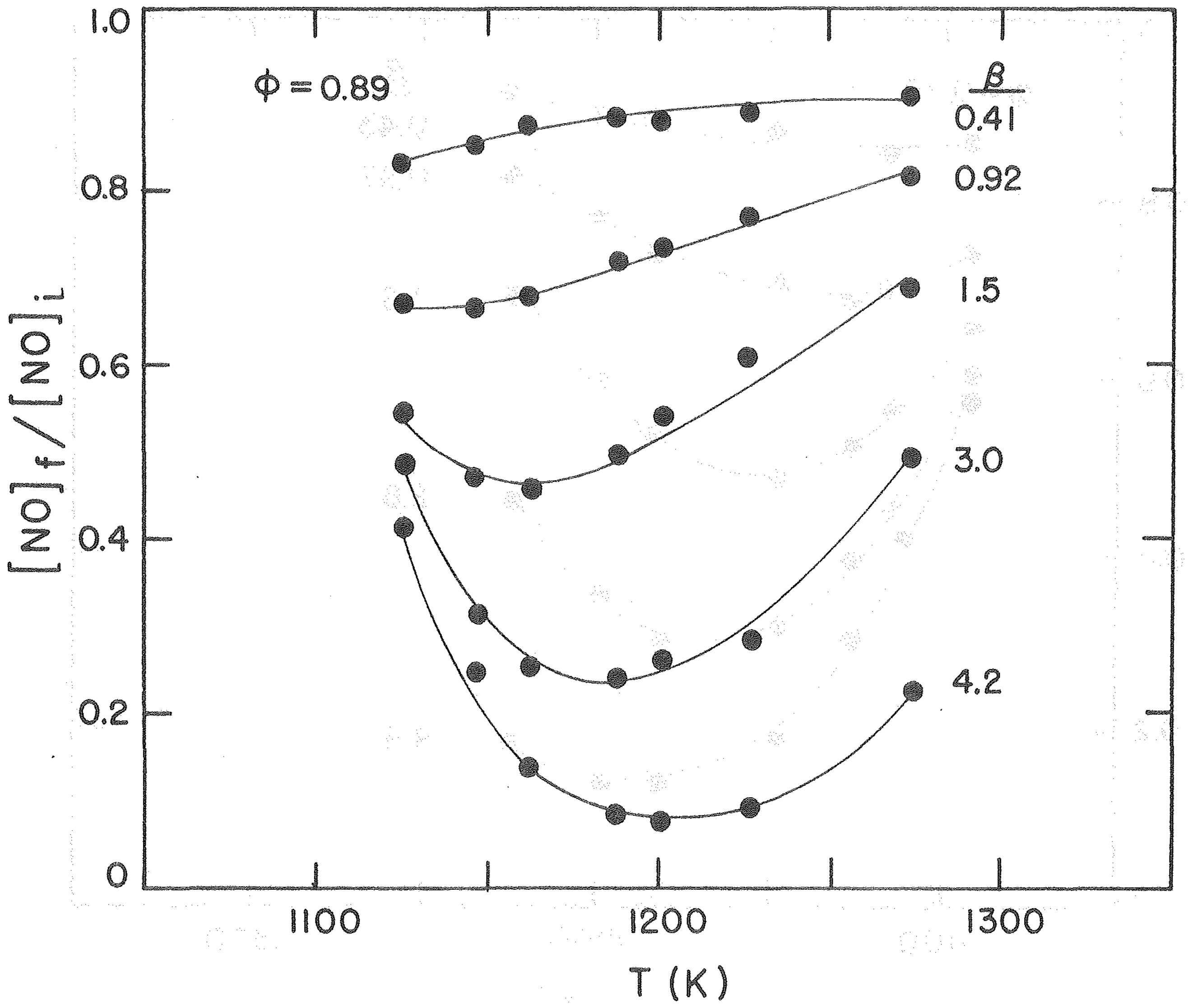

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Figure 13

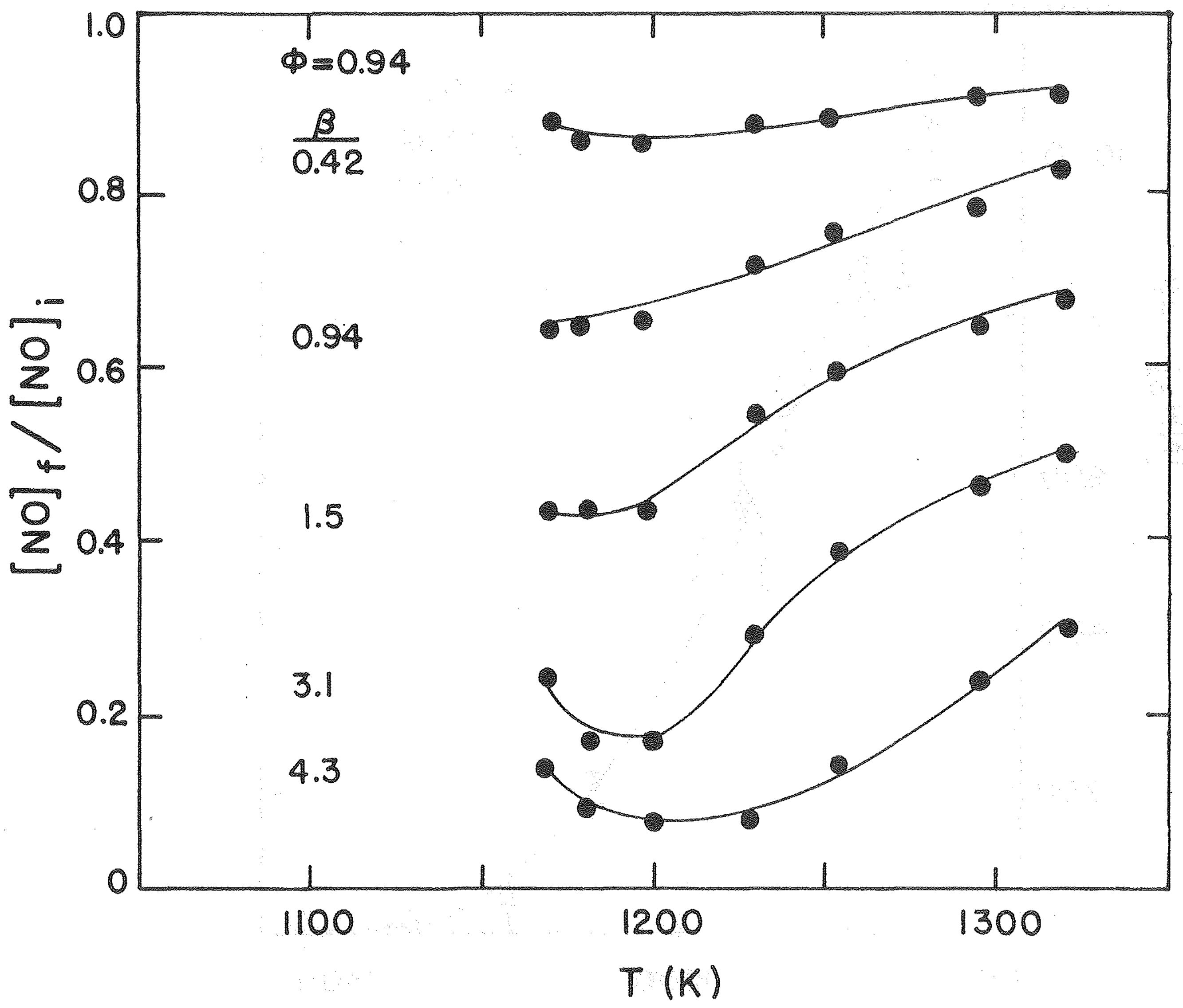

Figure 14

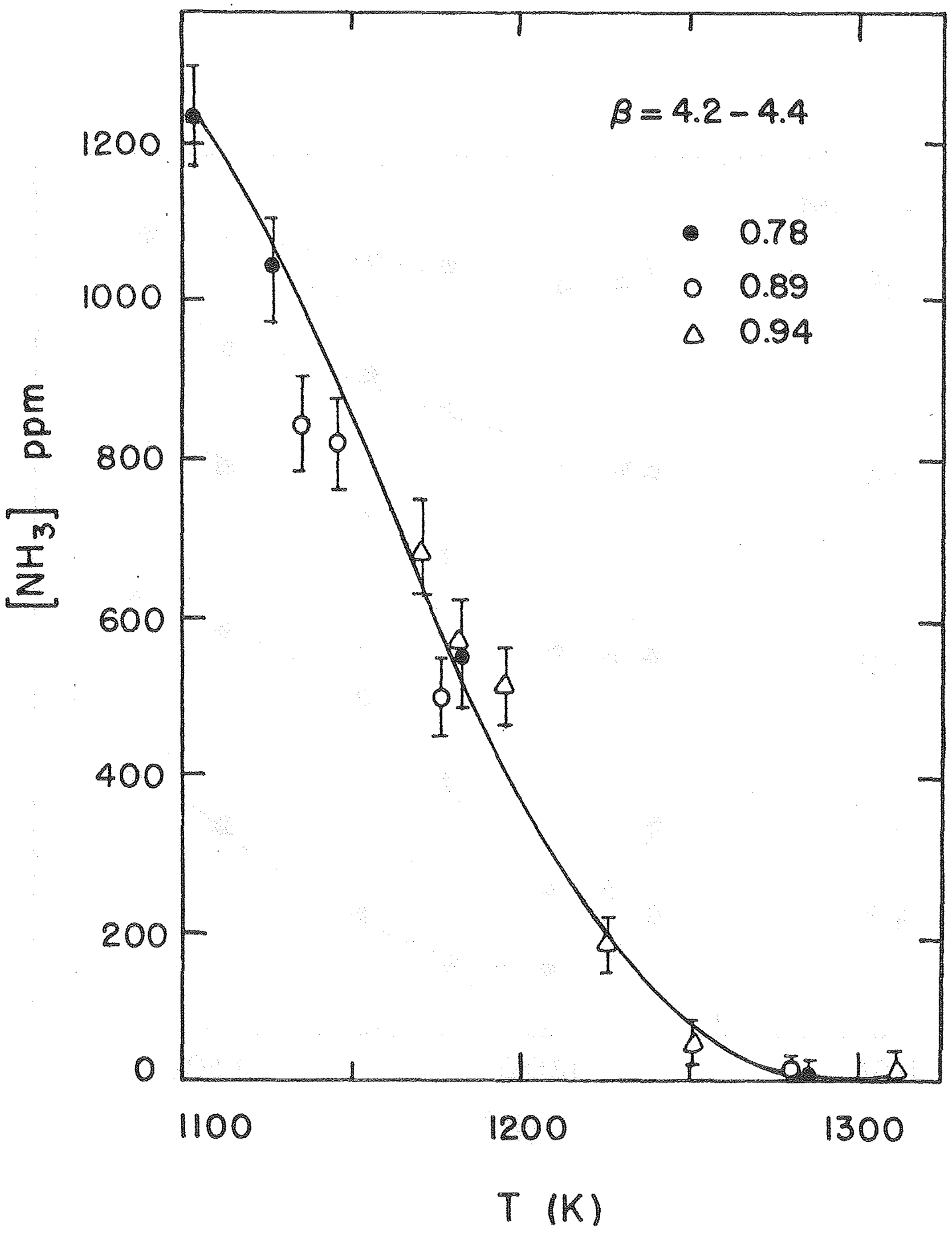
$\beta = 4.2 - 4.4$
● 0.78
○ 0.89
△ 0.94
$[NH_3]$ ppm
0
200
400
600
800
1000
1200
1100
1200
1300
T (K)

Figure 15