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Reaction Kinetics of Rocket Propellant Cases: I. - Rate of Decomposition of Nitric Oxide at Elevated Temperatures - and Appendix (Progress Report)

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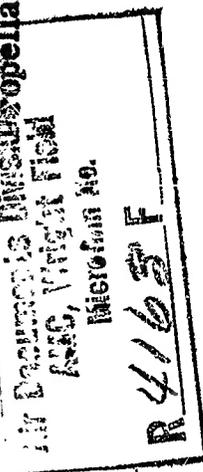
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REACTION KINETICS OF ROCKET PROPELLANT GASES:
I. RATE OF DECOMPOSITION OF NITRIC OXIDE
AT ELEVATED TEMPERATURES

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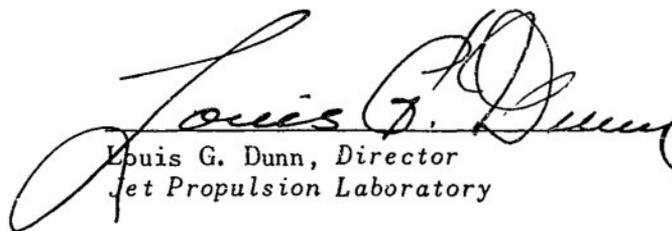
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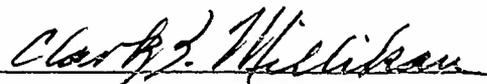
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Pasadena, California
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TABLE OF CONTENTS

	Page
I. Introduction and Summary	1
II. Review of Literature	2
III. Experimental Method	3
A. Description of Apparatus	3
B. Analysis of Decomposition Products	4
C. Purification of Nitric Oxide	5
D. Experimental Results	5
IV. Analysis of Results	6
Tables	8
Figures	11
Appendix	17
References	18

LIST OF TABLES

I. Rate of Decomposition of Nitric Oxide at Various Temperatures	8
II. Kinetics of Thermal Decomposition of Nitric Oxide	9
III. Activation Energy for Thermal Decomposition of Nitric Oxide in the Presence of Various Surfaces Below 1100°K	9
IV. Specific Reaction-Rate Constant at 1000°K in the Presence of Various Surfaces	10

LIST OF FIGURES

	Page
1. Schematic Diagram of Apparatus Used in Study of Rate of Thermal Decomposition of Nitric Oxide	11
2. Details of Quartz Reaction Vessel	12
3. Details of Apparatus for Measurement of Rate of Thermal Decomposition of Nitric Oxide	13
4. Calibration Curve for Analysis of Nitrogen Dioxide by Means of Gas Analyzer	14
5. Method for Purification of Nitric Oxide	15
6. Variation of Specific Reaction-Rate Constant with Temperature	16

I. INTRODUCTION AND SUMMARY

The extensive use of the oxides of nitrogen as oxidizers in solid and liquid rocket propulsion systems has emphasized the need for information on the kinetics of reaction of these compounds. Although the rates of decomposition of the oxides of nitrogen such as N_2O_5 (Cf. Refs. 1 and 2), N_2O_4 (Cf. Refs. 3, 4, and 5), NO_2 (Cf. Ref. 6), and N_2O (Cf. Ref. 7) have been the subjects of several investigations, the uncatalyzed rate of decomposition of nitric oxide has hitherto not been measured in great detail.

Thermodynamically NO shows a strong tendency to decompose into its elements even at room temperature, as may be judged by the following free-energy equation (Cf. Ref. 8):



Nevertheless, in spite of the large negative value for the standard free-energy change at 298°K, nitric oxide may be classified as a relatively stable gas since, as will be shown in Section III-D, the rates of decomposition are relatively small even at temperatures near 1500°K. Earlier calculations on the dissociation of NO during expansion through a rocket nozzle at temperatures below 2700°K have suggested that this equilibrium cannot be maintained because of the rapid rate of temperature drop (Cf. Ref. 9). This relative inertness of NO toward thermal decomposition suggests that perhaps one of the slow steps in the combustion of fuels with nitrogen oxides may be the reaction with NO. This report is the first in a series designed to study in detail the kinetic behavior of this molecule in order to interpret the combustion mechanisms in which nitrogen oxides participate.

A review of the experimental results reported for the reaction kinetics of NO (Cf. Section II) points to the need of additional information on the rate of decomposition of NO over a range of temperatures in the absence of metallic surfaces or refractories. In order to study more accurately the mechanism of this reaction at temperatures below 1300°K, a static system was chosen in which the residence time of the gas could be varied over wide limits not attainable in the dynamic method. The maximum temperature selected in this first phase of the study also permits the use of quartz in the construction of the reaction vessel which readily lends itself to subsequent investigations of the heterogeneous reaction rates.

Essentially the experimental procedure consists of introducing a known concentration of NO into the reaction vessel for a given time interval. The temperature of the gas during this period is accurately measured and maintained at the desired value. At the end of the reaction time the gas mixture is rapidly chilled by allowing the products of the reaction to expand into an evacuated vessel cooled by liquid nitrogen. The extent of the decomposition is determined by quantitative analysis of the decomposition products. From the results of these measurements, the kinetics of the reaction are given by two rate expressions. At temperatures above 1100°K the rate may be expressed by the following equation:

$$k = 1.4 \times 10^{11} e^{-56600/RT} \left(\frac{\text{mol}}{\text{cc}} \right)^{-1} \text{sec}^{-1}$$

whereas at lower temperatures an alternate rate expression applies as follows:

$$k = 1.4 \times 10^4 e^{-21400/RT} \left(\frac{\text{mol}}{\text{cc}} \right)^{-1} \text{ sec}^{-1}$$

Over the entire temperature region studied (700 to 1300°K) the decomposition of nitric oxide obeys a second-order rate law. It can be concluded that the observed reaction is a composite one made up of two or more concurrent reactions differently influenced by temperature.

II. REVIEW OF LITERATURE

A survey of the data published in the literature has shown that in the presence of platinum or iridium surfaces the rate of decomposition of NO is rapid. (Cf. Refs. 10, 11, and 12). Whereas the experimental results of Jellinek (Cf. Ref. 10) and of Green and Hinshelwood (Cf. Ref. 11) point to a first-order heterogeneous reaction, the measurements by Bachman and Taylor (Cf. Ref. 12) indicate a second-order rate law in the presence of platinum. The authors of References 11 and 12 also observed an inhibitory effect in the decomposition rate of NO due to the presence of oxygen formed in the reaction. Nitrogen, on the other hand, had no effect on the reaction rate.

In recent years renewed interest has been shown in the kinetics of formation of nitric oxide at elevated temperatures. The rate of formation of nitric oxide from air was determined by Nernst (Cf. Ref. 13) in a platinum and iridium furnace. More recently Zeldovich (Cf. Ref. 14), Polyakov and Genkina (Cf. Ref. 15), and Frank-Kamenetzky (Cf. Ref. 16) studied the mechanism of nitric oxide formation in the explosion of combustible mixtures composed of hydrogen, oxygen, and nitrogen. The oxidation of nitrogen to NO was also investigated by Muthman and Hofer (Cf. Ref. 17) in an electric arc. However, the results described in References 14 through 17 are of questionable accuracy because of the problem of temperature measurement during an explosion or in an electric discharge.

Research by Daniels and his coworkers (Cf. Refs. 18, 19, and 20) on the fixation of atmospheric nitrogen with the formation of NO has led to some interesting theoretical as well as experimental results on the reaction kinetics of this gas. At temperatures above 2000°K in a furnace filled with magnesia pebbles, the experimental measurements of the rate of decomposition of NO yielded an energy of activation of 70 kcal for this process (Cf. Ref. 18). In a theoretical analysis of the problem (Cf. Ref. 19) two rate expressions were derived for the decomposition of NO with activation energies of 50 and 70 kcal, respectively, both of which could be fitted to the experimental data by proper choice of the pre-exponential coefficient in the Arrhenius equation. Additional measurements of the rate of decomposition of NO in the presence of zirconia pebbles were carried out (Cf. Ref. 20). The results obtained suggest a complex mechanism for this reaction with a heterogeneous process of lower activation energy predominating at temperatures below 1300°K. Analytically these data parallel those obtained by Jellinek (Cf. Ref. 10), who employed porcelain tubes at temperatures up to about 1600°K. However, the studies reported in References 10, 18, and 20 utilized a flow method in which the NO was passed through a region of high temperature and then was collected for subsequent analysis. Since the rate of decomposition of NO is relatively slow at temperatures below 1200°K, the accuracy of the experimental measurements carried out in a flow system is greatly reduced because the mass rate of flow of gas cannot be varied sufficiently to increase the residence time of the gas in the hot zone.

III. EXPERIMENTAL METHOD

A. Description of Apparatus

A schematic drawing of the apparatus used in this study is shown in Figure 1. A purified sample of NO (a detailed description of the method of purification is given in Section III-C) is admitted from the bulb *A* to the reaction vessel *B*. It is composed of a quartz cylinder (120 mm in diameter and 150 mm in height) provided with a gas inlet 1 and outlet 2 and a thermocouple well which extends down the center of the vessel (Cf. Fig. 2). The reactor is located in an electrically heated furnace in which the temperature can be adjusted and maintained with a high degree of accuracy ($\pm 1^\circ\text{K}$) by means of variable voltage control (Variac) for the multiple-unit heating elements with a maximum power consumption of 1700 watts at 1350°K .

For temperature measurements inside the reaction vessel a shielded thermocouple [platinum—platinum rhodium (10%)] is employed which has previously been calibrated against a standard supplied by the National Bureau of Standards.* The hot junction of the thermocouple extends into the centrally located well of the reactor; the cold junction is in contact with ice water. The thermo-electric electromotive force generated by the thermocouple is read on a self-balancing Brown potentiometer with a sensitivity of $\pm \frac{1}{4}$ per cent. The temperature-sensing element is thus separated from the reacting gas mixture by a quartz wall; thus any catalytic effect of the thermocouple is eliminated (Cf. Fig. 2).

Over the range of temperatures studied (700 to 1300°K) the temperature profile of the reactor has shown a maximum variation of ± 1.2 per cent as the hot junction was moved from the lowest point in the well to a point near the top of the quartz vessel. A variation in temperature of similar magnitude was observed when in the absence of the quartz cylinder a horizontal thermocouple traverse was carried out at different heights inside the furnace.

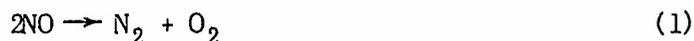
After a given time interval the hot-gas mixture contained in vessel *B* (Cf. Fig. 1) is rapidly expanded into the evacuated trap *C* cooled by liquid nitrogen. The section connecting *B* and *C* is made relatively short in order to allow fast cooling of the hot gases to a point where the composition of the mixture will not undergo any further change. In this manner the possibility of additional reaction of the gases during their passage from the reactor to the trap *C* is greatly reduced. Thus the composition of the mixture as found in *C* is essentially that which prevailed in the reactor at the end of the decomposition period. In several tests quantitative recovery of the gaseous products was ascertained by pumping on vessel *B* with the Toeppler pump *D* after the bulk of the gas mixture had been removed from *B* to *C* by the expansion method described. The recovery of the gases in *C* is aided not only by the large pressure gradient between *B* and *C*, which causes the products of reaction to pass into the evacuated trap as soon as the intervening stopcock (No. 2) is opened, but also by the large temperature difference between the two points in the system.

The entire apparatus is connected to the manifold of a vacuum line composed of an oil-diffusion pump and mechanical pump and is provided with McLeod and Pirani gages for the measurement of pressure in the system. A photograph of the essential parts of the apparatus is shown in Figure 3. Preceding each experimental measurement, the quartz reactor is outgassed for several hours at high temperatures and a pressure of less than 10^{-7} mm Hg in order to remove adsorbed surface films which may affect the course of the reaction.

*The calibration work was carried out by the instrument section of this Laboratory.

B. Analysis of Decomposition Products

In following the progress of the decomposition of NO the rate of disappearance of the reactant or the rate of formation of the products may be taken as an index of the rate process. Since the change in concentration of NO is relatively small even at the highest temperatures employed, it is difficult to measure accurately a small difference between two relatively large quantities. Instead, the quantitative detection of the products of decomposition offers a more satisfactory and accurate index of the rate of reaction. Thus one has the choice of determining either the concentration of nitrogen formed during the reaction according to the following equation:



or the concentration of NO_2 subsequently produced from the combination of undecomposed NO with O_2 yielded in the decomposition, namely,



The latter reaction proceeds at a fairly rapid rate at room temperature (Cf. Ref. 6). In the present experimental work, the concentration of N_2 and of NO_2 was analyzed at the end of each experiment.

Preceding the analysis, the gas sample stored in trap C (Cf. Fig. 1) is allowed to distill into vessel E, which is kept at room temperature. Sufficient time is allowed for the formation of NO_2 at room temperature according to Equation (2) before the vessel is surrounded with a Dewar flask containing liquid nitrogen. After all of the condensable components are frozen out, the gaseous nitrogen is passed into the calibrated vessel F by means of an automatic Toepller pump D. The transfer of N_2 with the aid of the pump is continued until no further pressure increase is noted on the mercury manometer attached to vessel F and read to ± 0.05 mm Hg with the aid of a cathetometer.*

For the analysis of nitrogen dioxide formed according to Equation (2) a spectrophotometer is employed. The details of this gas analyzer have previously been reported (Cf. Ref. 21). Essentially the instrument is composed of two absorption cells (10 mm ID and 482 mm long), provided with plane parallel windows at either end. A beam of light of constant intensity after passage through a collimating lens and light filter (maximum transmission at 4800° \AA) is interrupted by means of a mechanical chopper (1300 cyc/sec) before it alternately enters the two absorption cells. The transmitted light is then focused on a single photocell which responds to the light intensity received by it. With both absorption cells transparent to the wave-length region of light employed, an ac zero signal is registered by the photocell, since the light transmitted through the test absorption tube and that through the control cell are of equal intensity. However, when a sample of NO_2 is contained in the test cell, a fraction of the incident light, proportional to the concentration of NO_2 in the sample, is absorbed; the intensity of the light transmitted through this cell is now of a smaller magnitude than that striking the photocell from the control absorption tube. The magnitude of this difference in transmitted-light intensity is a measure of the

*In actual practice, cycling of the gas with the Toepller pump was kept up until a constant pressure increase per cycle was observed because of the partial pressure of nitric oxide at the temperature of liquid nitrogen.

concentration of NO_2 in the gas mixture. In order to suppress the formation of N_2O_4 (Cf. Eq. 2) the absorption cells are surrounded by a hot-water jacket maintained at 95°C .

The gas analyzer is calibrated by charging the apparatus with samples of known concentration of NO_2 and recording the photocell output after proper amplification. The wide range of concentrations of NO_2 which can be detected and the high degree of precision obtained with this instrument are best demonstrated by the calibration curve (Cf. Fig. 4). Beer's law is not obeyed over the entire concentration range because of the absence of monochromatic light. The high degree of sensitivity of the spectrophotometer to low concentrations of NO_2 in the gas mixture is especially useful since in this region the accuracy inherent in the manometric procedure of nitrogen analysis is reduced.

C. Purification of Nitric Oxide

The nitric oxide used in the experimental measurement was obtained from the Matheson Company. However, since the commercial sample was found to contain some impurities such as NO_2 and N_2O , it was subjected to purification as shown schematically in Figure 5. In order to remove the residual NO_2 , the NO as obtained from the tank was dispersed into an aqueous solution of 80 per cent sulfuric acid *A* and then into a column *B* containing 50 per cent aqueous potassium hydroxide. The gas then passed through the trap *C* cooled by a mixture of dry ice and acetone and a drying tube *D* filled with P_2O_5 before it was condensed in the liquid nitrogen trap *E* and kept in the solid state for subsequent removal of the remaining N_2O . Since the latter impurity is highly soluble in liquid NO , a small portion of this semifinal product was then distilled into the U-tube *F* cooled by liquid N_2 until it had collected to a depth of a few centimeters. By regulating the height of liquid N_2 in the Dewar flask surrounding the U-tube *F*, this material was kept in the liquid phase while the remaining portion of the semifinal product was slowly bubbled through it and collected in storage vessel *A* (Cf. Fig. 1) for subsequent use. Infrared spectrographic analysis of the purified sample indicated a purity in excess of 99.97 per cent with respect to NO .*

D. Experimental Results

Two parameters are of particular interest in the study of the kinetics of a reaction, (a) the order of the reaction which relates the rate to some function of the concentration of the reactants and (b) the energy of activation for the process which identifies the magnitude of the energy barrier to be overcome by the reacting system in its passage from initial to final state.

The order of the reaction involving the thermal decomposition of NO was determined by a study of the effect of concentration of NO on the reaction rate under isothermal conditions. Over the range of temperature and concentrations studied, the kinetics of decomposition were found to follow a second-order rate law as follows:

$$-\frac{d(\text{NO})}{dt} = k(\text{NO})^2 \quad (3)$$

*The spectrographic analysis of the material was carried out by S. S. Penner and Dwight Weber of this Laboratory.

That is, the rate of decomposition of NO is proportional to the square of its concentration at a given temperature.

From Equation (3) the specific reaction-rate constant may be evaluated. For this purpose Equation (3) is rewritten in the form

$$\frac{dx}{dt} = k(a-x)^2 \quad (4)$$

where a is the initial concentration of NO and x the amount decomposed in time t . Upon integration between the limits of zero to x and zero to t , respectively, one obtains

$$k = \frac{1}{t} \frac{x}{a(a-x)} \quad (5)$$

The specific reaction rates calculated from Equation (5) are summarized in Table I (column 6). The validity of the second-order rate law for this reaction is evidenced by the constancy of the rate constant k at a given temperature with variations in the initial concentration of NO.

The dependency of the reaction rate on temperature can subsequently be determined by means of the Arrhenius equation

$$k = Ae^{-E/RT} \quad (6)$$

Thus a plot of $\ln k$ vs the reciprocal of the temperature ($1/T$) yields a curve the slope of which is proportional to the energy of activation E . When such a plot is constructed from the experimental results presented in Table I, it becomes apparent that the data cannot be fitted by a single straight line (Cf. Fig. 6). Thus at temperatures below approximately 1000°K an energy of activation of $21.4 \text{ kcal/2 moles}$ of NO obtains, whereas at higher temperatures the value of E increases to $56.6 \text{ kcal/2 moles}$ of NO. Also the pre-exponential coefficients A in the Arrhenius equation differ by a factor of 10^7 for these two temperature regions (Cf. Fig. 6). The difference in the slope of the two curves is greatly in excess of the over-all experimental error which has been estimated to be ± 3.6 per cent.

The rate of decomposition of nitric oxide as a function of temperature can further be elucidated by a computation of the time $t_{1/2}$ required to decompose 1 atmosphere of NO to half its original value at the specified temperature (Cf. Table II).

In the calculations just presented, the effect of the reverse reaction, namely, the formation of nitric oxide from its products of decomposition, has been neglected. Over the temperature range studied, such an approximation is valid since the contribution of the reverse reaction on the over-all rate is relatively small as can be shown by evaluation of the complete rate expression given in the appendix.

IV. ANALYSIS OF RESULTS

From the data presented in Figure 6 it can be concluded that the observed reaction is a composite one, made up of two or more concurrent reactions differently influenced by temperature. In the low-temperature region one of the reactions predominates. Thus the shape of the curve corresponds to a value for the activation energy characteristic of the rate-determining step in this process. At higher temperatures the alternate reaction with its larger temperature coefficient will cause the reaction velocity to increase relative to that of the first, and alternately it

will constitute the major portion of the total change. The slope of the curve now corresponds to the larger value of the activation energy E proper to the high-temperature reaction.

Since the course of the chemical transformation at low temperatures involves a smaller activation energy, an extraneous influence of homogeneous or heterogeneous nature suggests itself. Thus it is a rather striking fact that nitric oxide is known to participate in several homogeneous termolecular reactions involving 2 molecules of this gas (Cf. Ref. 22). The paramagnetic properties of the nitric oxide molecule would favor a relatively inelastic collision between the molecules which would result in a temporary association to a complex, the likelihood of which diminishes with increasing temperature. Also at low temperatures one of the products of decomposition of nitric oxide may influence the rate of the reaction by a termolecular mechanism. This effect as well as that of other foreign gases remains to be investigated.

On the other hand some experimental evidence points to the existence of a heterogeneous reaction predominating in the low-temperature region. The degree of scatter of the experimental data is more pronounced in this range, as can be seen from Figure 6. Also in Jellinek's measurements of the rate of decomposition of nitric oxide in a porcelain vessel (Cf. Ref. 10) a plot of the variation of the rate constant with temperature exhibits a decrease in activation energy for this process as the temperature of the system is lowered (Cf. Fig. 6). Whereas at temperatures above 1150°K the rate of decomposition of nitric oxide in porcelain agrees closely with that found in quartz, at temperatures below that value the activation energy is diminished as shown in Table III. Similarly some experimental measurements of the decomposition rate of nitric oxide in a furnace filled with ZrO pebbles yields an activation energy of 24.5 kcal (Cf. Ref. 20).

These results suggest the specificity of the catalytic effect which is further elucidated in a comparison of the specific reaction-rate constants at 1000°K in the presence of these three surfaces (Cf. Table IV). The lack of correlation in reaction velocity is evident. Strictly the comparison is applicable to only the first two surfaces in Table IV, since in these two instances the surface area of the respective reaction zones was of the same order of magnitude. In the case of zirconia the surface area of the reaction zone was considerably increased by the addition of pebbles made of the same material. Nevertheless, these observations further elucidate the existence of a temperature region in the decomposition of nitric oxide in which the rate-determining step is a function of surface area and/or surface.

Furthermore, it is of particular interest to note that the energy of activation for the decomposition of NO in the high-temperature region ($E = 56.6$ kcal) is of the same order of magnitude as the value observed for the homogeneous thermal decomposition of N_2O for which a value of 58.5 kcal has been found (Cf. Ref. 22). Since the initial stage in the decomposition of nitrous oxide appears to be the rupture of a nitrogen-oxygen band, namely, $N_2O = N_2 + O$, it may be expected that in the decomposition of NO an activation energy of the same magnitude is required for the breakage of a similar bond between the nitrogen and oxygen atoms.

TABLE I
RATE OF DECOMPOSITION OF NITRIC OXIDE AT VARIOUS TEMPERATURES

Temperature T (°K)	Reciprocal Temperature $\frac{1}{T} \times 10^4$ (°K) ⁻¹	Concentration of NO $\left(\frac{\text{mol}}{\text{cc}} \times 10^6\right)$		Reaction Time t (sec)	Specific Reaction-Rate Constant k $\left[\left(\frac{\text{mol}}{\text{cc}}\right)^{-1} \text{sec}^{-1}\right]$
		Initial	Final		
872	11.468	7.330	7.292	10,000	0.07
872	11.468	5.943	5.913	10,500	0.08
872	11.468	4.698	4.681	10,000	0.08
878	11.390	9.207	9.155	10,500	0.06
899	11.123	6.444	6.412	10,000	0.08
901	11.099	10.015	9.951	9,000	0.07
901	11.099	4.282	4.264	12,000	0.08
918	10.893	5.353	5.318	11,020	0.12
951	10.515	4.791	4.761	6,000	0.22
980	10.204	9.677	9.558	6,000	0.21
980	10.204	8.246	8.145	7,000	0.22
1000	10.000	7.310	7.250	5,000	0.23
1001	10.000	3.164	3.145	8,000	0.24
1025	9.750	9.827	9.675	3,000	0.53
1025	9.750	8.141	8.050	3,000	0.46
1025	9.750	4.475	4.428	5,100	0.47
1057	9.461	3.939	3.844	10,000	0.63
1060	9.434	8.286	8.038	6,500	0.57
1080	9.259	5.273	5.194	3,600	0.80
1100	9.091	6.498	6.402	2,000	1.15
1109	9.071	6.228	6.107	3,000	1.06
1135	8.811	3.703	3.662	1,500	2.02
1173	8.525	8.721	6.327	8,000	5.42
1186	8.432	5.051	4.775	1,900	6.02
1186	8.432	4.391	4.291	1,000	5.31
1193	8.382	7.011	5.725	4,000	8.01
1275	7.843	6.825	6.584	200	26.82
1275	7.843	5.785	5.609	200	27.12
1275	7.843	2.775	2.677	500	26.45

TABLE II
KINETICS OF THERMAL DECOMPOSITION OF NITRIC OXIDE

Temperature T (°K)	Specific Reaction-Rate Constant k $\left[\left(\frac{\text{mol}}{\text{cc}} \right)^{-1} \text{sec}^{-1} \right]$	Half-Time* $t_{1/2}$ (sec)
700	0.0034	1.69×10^7
800	0.023	2.86×10^6
900	0.1	7.35×10^5
1000	0.33	2.52×10^5
1100	0.87	1.04×10^5
1200	7.72	1.28×10^4
1300	46.7	2.78×10^3
1400	231	6.06×10^2

*Time required to decompose 1 atmosphere of NO to half its original value at specified temperature.

TABLE III
ACTIVATION ENERGY FOR THERMAL DECOMPOSITION OF
NITRIC OXIDE IN THE PRESENCE OF VARIOUS
SURFACES BELOW 1100°K

Surface	Activation Energy Below 1100°K (kcal/2 moles NO)	Source
Quartz	21.4	this work
Porcelain	27.2	Ref. 10
ZrO	24.5	Ref. 20

TABLE IV
SPECIFIC REACTION-RATE CONSTANT AT 1000°K IN
THE PRESENCE OF VARIOUS SURFACES

Surface	Specific Reaction-Rate Constant k at 1000°K $\left[\left(\frac{\text{mol}}{\text{cc}} \right)^{-1} \text{sec}^{-1} \right]$	Source
Quartz	0.33	this work
Porcelain	1.02	Ref. 10
ZrO	55 (extrapolated)	Ref. 20

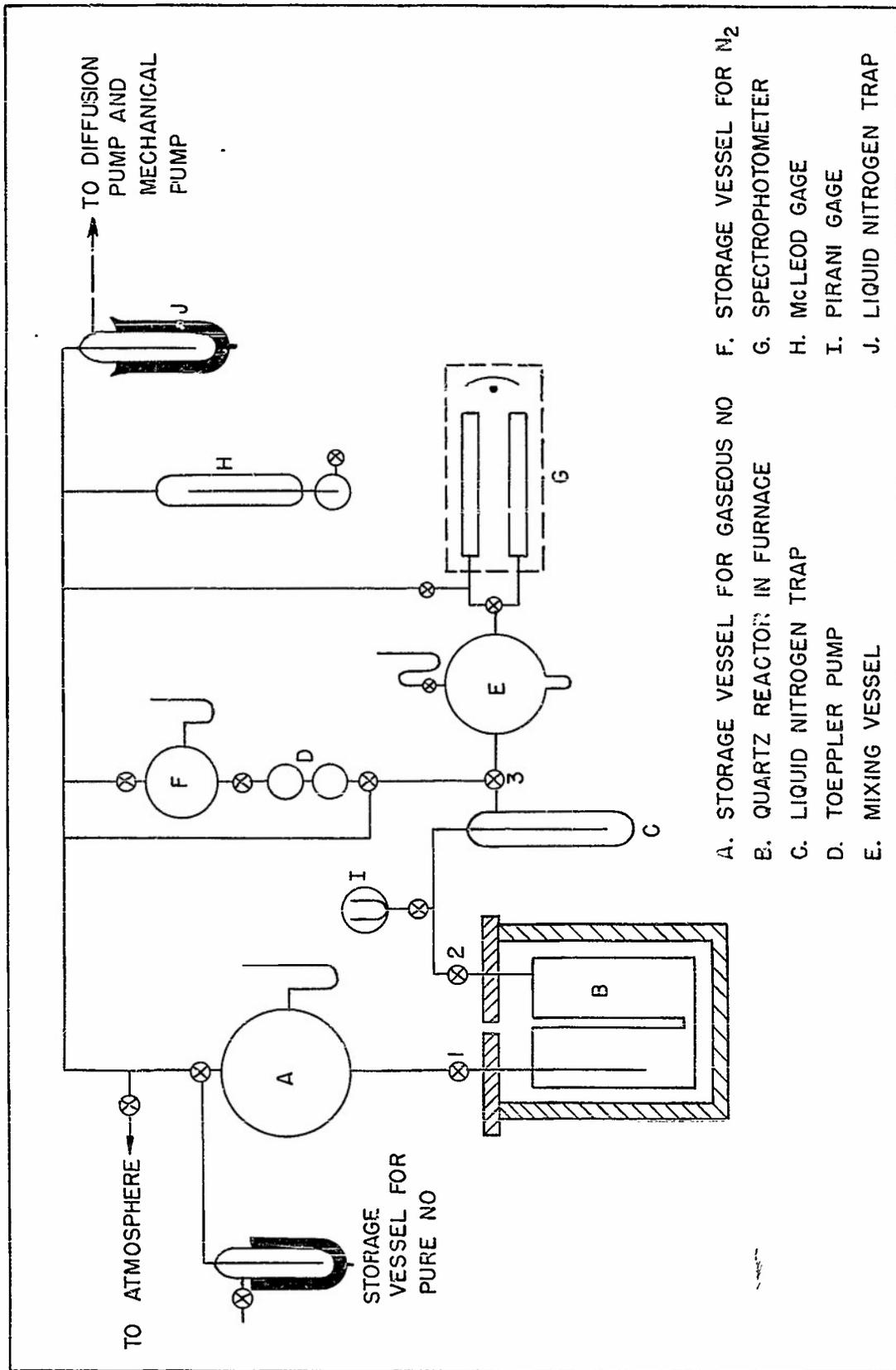


Figure 1. Schematic Diagram of Apparatus Used in Study of Rate of Thermal Decomposition of Nitric Oxide

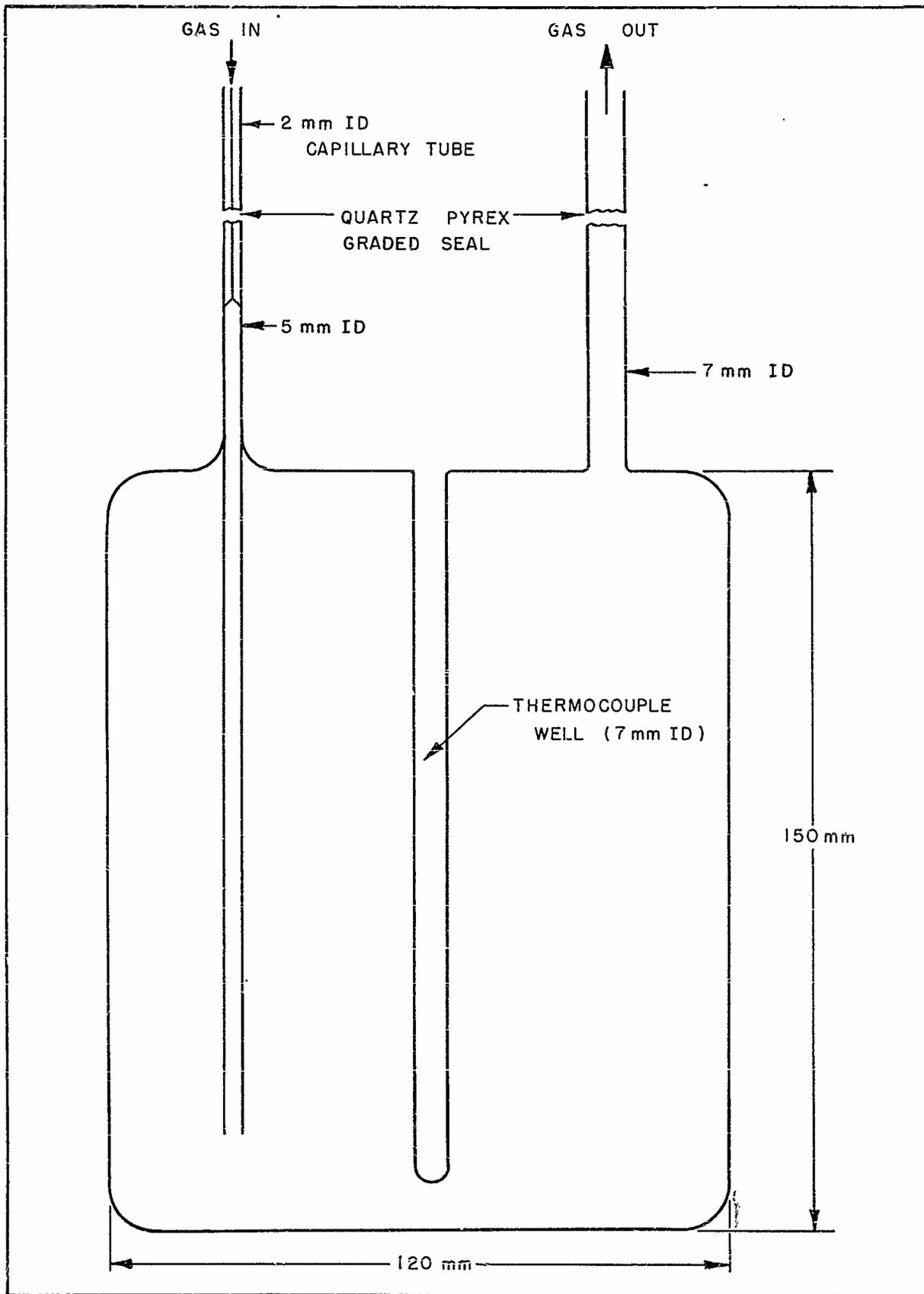


Figure 2. Details of Quartz Reaction Vessel

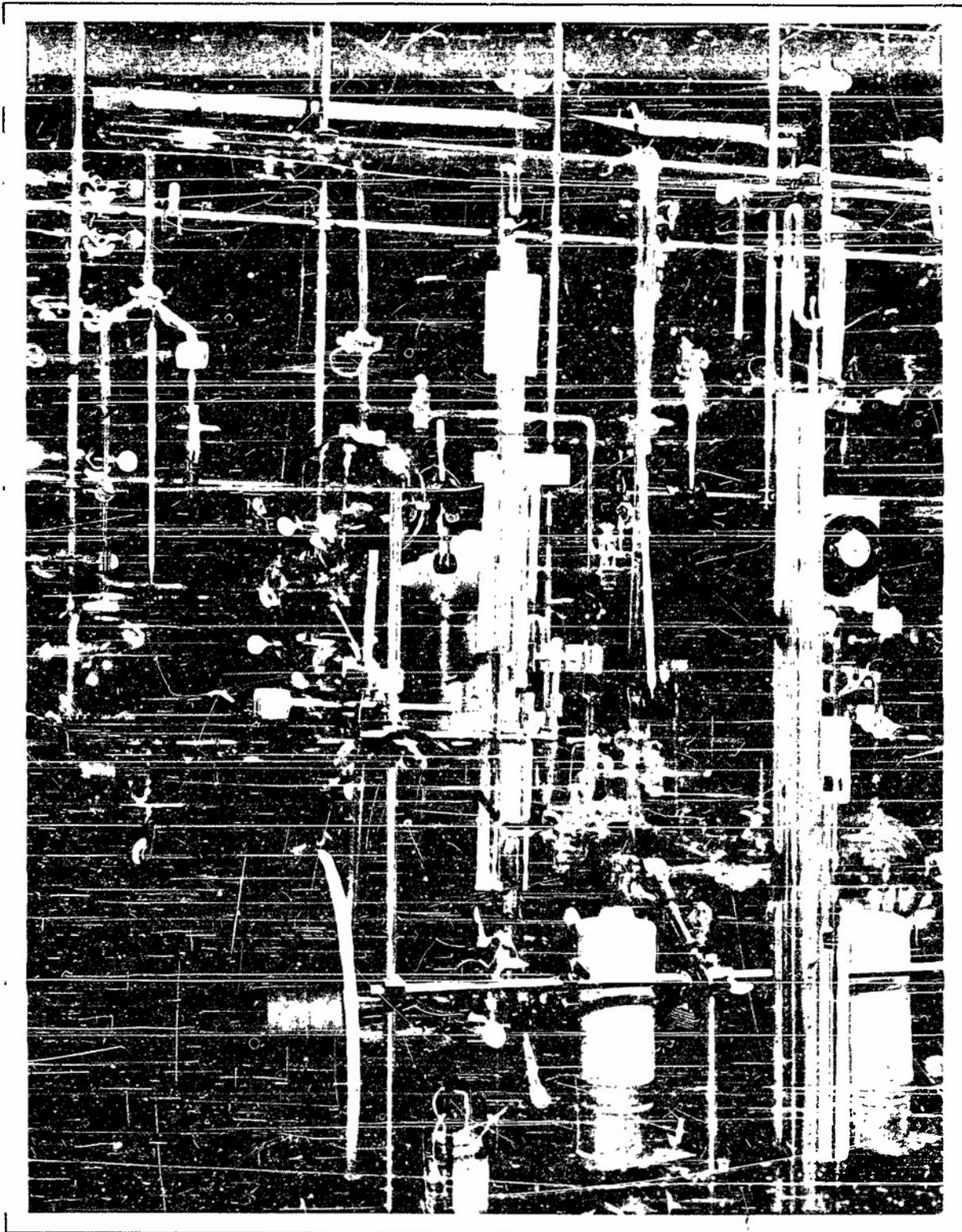


Figure 3. Details of Apparatus for Measurement of Rate of Thermal Decomposition of Nitric Oxide

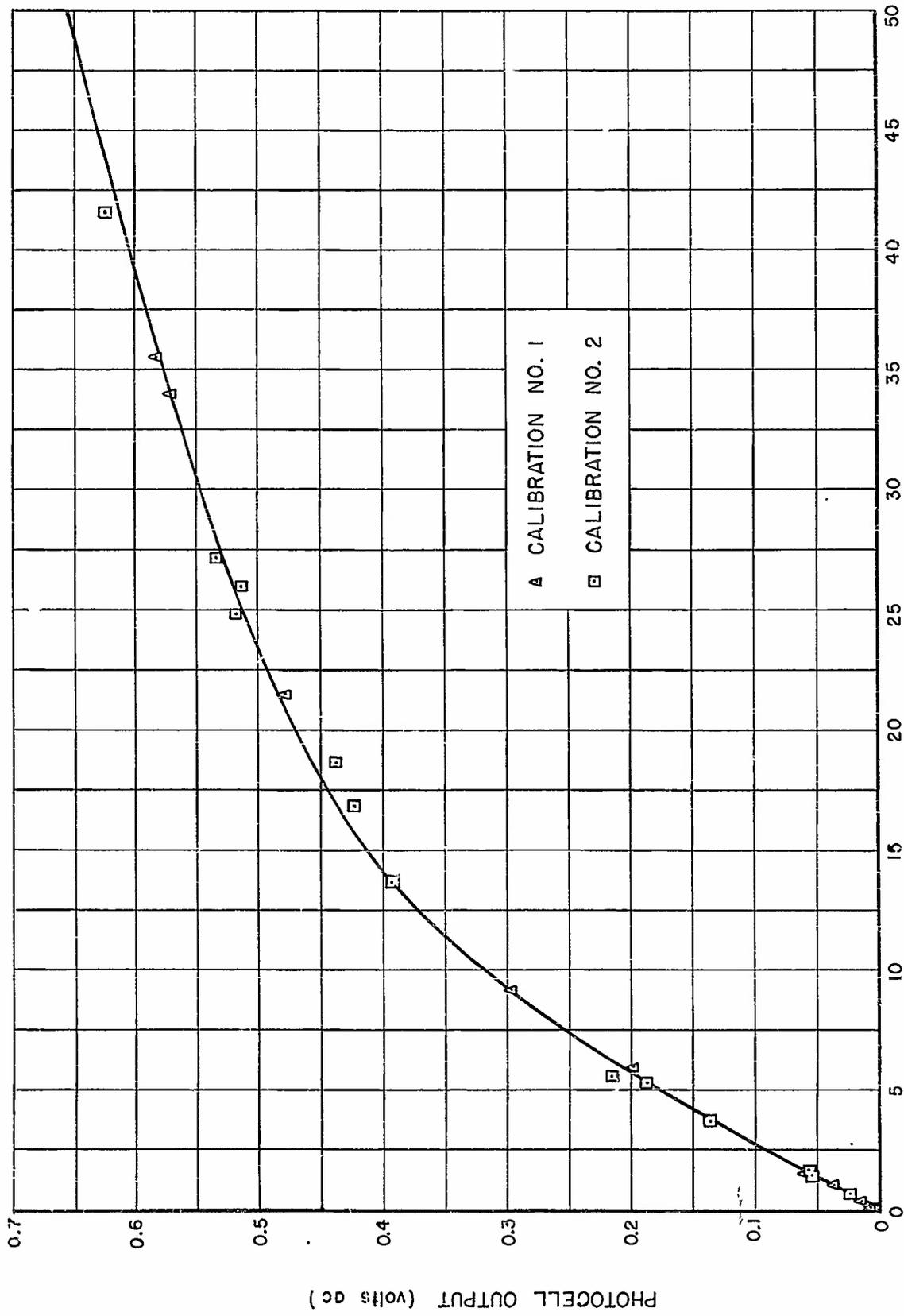


Figure 4. Calibration Curve for Analysis of Nitrogen Dioxide by Means of Gas Analyzer

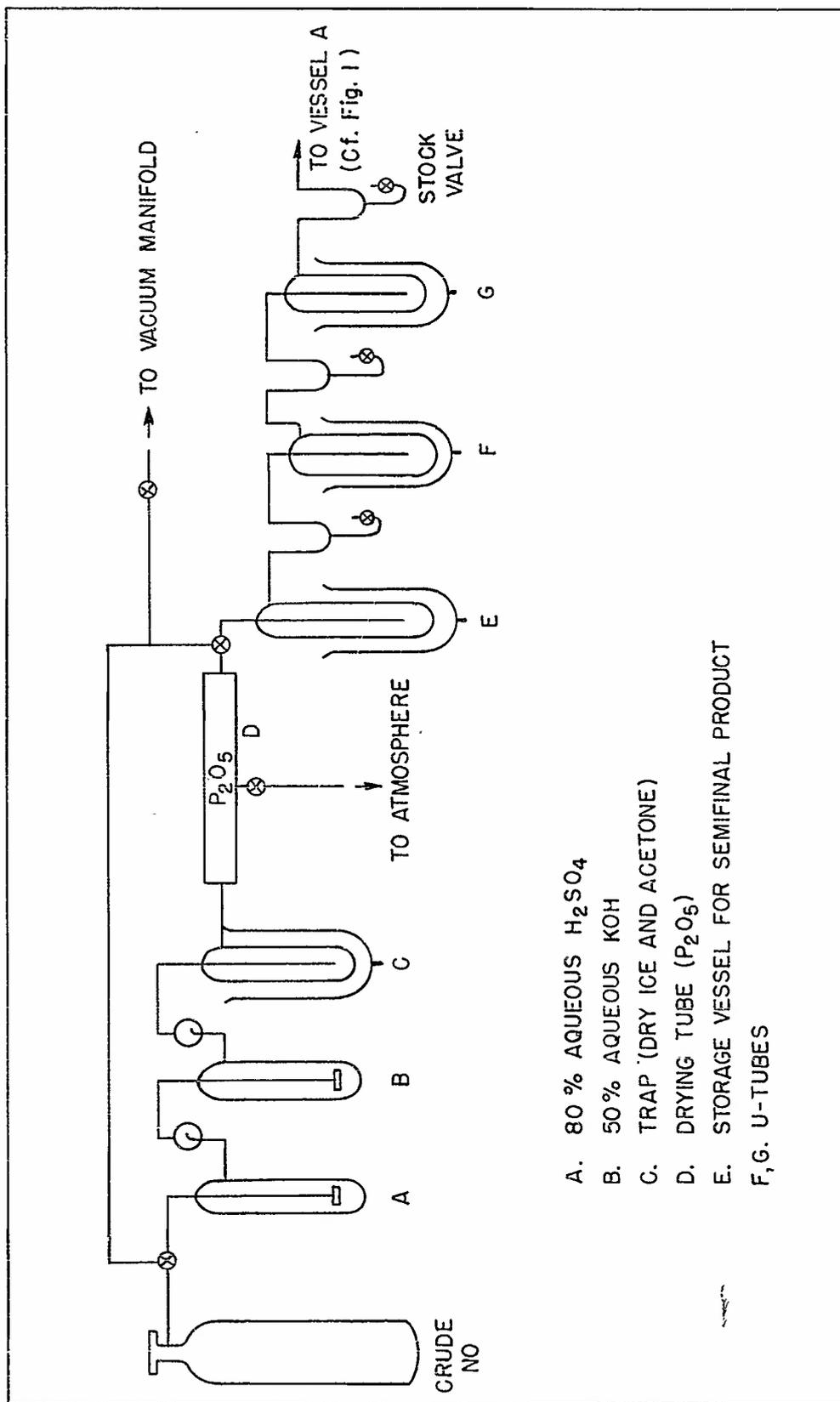


Figure 5. Method for Purification of Nitric Oxide

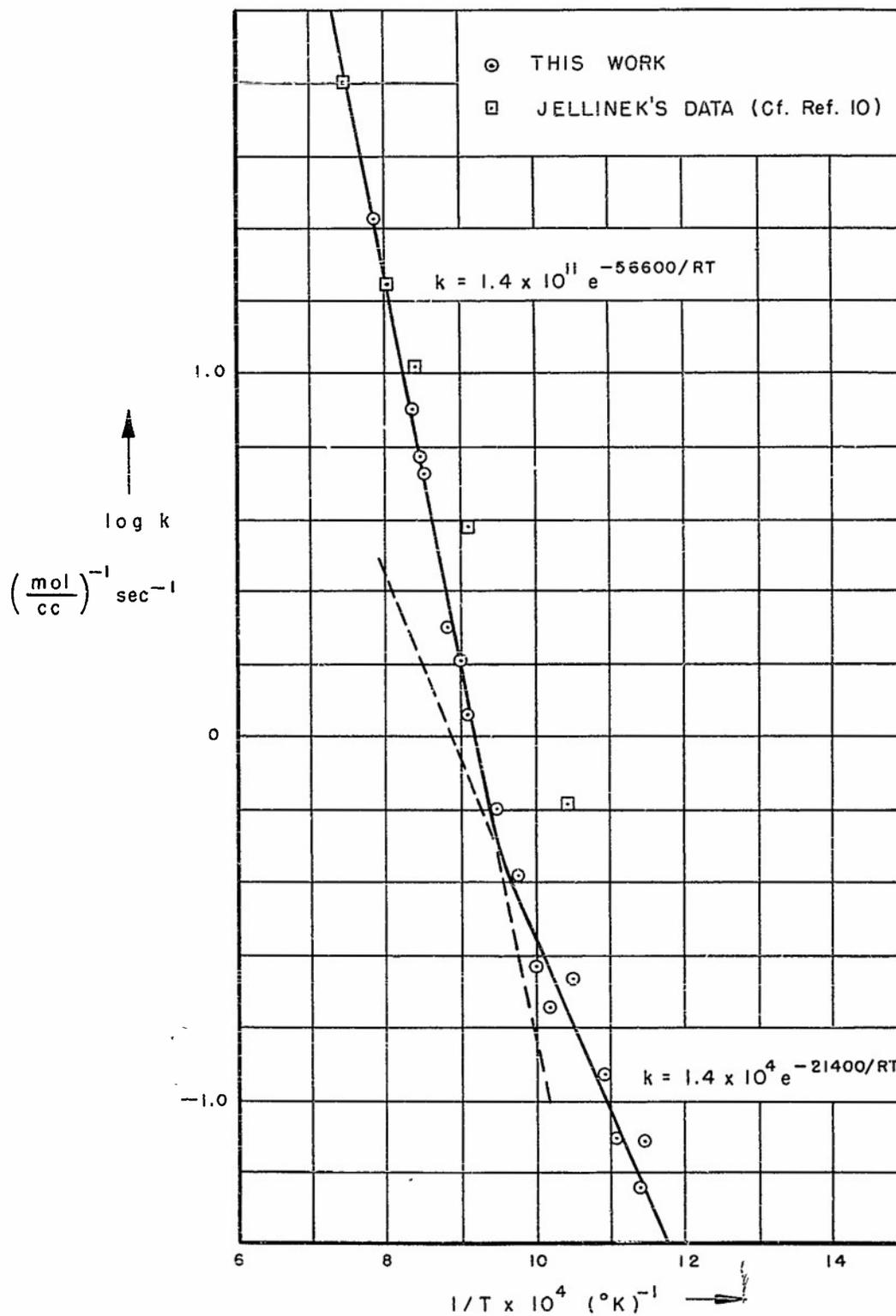


Figure 6. Variation of Specific Reaction-Rate Constant with Temperature

APPENDIX

EFFECT OF REVERSE REACTION ON RATE OF
DECOMPOSITION OF NITRIC OXIDE

For the reaction



the following complete rate expression applies:

$$-\frac{d(\text{NO})}{dt} = k_1(\text{NO})^2 - k_2(\text{N}_2)(\text{O}_2)$$

Upon integration one obtains

$$k_1 = \frac{K_e^{1/2}}{2at} \ln \left[\frac{(a-x)(K_e - K_e^2) + x(K_e^{1/2} - K_e^{3/2})}{(a-x)(K_e - K_e^2) - x(K_e^{1/2} - K_e^{3/2})} \right] \quad (\text{A-2})$$

where K_e is the equilibrium constant (equal to k_1/k_2); a , the initial concentration of NO; and x , the amount decomposed in time t . Over the temperature range studied, evaluation of k_1 by this procedure results in values identical with those obtained from Equation (5), in which the reverse reaction has been neglected. The equilibrium constants used in these calculations were based on data by Giaque and Clayton (Cf. Ref. 23).

It is to be noted that Equation (A-2) may be rewritten as

$$k_1 = \frac{K_e^{1/2}}{2at} \ln \left[1 + \frac{2x}{(a-x) K_e^{1/2} - x} \right] \quad (\text{A-3})$$

which may be expanded to

$$k_1 \approx \frac{K_e^{1/2}}{2at} \left[\frac{2x}{(a-x) K_e^{1/2} - x} \right] \quad (\text{A-4})$$

by neglecting the terms of higher order. Equation (A-4) may be further simplified by dividing by $K_e^{1/2}$

$$k_1 = \frac{1}{2at} \left[\frac{2x}{(a-x) - \frac{x}{K_e^{1/2}}} \right] \quad (\text{A-5})$$

When $x/K_e^{1/2}$ approaches zero (as would be the case for small values of x or small values of k_2 , which would tend to make K_e infinite), Equation (A-5) is identical with Equation (5), which was derived for the reaction rate in the absence of a reverse reaction.

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