

SOME PHYSICO-CHEMICAL PROPERTIES OF THE SYSTEM  
NITRIC ACID--NITROGEN DIOXIDE--WATER

- I. The Kinetics of the Thermal Decomposition  
of Nitric Acid in the Liquid Phase
- II. Electrolytic Conductance of the Ternary  
System Nitric Acid--Nitrogen Dioxide--  
Water at 32° F and Atmospheric Pressure

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ABSTRACT

Part I

The investigation of the kinetics of the decomposition of the liquid phase of nitric acid has indicated that the reaction probably proceeds by way of the unimolecular decomposition of dinitrogen pentoxide which exists in the pure acid. The effects of several inorganic additives in suppressing the rate of decomposition are in agreement with the postulate involving dinitrogen pentoxide. The magnitude of the inhibition of the decomposition by various additives has been found to be insufficient to prevent the eventual attainment of high equilibrium pressures resulting from decomposition when nitric acid is stored in closed containers. The solubility of oxygen in fuming nitric acid has been determined for oxygen pressures up to 21 atmospheres in the temperature range between 35° and 70° C. Under these conditions, the solubility of oxygen was found to increase with an increase in temperature.

Part II

The electrolytic conductance of the system nitric acid--nitrogen dioxide--water in the liquid phase was measured at 0° C and a pressure of 1 atmosphere for compositions containing more than 0.80 weight fraction nitric acid. The conductance of the associated binary systems nitric acid--water and nitric acid--

nitrogen dioxide has been measured over the entire range of compositions from 0 to 1.00 weight fraction nitric acid. The conductance measurements offer additional proof of the self-ionization of pure nitric acid and of the ionization of nitrogen dioxide dissolved in nitric acid.

TABLE OF CONTENTS

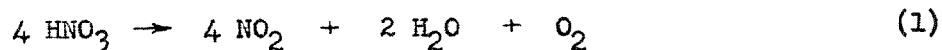
<u>Part</u>	<u>Title</u>	<u>Page</u>
I.	The Kinetics of the Thermal Decomposition of Nitric Acid in the Liquid Phase	
	Introduction . . . . .	1
	Description of Equipment, Methods, and Materials .	4
	Results . . . . .	8
	Discussion . . . . .	17
	Conclusions . . . . .	33
	Nomenclature . . . . .	35
	References . . . . .	37
	Tables . . . . .	39
	Figures . . . . .	43
	Appendix . . . . .	56
II.	Electrolytic Conductance of the Ternary System Nitric Acid -- Nitrogen Dioxide -- Water at 32° F and Atmospheric Pressure	
	Introduction and Summary . . . . .	78
	Description of Equipment and Methods . . . . .	78
	Results . . . . .	79
	Conclusions . . . . .	80
	Tables . . . . .	81
	Figures . . . . .	83
	References . . . . .	86

Part I. The Kinetics of the Thermal Decomposition  
of Nitric Acid in the Liquid Phase

## INTRODUCTION

The thermal decomposition of fuming nitric acid introduces many problems in the storage and handling of this important material which is used as an oxidant for rocket fuels and as a nitrating agent in chemical syntheses. It has been the aim of the experimental studies covered by this report to investigate as many of the factors involved in the kinetics of this decomposition as possible since any knowledge of the basic processes taking place will help in solving the many problems arising through the use of concentrated nitric acid.

The work of many previous investigators<sup>(1,2,3,4)</sup> has established the overall equation for the decomposition to be



for both the liquid and gas phase reactions. These products of decomposition have been observed over a temperature range from room temperature to 80° C for the liquid phase reaction<sup>(2)</sup> and to 475° C for the gas phase reaction<sup>(3)</sup>. At the temperatures encountered in the present investigation, the formation of nitric oxide by the decomposition of nitrogen dioxide\*, according to the equation

\* For the sake of brevity, the term nitrogen dioxide, unless otherwise specified, is used throughout this paper to designate the equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide.



does not occur to any appreciable extent since the equilibrium position lies very far to the left. Also, the attainment of this equilibrium is very rapid at these temperatures and nitric oxide formed from any other reaction would be oxidized quickly to nitrogen dioxide to satisfy equilibrium 2. Reference 5 contains a summary of the equilibrium and rate constants applying to equation 2.

Reaction 1 is reversible and nitric acid can be produced by allowing nitrogen dioxide, water, and oxygen to react under favorable conditions. This is the reaction involved in the commercial preparation of fuming nitric acid by the Fauser process<sup>(6)</sup>. It will be shown later (cf Results) that this reverse reaction is of minor importance under the conditions prevailing during the kinetic studies of the decomposition reaction.

Because the oxygen formed in the reaction described by equation 1 is relatively insoluble in liquid nitric acid, a high equilibrium pressure results if the acid is stored in a closed container for a prolonged period of time. A study of the conditions at chemical and physical equilibrium of the ternary system nitric acid--nitrogen dioxide--water is in progress at this Laboratory, and a report describing the earlier work of this project is available<sup>(7)</sup>.



Other experiments<sup>(3,4)</sup> have shown that the rate of decomposition of nitric acid in the vapor phase by either a photochemical or a thermal mechanism, or by a combination of both, is not sufficient to account for the rates of pressure rise observed under actual storage conditions with both liquid and gas phases present. Therefore, a study of the kinetics of the liquid phase decomposition was undertaken.

The data of Reference 7 indicate that the high equilibrium pressure of pure nitric acid can be substantially reduced by the addition of nitrogen dioxide and water. It is also conceivable that the high pressures encountered under storage conditions might be eliminated if some substance could be found which, when added to the acid, so reduced the rate of decomposition that chemical equilibrium was never attained during the storage period. In Table I are shown the initial rates of decomposition of nitric acid samples to which various compounds, present to the extent of about 0.1 mole fraction, have been added. The rates are expressed as the pressure rise based on a 24-hour day, that would be observed if the acid were stored at 25% ullage.\* The magnitude of the reduction in rate caused by these additives is not sufficiently large to insure that high equilibrium pressures would not be attained during prolonged storage.

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\* Ullage is a term used to describe the volume distribution in a gas—liquid system. Thus, 25% ullage means that the gas phase occupies 25% of the total volume of the system.

In order to interpret the kinetic data, it was necessary to know the solubility of oxygen in nitric acid. The solubility of oxygen in fuming nitric acids\* of various compositions has been measured at oxygen pressures up to 21 atmospheres and over a temperature range from 35° to 70° C. Under these conditions the solubility was found to possess a positive temperature coefficient.

#### DESCRIPTION OF EQUIPMENT, METHODS, AND MATERIALS

The usual method of following the course of a chemical reaction is to observe the change in concentration of one of the products or reactants as the reaction proceeds. It is frequently more convenient, although not always feasible, to observe some physical property of the system which is related to the concentration of one of the species. In the present system, either electrolytic conductance or optical absorbance could have been observed, since they have been shown to vary with the composition of the acid<sup>(8,9)</sup>. However, their use as analytical tools would have required lengthy calibration procedures and for this reason they were not utilized.

The increase in pressure resulting from the formation of oxygen offered a more easily interpreted measure of the rate at which the reaction was occurring. A schematic diagram of the apparatus employed for following the course of the reaction by this method

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\* The term "fuming nitric acid" is used throughout this report to describe systems which contain more than 0.80 weight fraction nitric acid.

is shown in Figure 1. A sample of nitric acid was confined in a 3-mm I.D. precision-bore glass capillary tube by an inert fluorinated hydrocarbon liquid,\* the density of which exceeded that of the liquid acid. The liquid and gas phase volumes of the sample were determined by locating the gas--liquid and liquid--liquid interfaces with a cathetometer which could be positioned with an error of less than  $\pm 0.005$  cm. Surrounding the capillary tube was a vacuum-jacketed oil bath whose temperature could be controlled to within  $\pm 0.05^\circ$  C of any desired value between  $35^\circ$  and  $90^\circ$  C. Agitation was produced within the liquid phase and at the gas--liquid interface of the sample by a magnetically-driven iron pellet encased in glass. The agitator moved back and forth through the entire length of the liquid phase once during each second.

The pressure within the capillary tube was transmitted from the confining fluid through a mercury U-tube to an oil-filled pressure balance which was capable of measuring pressure with a precision of  $\pm 0.005$  atmospheres up to a total pressure of 22 atmospheres. This balance had been calibrated against the laboratory standard balance which was periodically checked against the vapor pressure of solid carbon dioxide.

In the kinetic measurements, a volume of liquid sample of about one milliliter was maintained at approximately 25% ullage

\* "Fluorolube S" - manufactured by Hooker Electrochemical Co.,  
Niagara Falls, N. Y.

and the pressure required to keep the total volume constant was recorded. The rate of pressure change with time could then be related to the rate at which nitric acid was decomposing. The Appendix contains the relationships and assumptions employed in interpreting the kinetic data.

In the measurements of the solubility of oxygen, it was introduced into the capillary tube with the acid sample. The volume was then regulated so as to raise the pressure to about 40 atmospheres and the liquid phase was agitated until it was almost saturated with oxygen. The pressure was next lowered, with agitation, to about 22 atmospheres and the evolution of gas bubbles during this process was taken as an indication that the liquid was saturated with oxygen at the lower pressure. The gas phase volume and pressure were recorded and the pressure was again lowered to about 8 atmospheres with agitation and the new gas phase volume and pressure were measured after gas bubbles ceased to appear in the liquid phase. The time involved in the last step of the procedure was kept as small as possible to minimize the correction made necessary by the evolution of oxygen resulting from the decomposition of the acid. The volume of the liquid phase, which remained constant within the precision of the measurements, was also recorded. The method used to interpret the data is presented in the Appendix.

All samples were prepared by mixing weighed quantities of the desired constituents. To prevent decomposition, samples were stored

at  $-30^{\circ}$  C until used. Liquids were transferred by means of glass syringes fitted with stainless steel hypodermic tubing.

Nitric acid was prepared by vacuum distillation at  $40^{\circ}$  C from a mixture of potassium nitrate and sulfuric acid. The product was condensed at  $-79^{\circ}$  C and subsequently stored under refrigeration at  $-30^{\circ}$  C. The acid thus prepared was analyzed for water by acidimetric titration with sodium hydroxide and was always found to contain less than 0.001 weight fraction water. Previous experience with optical absorbance<sup>(9)</sup> has shown that quantities of nitrogen dioxide too minute to be determined easily by chemical analysis were sufficient to impart a definite yellow color to nitric acid at  $0^{\circ}$  C. Therefore, no specific test for nitrogen dioxide was made, but the acid was considered to be free of this species if a test portion remained colorless when warmed to room temperature. Commercial nitrogen dioxide was fractionated and dried over phosphorous pentoxide. Distilled water was obtained from the available laboratory supply.

Materials used as additives in the kinetic studies were obtained from various sources. Anhydrous ammonium nitrate, potassium nitrate, and potassium bisulfate of C.P. quality were carefully dried under vacuum to remove any traces of adsorbed moisture. Nitrosonium bisulfate was prepared from nitrogen dioxide and concentrated sulfuric acid in accordance with a method tested by Elliott et al<sup>(10)</sup>. Dinitrogen pentoxide, containing about 0.05 weight fraction of a

mixture of nitric acid and nitrogen dioxide, was obtained by distilling nitric acid to which an excess of phosphorous pentoxide had been added. Because this material was used only to indicate the qualitative effect of dinitrogen pentoxide on the rate of decomposition of nitric acid, no further purification was attempted.

Anhydrous sulfuric acid was prepared by mixing concentrated sulfuric acid and oleum until an acidimetric titration indicated that an excess of 0.005 weight fraction sulfur trioxide existed. Commercial, concentrated perchloric acid, containing 0.30 weight fraction water, was mixed with an excess of sulfuric acid and distilled to yield a product which contained less than 0.006 weight fraction water as indicated by titration with sodium hydroxide.

## RESULTS

To determine the practicability and limits of the method chosen to follow the course of the reaction, several preliminary experiments were performed. For example, since oxygen was being produced within the liquid phase, it became necessary to know if any supersaturation of the liquid phase by oxygen occurred. In Figure 2 are shown two pressure vs time curves for identical samples of nitric acid at 71.1° C. The data taken without agitation of the liquid phase are erratic and of little value for measuring the rate of decomposition of nitric acid while those obtained with agitation lie on a smooth curve. For this reason,

all kinetic data were obtained under similar conditions of agitation. This rate of agitation, in which the glass-encased iron pellet moved back and forth through the liquid phase once during each second, was assumed to be sufficient to maintain physical equilibrium between the gas and liquid phases. At  $87.8^{\circ}$  C, the supersaturation of the liquid phase by oxygen was less noticeable than it was at  $71.1^{\circ}$  C. Curve A of Figure 3, which was obtained without agitation, is relatively smooth and corresponds fairly well with curve B which was obtained with agitation.

To show whether or not the liquid phase reaction was a heterogeneous one, the acid-glass interfacial area was increased tenfold by adding glass wool to the liquid phase. The presence of the glass wool prevented agitation and thus permitted supersaturation of the liquid phase by oxygen. This effect was minimized, however, by conducting the experiment at  $87.8^{\circ}$  C where the lack of agitation was shown to have a small effect. The data obtained when the glass wool was present are shown in Figure 3 to agree very closely with curve A, which was obtained for similar conditions without the presence of glass wool. This agreement indicates that the reaction which occurred in the liquid phase was homogeneous and therefore no "scale-effect" was inherent in the apparatus.

It is known that nitric acid can decompose under the influence of light<sup>(1,4,11)</sup>. However, Reynolds and Taylor<sup>(4)</sup> have shown that light acts only on the gas phase and that the rate of the photochemical reaction is of an entirely different order of magnitude

from that of the liquid phase thermal reaction being studied. To determine that the rate of the photochemical reaction was negligible under the conditions encountered in the present work, nitric acid vapor in a 250-cc spherical flask was subjected to artificial light from the same type of source and of the same intensity as existed in the kinetic studies. The constancy of pressure with time for this system at 80° C, as shown in Figure 4, indicated that no appreciable decomposition had occurred.

Data obtained by Johnston et al<sup>(3)</sup> for the gas phase thermal reaction indicate that it is heterogeneous in nature and probably slow when compared to the liquid phase reaction at the temperatures investigated in the present work. The lowest temperature to which Johnston et al carried their work was about 130° C. Although there was considerable scatter in the data, an extrapolation of the highest values of the reported rate constants to 87.8° C yields the maximum possible value of  $2 \times 10^{-5}$  moles/liter·sec for the rate of disappearance of nitric acid in the gas phase. Thus at 25% ullage, an upper limit on the amount of nitric acid decomposing in the gas phase above one liter of pure nitric acid is  $0.7 \times 10^{-5}$  moles/sec as compared to  $140 \times 10^{-5}$  moles/sec decomposing in the liquid phase. This comparison is subject to considerable error, however, since the uncertainty in the gas phase data prevents an unambiguous extrapolation to lower temperatures and also since nitrogen dioxide, and water in the vapor phase were observed by Johnston et al to have a marked inhibiting effect on the heterogeneous



reaction. The comparison does, nevertheless, indicate the maximum possible effect of any gas phase reaction. The gas phase reaction at these lower temperatures is undoubtedly complex and an evaluation of the rate and the various factors influencing it must await a thorough experimental investigation. The energy of activation of the heterogeneous gas phase reaction is about 5 kcal/mole while the experimental energy of activation measured in the present work is of the order of 32 to 37 kcal/mole. The large temperature dependence shown by the systems described by this report in which both liquid and gas phases are present indicates that the rate of the heterogeneous gas phase reaction is not the controlling one. Since no specific information on the heterogeneous gas phase reaction is available, it has been assumed that its rate is negligible and no corrections for it have been applied to the results in Table II.

Water and nitric acid are immiscible with "Fluorolube S" but nitrogen dioxide appears to be soluble in all proportions. There is also some doubt that "Fluorolube S" is completely inert toward nitric acid at elevated temperatures. For these reasons, the method employed here might be open to question if used to follow the course of the reaction over extended periods of time, or if used as a means of measuring conditions at chemical equilibrium. In a reaction, such as has been studied here, in which the products of decomposition have a marked effect on the rate of the reaction and in which the reverse reaction also exerts an influence as the

products increase in concentration, it is the initial rate which is of primary interest. For the kinetic data reported in Table II, the initial rates were established adequately in experiments which did not exceed an hour in duration. No attack of the "Fluorolube S" by nitric acid was ever observed and the loss of nitrogen dioxide from the system by diffusion was visibly insignificant. The method was capable of reproducing kinetic rates to within  $\pm 1\%$ .

The qualitative effects of a few additives on the pressure vs time relationship of nitric acid decomposing at  $87.8^{\circ}\text{C}$  ( $190.0^{\circ}\text{F}$ ) are shown in Figure 5. These data have all been corrected to 25% ullage so that comparisons may be properly made. The method of correction of the observed data from the experimental ullage to a common ullage is included in the Appendix. The increase in rate resulting from the addition of ammonium nitrate, contrasted with the marked decrease caused by added potassium nitrate, is attributed to the presence of the noncondensable gases nitrogen and nitrous oxide formed by the decomposition of ammonium nitrate or as a result of its reaction with nitric acid. The rates of decomposition of nitric acid and nitric acid-additive systems, with the exception of the nitric acid--water system, were too great at  $87.8^{\circ}\text{C}$  to permit accurate determination of the initial values. For this reason, the majority of the kinetic studies were conducted at a temperature of  $71.1^{\circ}\text{C}$  ( $160.0^{\circ}\text{F}$ ).

Since the appearance of oxygen was being used to follow the course of the reaction, it was necessary to know how much of the oxygen formed passed into the gas phase, where it was determined by the measurement of pressure, and how much remained dissolved in the liquid phase. Experiments were performed which indicated the solubility of oxygen in acids of varying composition under as nearly the same conditions of pressure and temperature as possible to those of the kinetic measurements. Within the precision of the solubility measurements,  $\pm 5\%$ , and over the pressure range investigated, the system was found to obey Henry's Law<sup>(12)</sup>.

Constants which permit the calculation of the concentration of oxygen in acids of various compositions within certain temperature limits and at oxygen pressures up to 22 atmospheres, are given in Figure 6. The Appendix contains the original data and the methods of calculating the solubility constants. The observed increase of solubility with an increase in temperature, while unusual, is not unique. Similar positive temperature coefficients have been reported for other systems involving slightly soluble gases<sup>(13,14)</sup>.

A brief summary of the effect on the initial rate of decomposition at  $71.1^{\circ}\text{C}$  of various additives, all present to the extent of about 0.1 mole fraction, is presented in Table I. To emphasize their order of magnitude, these initial rates are expressed as the pressure rise that would be observed in a 24-hour day if the acid were confined at 25% ullage. Table II is a complete tabulation of all the kinetic results obtained. A graphical presentation

of some of the results from Table II has been made in Figures 7 and 8. The original data and the methods by which these data have been treated to give the results of Table II are presented in the Appendix. The density data for the nitric acid-nitrogen dioxide-water system which were used to convert composition on a weight fraction basis to concentration in moles/liter were obtained from the literature<sup>(15,16)</sup> and are shown in Figure 9. The densities of the systems containing salts were obtained by assuming that the partial volume of the additive was negligible. The assumption of additive volumes was employed to calculate the density of the samples containing sulfuric and perchloric acids.

To determine the effect of temperature upon the kinetics, rate measurements with pure nitric acid were made at 71.1°, 62.9°, and 54.4° C (160.0°, 145.0°, and 130.0° F). The pressure vs time curves for these experiments are shown in Figure 10. By the method shown in the Appendix the slopes of these curves can be expressed in terms of the rate of oxygen formation which is related by the overall stoichiometry of equation 1 to the rate of decomposition of nitric acid. If the variation of specific rate constants with temperature were known, then the Arrhenius equation could be used to determine the energy of activation of the rate-determining step of the reaction. This equation takes the form

$$\frac{d \ln k}{dT} = \frac{E_{ACT}}{RT^2} \quad (3)$$

or

$$\frac{d \ln k}{d\left(\frac{1}{T}\right)} = - \frac{E_{ACT}}{R} \quad (4)$$

The meaning of the various symbols is given in Nomenclature. For a general discussion of the Arrhenius equation and its applicability see Reference 17.

In the present work, the actual concentration of the reacting species was not determinable and consequently no specific rate constants could be calculated. However, an apparent, or experimental, energy of activation,  $E_{EXP}$ , was obtained by employing a relationship of the form of the Arrhenius equation, thus

$$\frac{d \log \text{Rate}}{d\left(\frac{1}{T}\right)} = - \frac{E_{EXP}}{2.303 R} \quad (5)$$

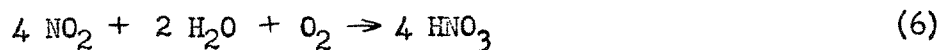
where

$$\text{Rate}^* = - \frac{d [\text{HNO}_3]}{dt} \quad \text{in moles/liter}\cdot\text{sec}$$

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\* For the sake of brevity, the word "Rate" will be used throughout this report to designate the rate of disappearance of nitric acid in moles/liter·sec unless otherwise specified. Since the liquid phase reaction is controlling, the rate is expressed in terms of a unit volume of liquid.

From the form of equation 5 it can be seen that a plot of  $\log$  Rate vs  $\frac{1}{T}$  should yield a straight line of slope  $-\frac{E_{\text{EXP}}}{2.303 R}$  if  $E_{\text{EXP}}$  is a constant over the temperature range investigated. Figure 11 shows the results of such a plot for rate measurements of pure nitric acid at three different temperatures and for mixtures of nitric acid with water and with perchloric acid at two different temperatures. The values of the experimental energy of activation calculated from the slopes of the straight lines for these three systems are presented in Table III.

The shapes of the three curves in Figure 10 indicate that the reverse reaction

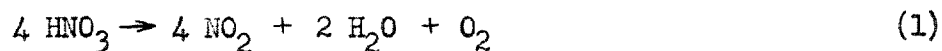


was not taking place to any appreciable extent during the period in which the initial rates were being determined. Although this reverse reaction has not been investigated in the composition range encountered here and its mechanism is not known, it is reasonable to assume that its rate will be a function of the concentration of any or all of the species on the left hand side of equation 6. For the experiments represented in Figure 10, the nitrogen dioxide concentration was initially negligible and increased steadily because of the decomposition of nitric acid during the period of observation. If the rate of the reverse reaction

were of any importance, such a large change in the concentration of one of the participating species would have caused a marked change in the magnitude of the reverse rate and thus would have produced a noticeable curvature of the pressure vs time curves of Figure 10. The same argument applied to all samples shown in Table II except those which initially contained an appreciable amount of nitrogen dioxide. Even in experiments with the latter systems, some curvature would have been expected since the oxygen concentration also underwent a significant change as the decomposition occurred. The absence of such a curvature during the period used to determine the initial rate for each of the samples of Table II has been considered sufficient evidence that the rate of the reverse reaction is negligible.

#### DISCUSSION

One of the purposes of the kinetic study of the thermal decomposition of liquid nitric acid is to determine the mechanism of the reaction; i.e., the actual step or series of steps by which the products are formed from the reactants. In the present study, the equation which describes the overall effect of the decomposition is



but it is not to be supposed that four nitric acid molecules simultaneously react to form the indicated products. Probably the reaction consists of a series of steps, one of which is sufficiently slower than the others that it alone controls the observed rate.

Frank and Schirmer<sup>(2)</sup> observed the decomposition of pure nitric acid and determined a rate expression of the form

$$\frac{-d [\text{HNO}_3]}{dt} = k_7 \frac{[\text{HNO}_3]^2}{[\text{H}_2\text{O}]} \quad (7)$$

They did not indicate the range of compositions over which their investigation extended. An equation of the type



can be written for the dissociation of nitric acid. Application of simple equilibrium concepts<sup>(12)</sup> to equation 8 yields the following expression for the concentration of dinitrogen pentoxide:

$$[\text{N}_2\text{O}_5] = K_9 \frac{[\text{HNO}_3]^2}{[\text{H}_2\text{O}]} \quad (9)$$

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\* The subscripts on constants refer to the number of the equation by which they are defined or in which they first appear.

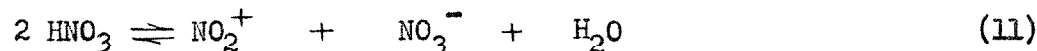


If equations 7 and 9 are combined, a rate equation in terms of the concentration of dinitrogen pentoxide can be obtained

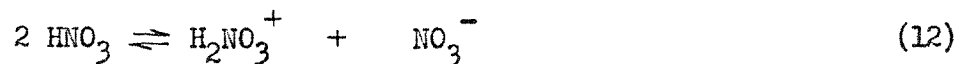
$$\frac{-d [\text{HNO}_3]}{dt} = k_7 (K_9)^{-1} [\text{N}_2\text{O}_5] = k_{10} [\text{N}_2\text{O}_5] \quad (10)$$

Equation 10 suggests that the nitric acid decomposition reaction may be just the first order decomposition of dinitrogen pentoxide. Frank and Schirmer<sup>(2)</sup> proposed such a mechanism and measured the rate of decomposition of acid samples containing excess dinitrogen pentoxide. By assuming that pure nitric acid contained about 0.008 weight fraction dinitrogen pentoxide, they were able to obtain rate expressions in which the empirical value of  $k_{10}$  varied from a constant value by only about  $\pm 10\%$ .

The work of Frank and Schirmer was done before the recent evidence for the self-ionization of pure nitric acid was available<sup>(8,9,18,19,20,21)</sup>. It has been shown that the following ionic equilibrium exists in pure nitric acid:



This ionization is thought really to occur in two steps. The first step is a proton shift with the formation of the nitricacidium ion ( $\text{H}_2\text{NO}_3^+$ ), thus

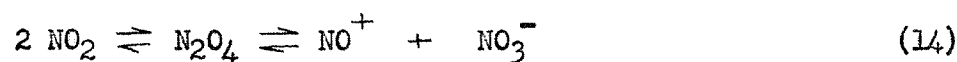


The nitricacidium ion then almost completely dissociates into nitronium ion ( $\text{NO}_2^+$ ) and water,



and the net result is the same as is shown in equation 11.

Nitrogen dioxide and dinitrogen pentoxide also ionize in nitric acid solution in accordance with the equations



and



The equilibrium position of equation 15 has been shown<sup>(21)</sup> to lie

far to the right, even at dinitrogen pentoxide concentrations as high as 0.6 molar.

The existence of such ionization equilibria prevent the rate expression of equation 10 from being exact unless the actual concentration of the molecular species dinitrogen pentoxide is known. There is also a possibility that the reacting species may not be dinitrogen pentoxide but may instead be one of the products of its ionic dissociation. Since the nitrate ion is relatively stable, the nitronium ion ( $\text{NO}_2^+$ ) may perhaps be the reactive species. Any mechanism which requires that the nitric acid molecule or the nitricacidium ion be the reactive species involved in the rate determining step is ruled out by the marked decrease in rate caused by additional water, see Figure 7. The limited dilution of nitric acid by water made in the present experiments caused only a small change in the concentration of the nitric acid molecule and the corresponding effect on the rate would thus be expected to be smaller than the observed effect. An increase in water concentration actually causes an increase in nitricacidium ion as indicated by equation 13, and therefore an increase in rate would be predicted if nitricacidium ion were the reactive species.

A choice between the dinitrogen pentoxide and nitronium ion mechanisms can be made on the basis of the data given in Table II. In qualitative agreement with the observed data, both theories predict that the presence of additional dinitrogen pentoxide should increase the rate and that added water should decrease it. The

quantitative effect of added water, as shown in Figure 7, can be examined in more detail. If it is postulated that the rate of disappearance of nitric acid is given by the expression

$$\text{Rate} = k_{16} [\text{N}_2\text{O}_5] \quad (16)$$

in which  $[\text{N}_2\text{O}_5]$  represents the actual molecular concentration of dinitrogen pentoxide and in which  $k_{16}$  is a true specific rate constant, then

$$\log \text{Rate} = \log k_{16} + \log [\text{N}_2\text{O}_5] \quad (17)$$

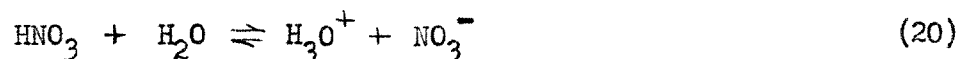
A combination of equation 9 with equation 17 yields

$$\log \text{Rate} = \log k_{16} + \log K_9 + \log [\text{HNO}_3]^2 - \log [\text{H}_2\text{O}] \quad (18)$$

Differentiating both sides and dividing by  $d \log [\text{H}_2\text{O}]$ , there is obtained the expression

$$\frac{d \log \text{Rate}}{d \log [\text{H}_2\text{O}]} = \frac{d \log [\text{HNO}_3]^2}{d \log [\text{H}_2\text{O}]} - 1 \quad (19)$$

From a consideration of the change in density of nitric acid as it is diluted with water, see Figure 9, an approximate value of -0.04 can be obtained for the term involving the concentration of nitric acid. Therefore, a plot of log Rate vs log  $[H_2O]$  should give a straight line with a slope of about -1.04. Such behavior is exhibited approximately by the data, as shown in Figure 7, for concentrations of water up to 2.5 moles/liter (0.03 weight fraction). It has been shown by conductance measurements at 0° C<sup>(8)</sup> that the ionization of nitric acid proceeds primarily in accordance with equation 11 for systems containing less than 0.03 weight fraction water. As the amount of water in the acid is increased from 0.03 weight fraction, the normal mode of ionization in aqueous solutions begins to occur, namely



The marked increase in the inhibiting effect of water on the decomposition reaction when present at concentrations greater than 2.5 moles/liter may be due to the influence of the same conditions which cause the change in mode of ionization. No quantitative explanation for this effect is offered.

The effect of water on the rate as predicted by a mechanism involving nitronium ion is different from that for the dinitrogen pentoxide hypothesis presented above. Since in pure nitric acid

the principal ionization occurs by way of equation 11, the nitronium and nitrate ion concentrations will be approximately equal for samples containing less than 0.03 weight fraction water. The nitronium ion concentration can thus be related to the nitric acid and water concentrations by the expression

$$[\text{NO}_2^+] = \left( \frac{K_{11}}{[\text{H}_2\text{O}]} \right)^{\frac{1}{2}} [\text{HNO}_3] \quad (21)$$

If the rate is given by

$$\text{Rate} = k_{22} [\text{NO}_2^+] \quad (22)$$

Then, by the same method by which equation 19 was obtained,

$$\frac{d \log \text{Rate}}{d \log [\text{H}_2\text{O}]} = \frac{d \log [\text{HNO}_3]}{d \log [\text{H}_2\text{O}]} - \frac{1}{2} \quad (23)$$

In order to make the nitronium ion theory agree with the data of Figure 7 for less than 0.03 weight fraction water, it is therefore necessary to assume that

$$\text{Rate} = k_{24} [\text{NO}_2^+]^2 \quad (24)$$

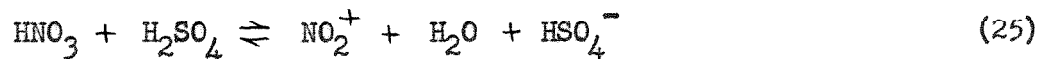
from which is obtained by the previously discussed mathematical procedure, an expression identical to equation 19.

The mechanism requiring the second order dependence on nitronium ion is not plausible if treated by simple collision theory<sup>(23)</sup>. Even if every collision between two nitronium ions led to a reaction, by the experimental results there are still about  $10^8$  more molecules decomposing than there could be bimolecular collisions between nitronium ions according to theory. Although reactions between ions of like charge do occur in solutions, the observed rates never exceed those predicted by the simple collision theory and usually are lower by a factor of  $10^2$  or  $10^3$ .<sup>(23)</sup>

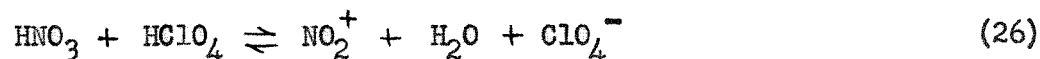
One means of differentiating between the two mechanisms would be to alter the system so that either dinitrogen pentoxide or nitronium ion is increased in concentration while the other is simultaneously decreased. A method for accomplishing this is to add excess nitrate ion since it suppresses the nitronium ion and water in equation 11 and this decrease in water causes an increase in dinitrogen pentoxide as shown by equation 8. Both potassium nitrate and nitrogen dioxide, which ionizes to a certain extent in accordance with equation 14, have been used as a source of additional nitrate ion. Coincident with any effect caused by the influence of the extra nitrate ion on the dissociation equilibrium is the general salt effect due to the increase in ionic strength of the solution by the added salt. Thus, before the specific effect of the added nitrate species on the reaction kinetics can be determined quantitatively, the magnitude of the salt effect must be

evaluated.

It has been shown from Raman spectra<sup>(22)</sup> that acids which are stronger than nitric acid can donate a proton to the nitric acid to form the nitricacidium ion which dissociates as shown in equation 13. The overall effects for mixtures of sulfuric and perchloric acids with nitric acid are



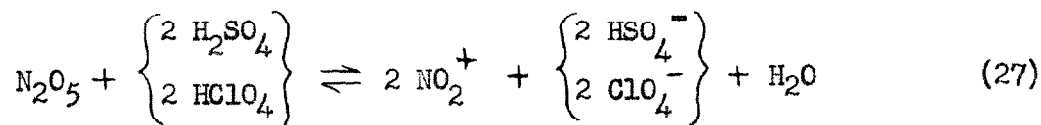
and



The position of the equilibrium lies very far to the right even at sulfuric and perchloric acid concentrations as high as 0.1 mole fraction. For this reason, potassium bisulfate and potassium perchlorate would be considered neutral salts since they would exert no mass action effect on the ionic equilibrium of equation 11 involving nitronium ion. Only potassium bisulfate was soluble enough to permit its use for evaluating the general salt effect of additives in the concentration range of the data of Table II. The change in the decomposition rate caused by the addition of this salt to nitric acid is shown in Figure 8, where it can be easily



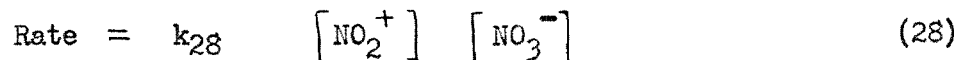
compared with the other experimental results. The behavior of sulfuric and perchloric acids in nitric acid, as given in equations 25 and 26, offers another situation in which the additive causes an increase in the nitronium ion concentration while the water formed suppresses dinitrogen pentoxide. The combination of equation 8 with equations 25 and 26 shows the overall effect to be:



Raman spectrum studies<sup>(22)</sup> have shown that the position of equilibrium lies very far to the right.

After the salt effect has been taken into account, the specific influence of added nitrate ion and of acids stronger than nitric acid on the rate indicates that dinitrogen pentoxide is the reactive species since the rate varies directly as a function of its concentration. The decrease in rate caused by nitrosonium bisulfate ( $\text{NOHSO}_4$ ) indicates not only the salt effect, as shown by potassium bisulfate, but also a specific effect due to the nitrosonium ion ( $\text{NO}^+$ ). Some of the nitrosonium ion removes nitrate ion to form nitrogen dioxide in accordance with equation 14. This decrease in nitrate ion requires a shift in the equilibrium of equation 15 which lowers the concentration of dinitrogen pentoxide. Thus in agreement with experiment, nitrosonium bisulfate should cause more of a reduction in rate than potassium bisulfate.

No mention has been previously made of the possibility that the rate of reaction might be expressed by the equation



This mechanism is subject to the same criticism with respect to the number of bimolecular collisions as is the second order nitronium ion theory, although reactions in solutions between ions of unlike charge are known to proceed at rates in excess of those predicted by the simple collision theory<sup>(23)</sup>. It is possible that the decomposition proceeds by a combination of each of the rate determining steps described by equations 16 and 28. The present data do not appear adequate to permit a differentiation between these two mechanisms.

The decrease in rate caused by the inert salt, potassium bisulfate can be explained qualitatively in terms of its effect on the mechanisms involved in both equations 16 and 28. The normal result of an increase in ionic strength is to decrease the rate of a reaction occurring in solution between two ions of unlike charge, and to increase the rate of a reaction in which two ions of like charge are participating<sup>(23)</sup>. Thus the effect of potassium bisulfate is in agreement with equation 28 but not equation 24 which has already been disproved by other arguments.

In the earlier parts of this discussion, it has been tacitly

assumed that the various equilibrium expressions were correct when written in terms of the concentrations of the species involved. The equilibrium equations can be expected to be obeyed accurately only if they are expressed in terms of the activities of the species involved. Since neither the activities nor the actual concentrations of most of the species are known, the distinction between activity and concentration has not been considered in the qualitative discussion of the rates. To explain the salt effect in conjunction with equation 16, it is necessary to make the reasonable assumption that the activity coefficients of the various ionic species decrease with increasing ionic strength at least in the composition ranges investigated here. The net effect of such a decrease in activity coefficients is to cause an increase in concentration of the ionic species involved in equation 11 with the accompanying increase in water concentration. In accordance with equation 8 such an increase in water concentration requires a decrease in the concentration of dinitrogen pentoxide and this would result in a decrease in rate as indicated by equation 16. For a general discussion of the effect of ionic strength on activity coefficients see Reference 12. No theories have been developed which would allow a quantitative prediction of the effects to be observed in systems with as large ionic concentrations as exist in the systems under investigation here.

The experimental energies of activation determined in this work differ from the energies of activation which would be calculated from the Arrhenius equation. For example, if the actual

concentration of the molecular species dinitrogen pentoxide were known, then a specific rate constant,  $k_{16}$ , could be calculated from the observed rate of decomposition by applying equation 16. The energy of activation,  $E_{ACT}$ , could then be obtained from the Arrhenius equation

$$\frac{d \log k_{16}}{d \left( \frac{1}{T} \right)} = - \frac{E_{ACT}}{2.303 R} \quad (29)$$

The relationship between the experimental and Arrhenius activation energies can be obtained from equation 18,

$$\log \text{Rate} = \log k_{16} + \log K_9 + \log \frac{[\text{HNO}_3]^2}{[\text{H}_2\text{O}]} \quad (18)$$

If equation 18 is differentiated with respect to  $\frac{1}{T}$ , there is obtained the expression

$$\frac{d \log \text{Rate}}{d \left( \frac{1}{T} \right)} = \frac{d \log k_{16}}{d \left( \frac{1}{T} \right)} + \frac{d \log K_9}{d \left( \frac{1}{T} \right)} + \frac{d}{d \left( \frac{1}{T} \right)} \left\{ \log \frac{[\text{HNO}_3]^2}{[\text{H}_2\text{O}]} \right\} \quad (30)$$

which, by definition, is equal to

$$- \frac{E_{\text{EXP}}}{2.303 R}$$

as given by equation 5. The term involving the equilibrium constant  $K_0$  is related by the Van't Hoff equation<sup>(12)</sup> to the heat of isobaric reaction  $\Delta H_0$ , for the reaction described by equation 9. The term involving the concentrations of nitric acid and water is a function of temperature, pressure, and composition and as such would be sensitive to the temperature dependence of all other equilibria involving nitric acid and water. Examples of such equilibria are given in equations 11, 20, 25, and 26. The relationship between the experimental and Arrhenius energies of activation is thus

$$E_{\text{ACT}} = E_{\text{EXP}} - \Delta H_0 - 2.303 R (\text{function of } T, P, \text{ and composition}) \quad (31)$$

At the present time, insufficient information is available for the nitric acid system to permit evaluation of all of the terms on the right hand side of equation 31.

The energy of activation for the decomposition of nitric acid reported by Frank and Schirmer<sup>(2)</sup> of about 24 kcal/mole included some of the  $\Delta H$  terms since the specific rate constants

were obtained on the assumption that all of the analytically measured dinitrogen pentoxide was present as that molecular species. Eyring and Daniels<sup>(24)</sup> studied the decomposition of dinitrogen pentoxide in inert solvents and in nitric acid. The observed energy of activation in inert solvents, approximately 24 kcal, and the rate of reaction agreed with the energy of activation and the rate observed for the gas phase decomposition of dinitrogen pentoxide. In nitric acid solution, the rate was found to be only one-twentieth as large as the gas phase rate at the same temperature; and the energy of activation, obtained by employing the same assumption regarding concentration as did Frank and Schirmer, was calculated to be 28 kcal/mole. The decrease in the rate of decomposition was attributed to a solvation effect; but, in view of the recent disclosures of the ionization phenomena occurring in fuming nitric acid, this decrease in rate is explained by the extensive ionization of the dissolved dinitrogen pentoxide. The experimental energies of activation found in the present investigation are shown in Table III to vary between 32 and 37 kcal/mole.

It has been suggested<sup>(25)</sup> that the techniques of infra-red spectrophotometry might be employed to determine the actual or relative concentrations of the various species present in analytically pure nitric acid and in solutions of other compounds in fuming nitric acid. The observation of the change in concentration of the various species with temperature would permit the estimation

of the unknown heat quantities in equation 31.

### CONCLUSIONS

The present investigation presents the effects of several additive materials on the rate of the thermal decomposition of nitric acid in the liquid phase. It has been shown that the presence of any of these additives in quantities up to 0.1 mole fraction will not, from a kinetic standpoint, prevent the attainment of any equilibrium pressures which pure nitric acid under the same storage conditions would exhibit.

The kinetic studies indicate that the rate determining step in the decomposition reaction involves the first order decomposition of the molecular species dinitrogen pentoxide. An experimental energy of activation has been determined for the decomposition of pure nitric acid and for the nitric acid-water and nitric acid-perchloric acid systems.

The solubility of oxygen in fuming nitric acid has been measured since a knowledge of its magnitude was necessary in the interpretation of the kinetic data. In the temperature range investigated, the solubility of oxygen in fuming nitric acid was observed to increase with increasing temperature.

In order to emphasize the effects of various additives in this work, most of the additives have been present to the extent of about 0.1 mole fraction. It is realized that this concentration

is so great that most of the theoretical treatments of liquid phase kinetics cannot be applied. If further work in this field is undertaken, it is suggested that more dilute solutions be investigated. Such a procedure will not only allow a closer approach to ideal conditions but will also permit the use of many additives, which, by virtue of their low solubility in nitric acid, could not be investigated in the present work. The application to this acid system of theories valid only at low ionic strength cannot be expected to yield the same results as their application to dilute aqueous systems, since, at 70° C, the self ionization of nitric acid alone is sufficient to give an ionic strength of about 0.2 moles/liter.



## NOMENCLATURE

### Symbols

d differential operator

$E_{ACT}$  activation energy in kcal/mole as defined by the Arrhenius equation

$E_{EXP}$  experimental activation energy in kcal/mole obtained from the variation of experimental rate with temperature

K thermodynamic equilibrium constant

k specific rate constant

n number of gram moles of a constituent

P pressure, in atmospheres

R universal gas constant

T temperature, in °K, unless otherwise specified

t time, in seconds

U ullage, defined as  $\frac{V_G}{V_G + V_L} \times 100$ , in %

V volume in liters

$\alpha$  Henry's law constant, in moles/liter·atm

$\Delta H$  thermodynamic heat of isobaric reaction in kcal/mole

[A] brackets indicate concentration of species A in moles/liter

### Subscripts

A refers to acid constituents including nitrogen dioxide, water, and additives

d refers to oxygen formed as a result of decomposition of acid

G refers to gas phase

$HNO_3$  refers to nitric acid molecules only

- I refers to inert materials, primarily nitrogen
- L refers to liquid phase
- O refers to oxygen
- 1,2 refer to conditions specified in text

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LIST OF TABLES

- I. Summary of the Effect of Various Additives on the Initial Rate of Decomposition of Liquid Nitric Acid at 71.1° C
- II. Summary of Kinetic Data
- III. Experimental Energy of Activation of Fuming Nitric Acid

Table I

Summary of the Effect of Various Additives  
on the Initial Rate of Decomposition  
of Liquid Nitric Acid at 71.1°C

Additive <sup>a</sup>	Initial Rate of Decomposition <sup>b</sup> atm/24-hour day
N <sub>2</sub> O <sub>5</sub>	1570
None	194
N <sub>2</sub> O <sub>4</sub>	90
KNO <sub>3</sub>	57
KHSO <sub>4</sub>	44
H <sub>2</sub> SO <sub>4</sub>	25
NOHSO <sub>4</sub>	20
HClO <sub>4</sub>	16
H <sub>2</sub> O	10

<sup>a</sup> Additives present initially in amounts  
of about 0.1 mole fraction.

<sup>b</sup> The initial rate of decomposition is  
expressed in terms of pressure rise  
per 24-hour day for acid stored at  
25% ullage.

Table II

Summary of Kinetic Data

Composition <sup>a</sup> of the System	Concentration <sup>b</sup> of Additive	Mole Fraction <sup>b</sup> of Additive	T	$-\frac{d[\text{HNO}_3]}{dt}$
weight fraction	moles/liter		°C	moles/liter-sec x 10 <sup>5</sup>
1.00 HNO <sub>3</sub>	0	0	71.1	16.1
1.00 HNO <sub>3</sub>	0	0	62.8	5.06
1.00 HNO <sub>3</sub>	0	0	54.4	1.49
0.0088 H <sub>2</sub> O	0.69	0.030	71.1	3.34
0.0088 H <sub>2</sub> O	0.68	0.030	87.8	33.4
0.0304 H <sub>2</sub> O	2.39	0.099	71.1	0.85
0.0304 H <sub>2</sub> O	2.34	0.099	87.8	10.5
0.0600 H <sub>2</sub> O	4.59	0.183	87.8	1.84
0.0509 N <sub>2</sub> O <sub>4</sub>	0.80	0.035	71.1	11.1
0.0971 N <sub>2</sub> O <sub>4</sub>	1.56	0.069	71.1	8.60
0.1536 N <sub>2</sub> O <sub>4</sub>	2.50	0.111	71.1	6.30
0.0089 H <sub>2</sub> O } 0.0866 N <sub>2</sub> O <sub>4</sub> }	0.73 1.38	0.031 0.060	71.1	2.51
0.165 N <sub>2</sub> O <sub>5</sub>	2.5	0.103	71.1	131
0.1586 KNO <sub>3</sub>	2.6	0.105	71.1	4.78
0.2085 KHSO <sub>4</sub>	2.7	0.109	71.1	3.85
0.1836 NOHSO <sub>4</sub>	2.5	0.100	71.1	1.60
0.1584 H <sub>2</sub> SO <sub>4</sub>	2.4	0.108	71.1	2.03
0.1363 HClO <sub>4</sub>	2.0	0.090	71.1	1.31
0.1363 HClO <sub>4</sub>	2.0	0.090	87.8	13.3

<sup>a</sup> When not expressed, the remainder of the sample consists of HNO<sub>3</sub>.

<sup>b</sup> The given values of concentration and mole fraction for the additives are those which would exist if no ionization occurred.

Table III

Experimental Energy of Activation  
of Fuming Nitric Acid

System	$E_{\text{EXP}}$ kcal/mole
Pure $\text{HNO}_3$	32
$\text{HNO}_3$ + 0.136 weight fraction $\text{HClO}_4$	34
$\text{HNO}_3$ + 0.030 weight fraction $\text{H}_2\text{O}$	37



LIST OF FIGURES

1. Schematic Diagram of Apparatus
2. The Effect of Agitation of the Liquid Phase on the Observed Pressure Increase for Nitric Acid at  $71.1^{\circ}\text{C}$
3. The Effect of Increased Surface Area on the Decomposition Rate at  $87.8^{\circ}\text{C}$
4. The Stability of Nitric Acid Vapor in the Presence of Light at  $80^{\circ}\text{C}$
5. The Effect of Various Additives on the Rate of Decomposition of Nitric Acid at  $87.8^{\circ}\text{C}$
6. The Solubility of Oxygen in Fuming Nitric Acid
7. The Effect of Water on the Rate of Decomposition of Nitric Acid
8. The Effect of Several Additives on the Rate of Decomposition of Nitric Acid at  $71.1^{\circ}\text{C}$
9. The Effect of Temperature on the Density of Fuming Nitric Acid
10. The Effect of Temperature on the Rate of Decomposition of Pure Nitric Acid
11. The Variation with Temperature of the Rate of Decomposition of Fuming Nitric Acid
12. The Effect of Temperature on the Total Pressure of Vapor above Fuming Nitric Acid

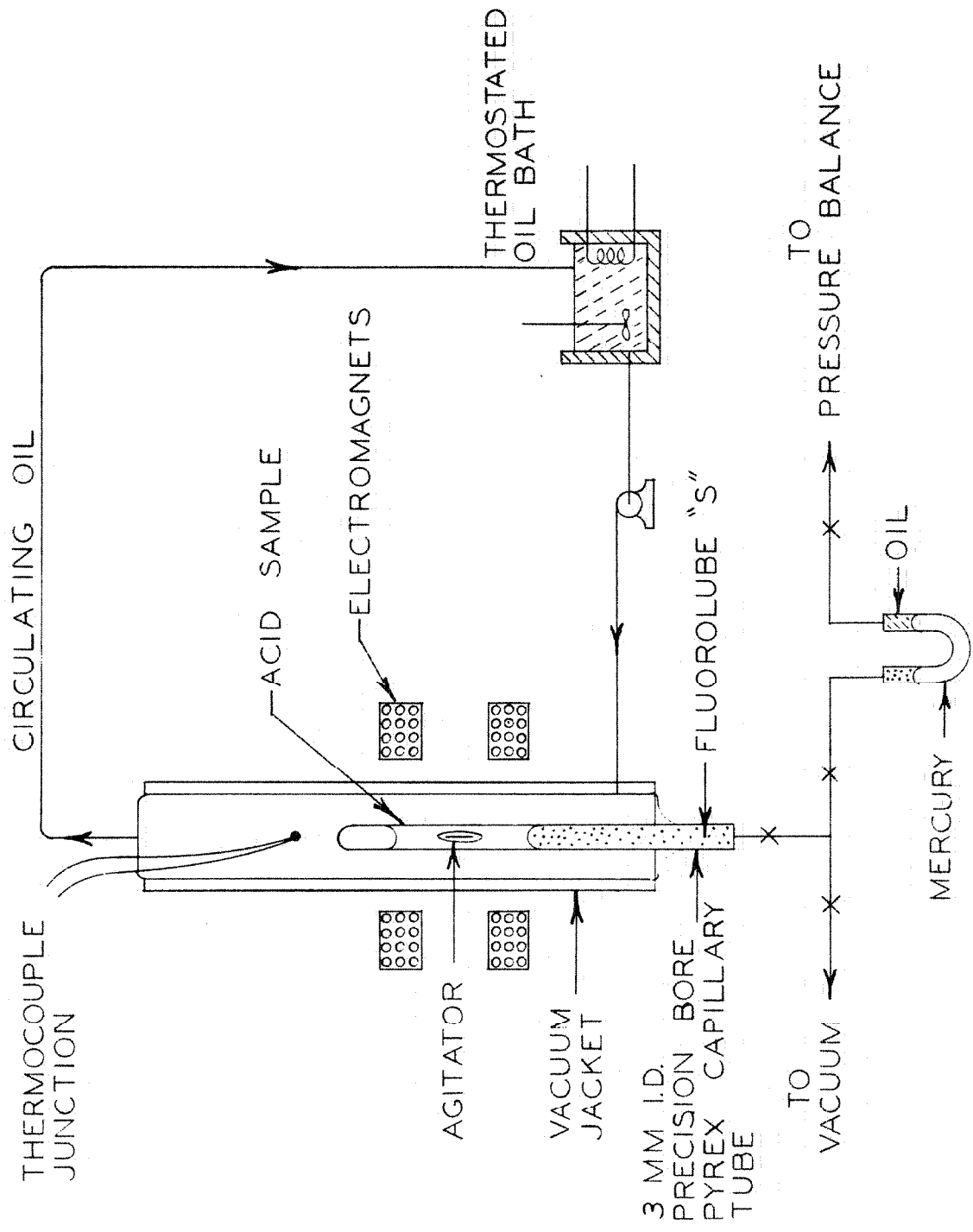


Figure 1. Schematic Diagram of Apparatus

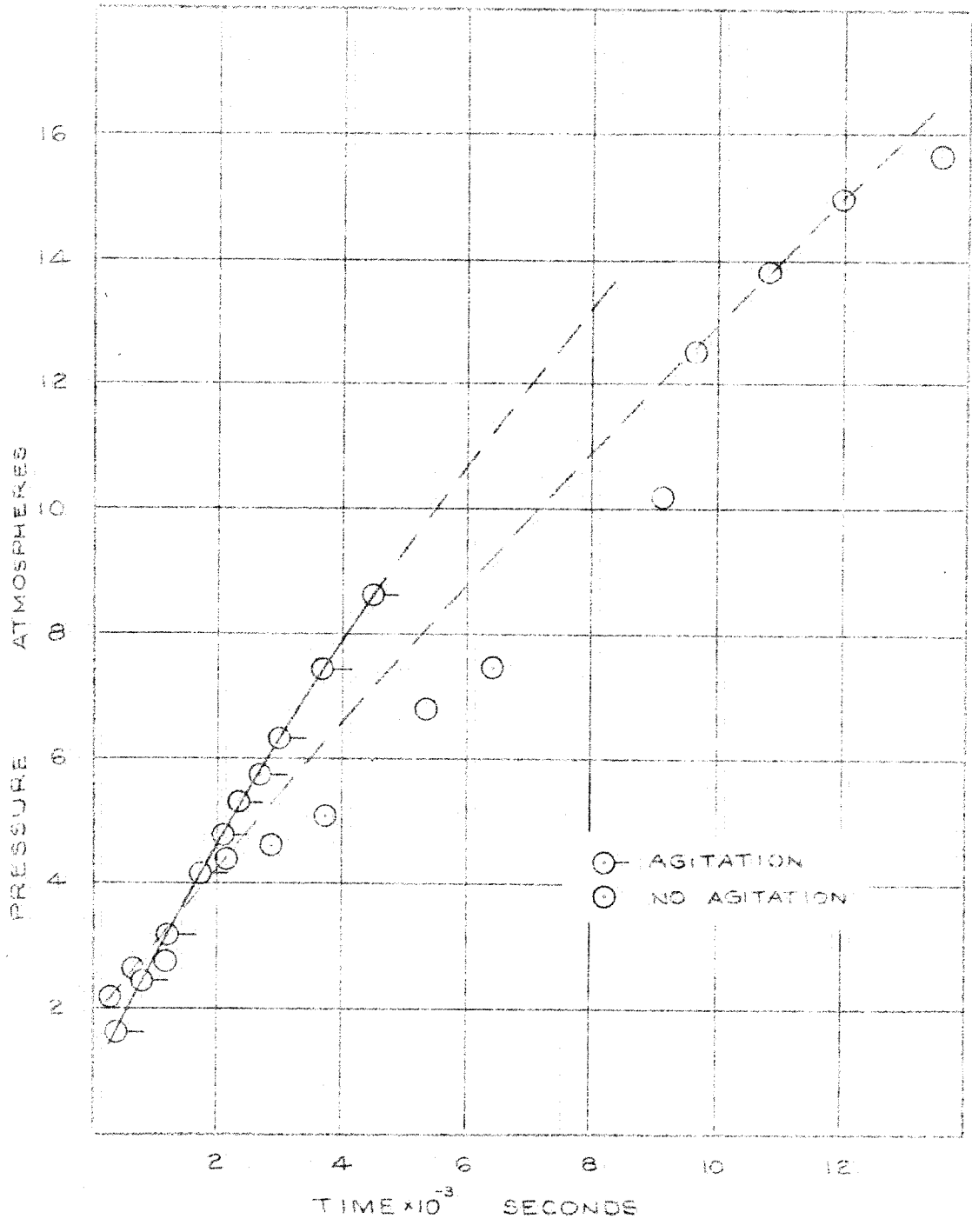


Figure 2. The Effect of Agitation of the Liquid Phase on the Observed Pressure Increase for Nitric Acid at 71.1°C

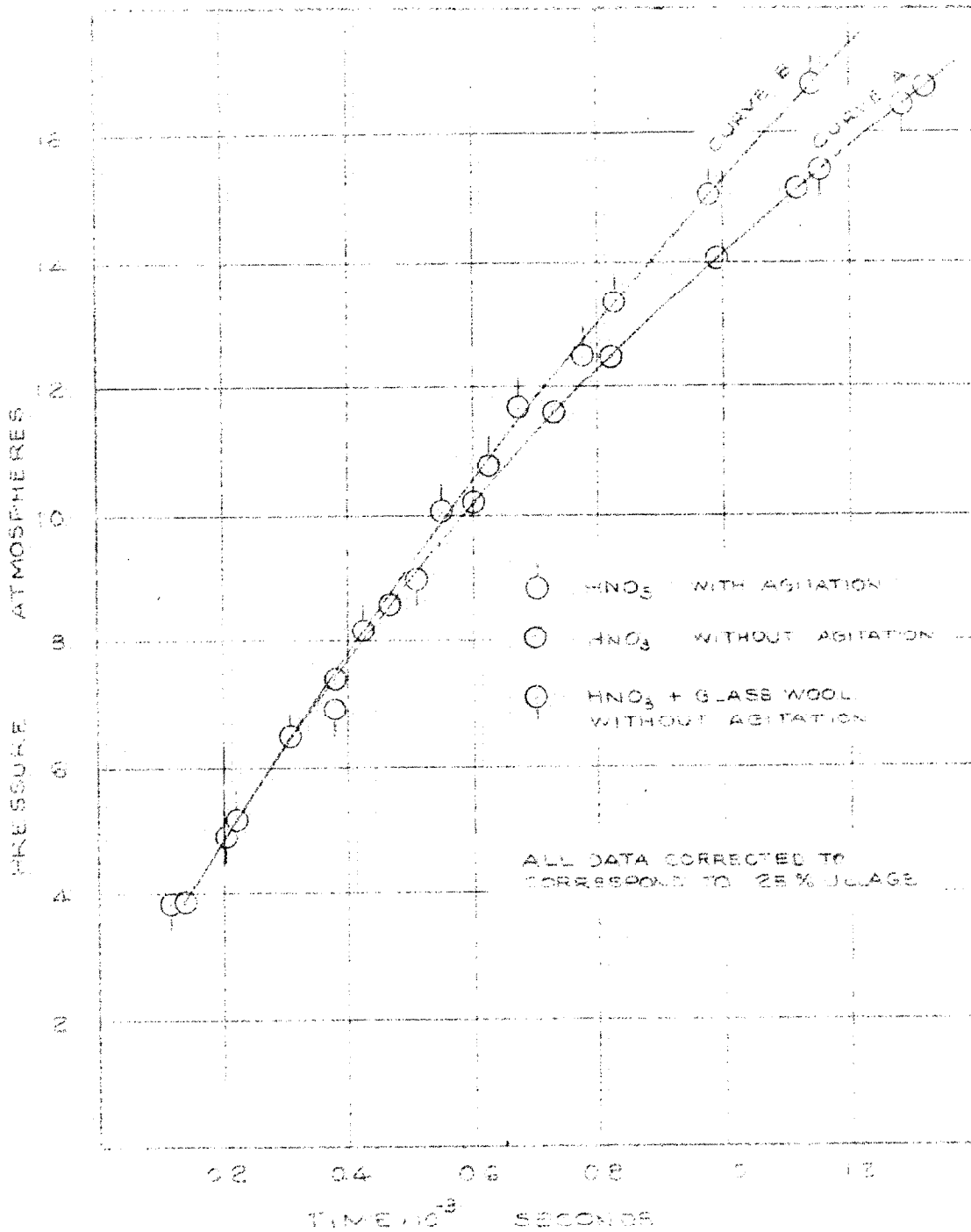


Figure 3. The Effect of Increased Surface Area on the Decomposition Rate at 87.8 °C

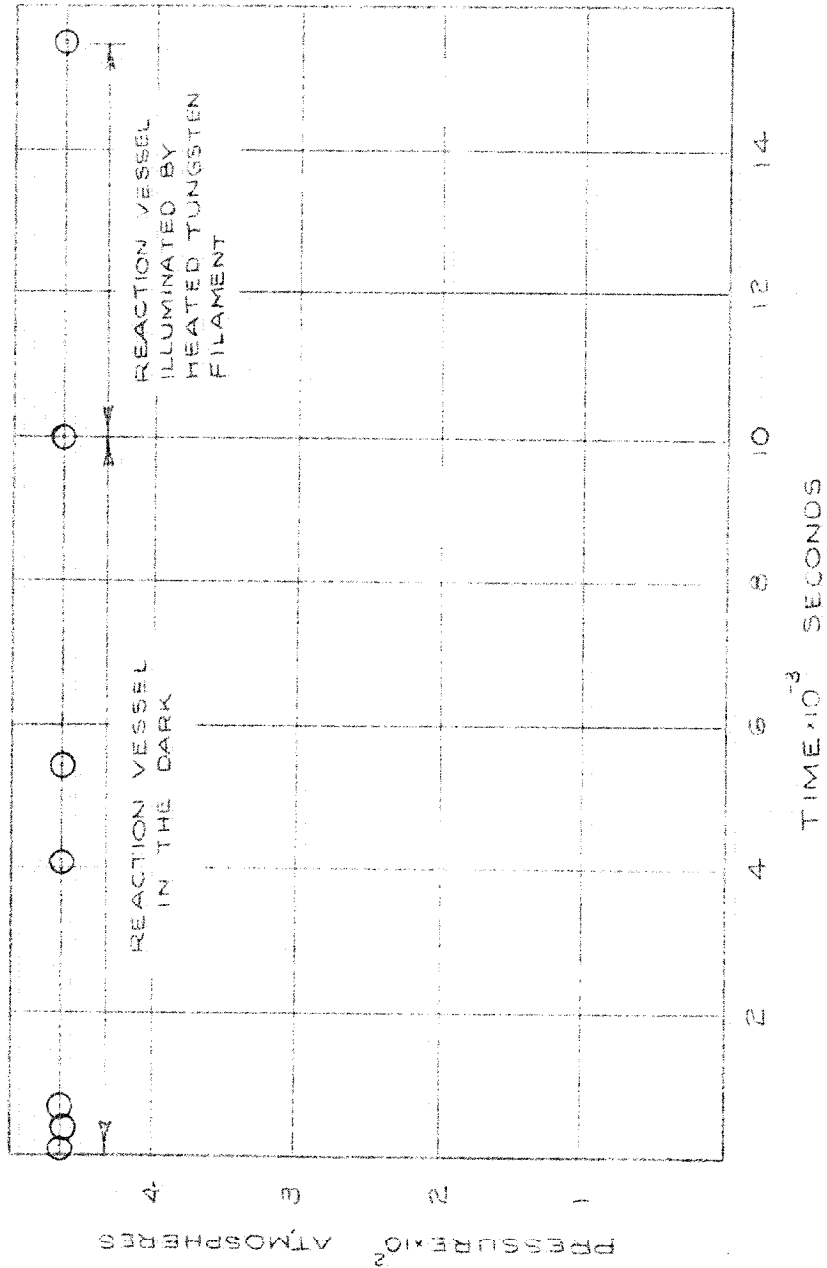


Figure 4. The Stability of Nitric Acid Vapor in the Presence of Light at 80° C

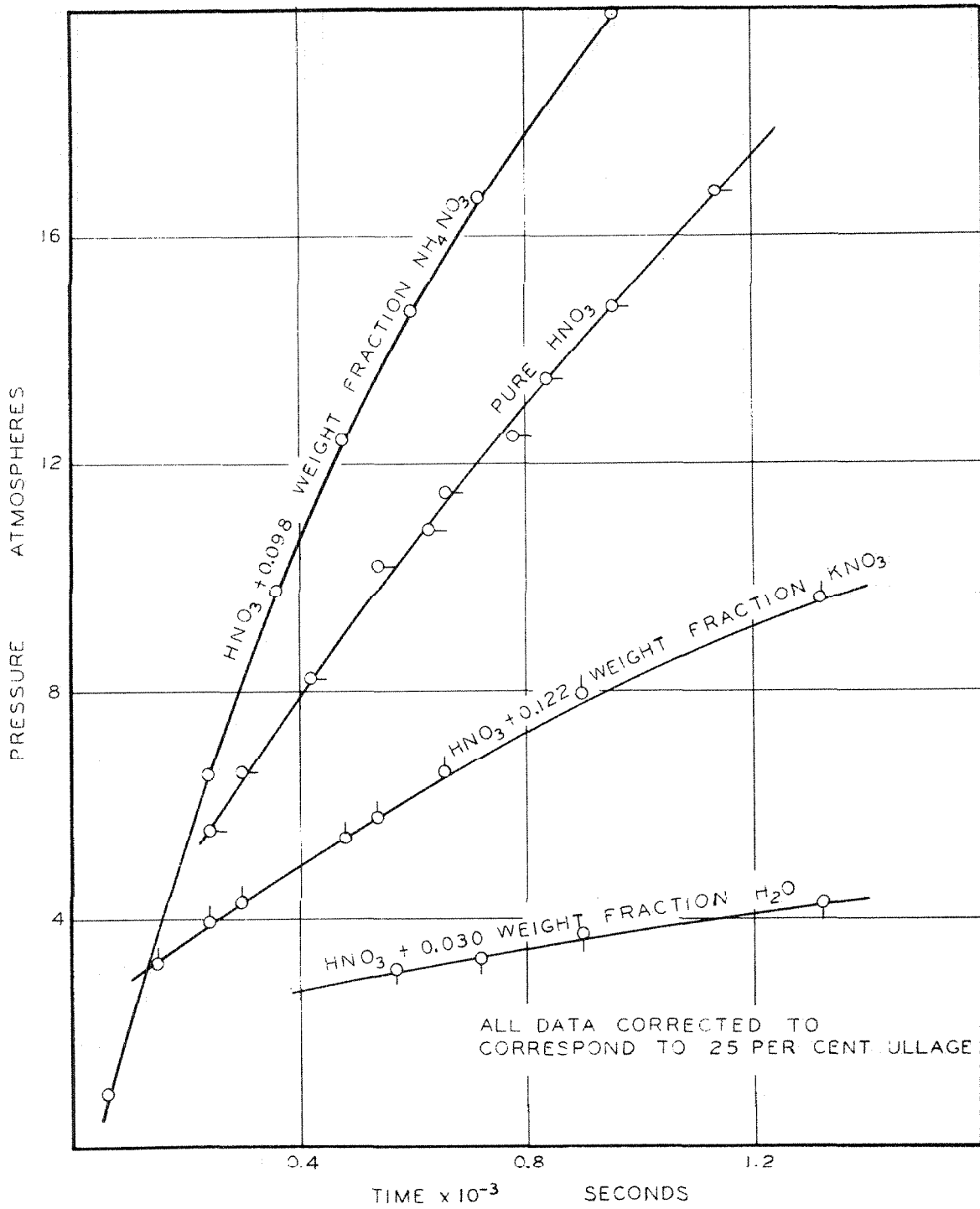


Figure 5. The Effect of Various Additives on the Rate of Decomposition of Nitric Acid at 87.8° C

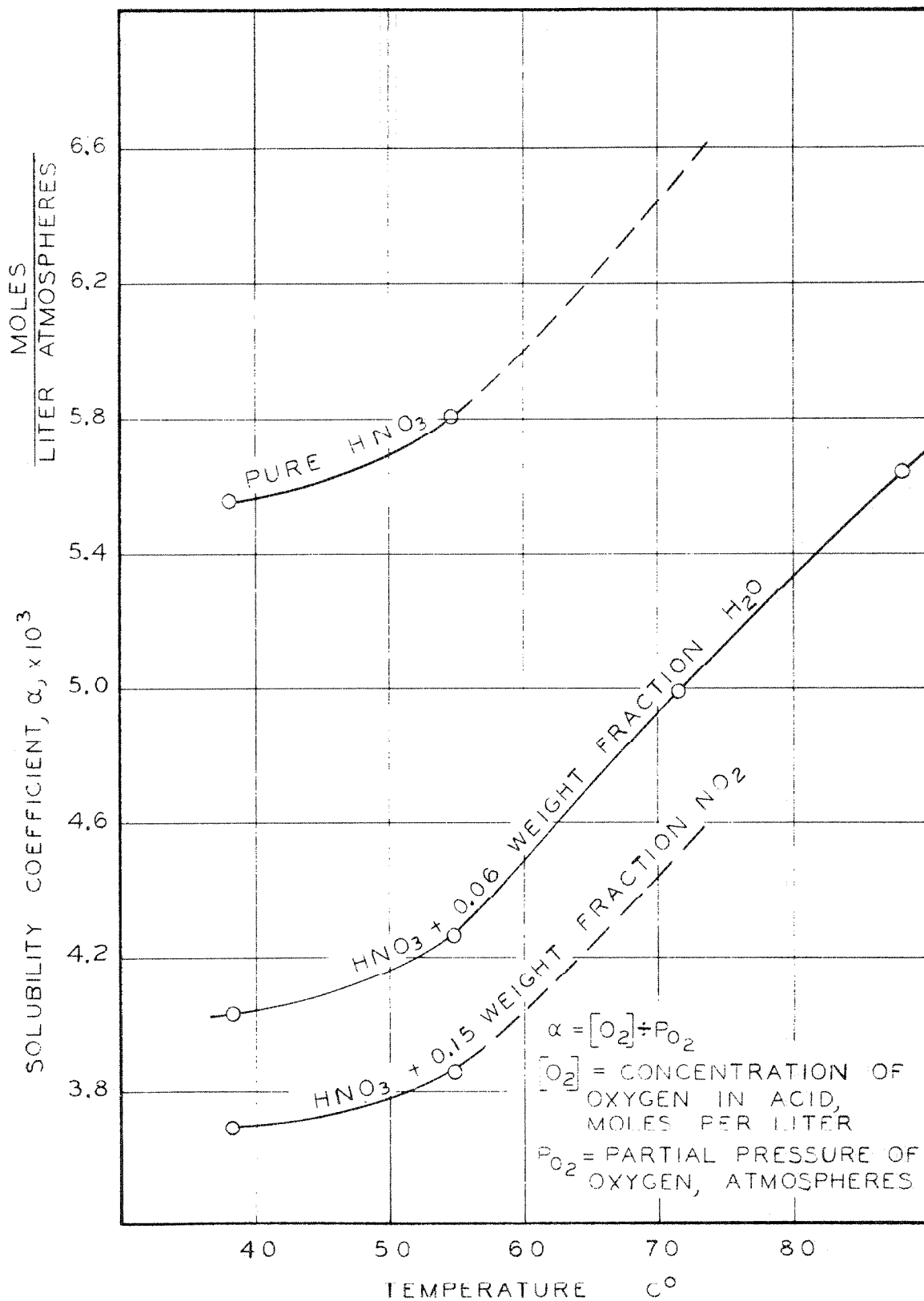


Figure 6. The Solubility of Oxygen in Fuming Nitric Acid

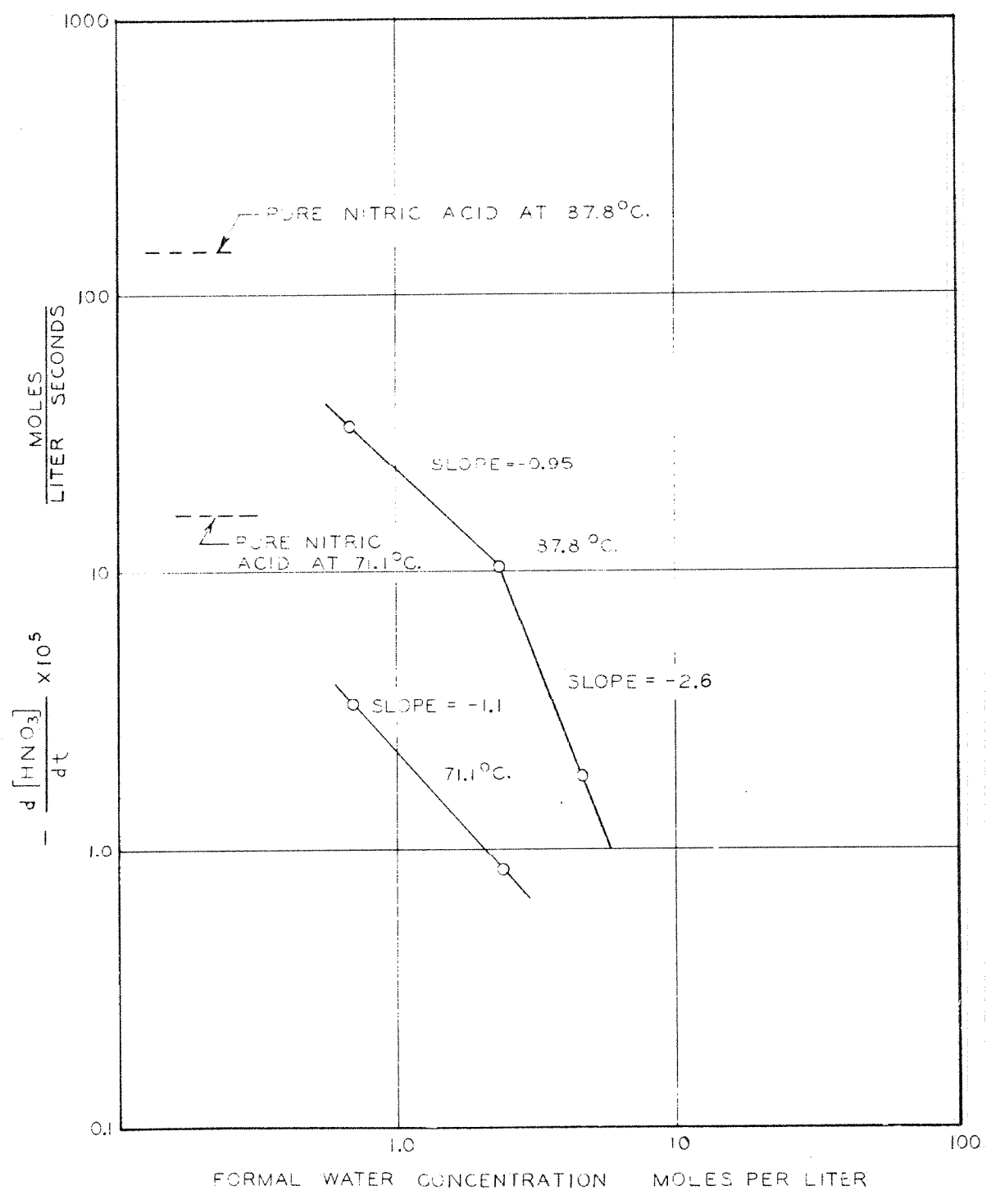


Figure 7. The Effect of Water on the Rate of Decomposition of Nitric Acid



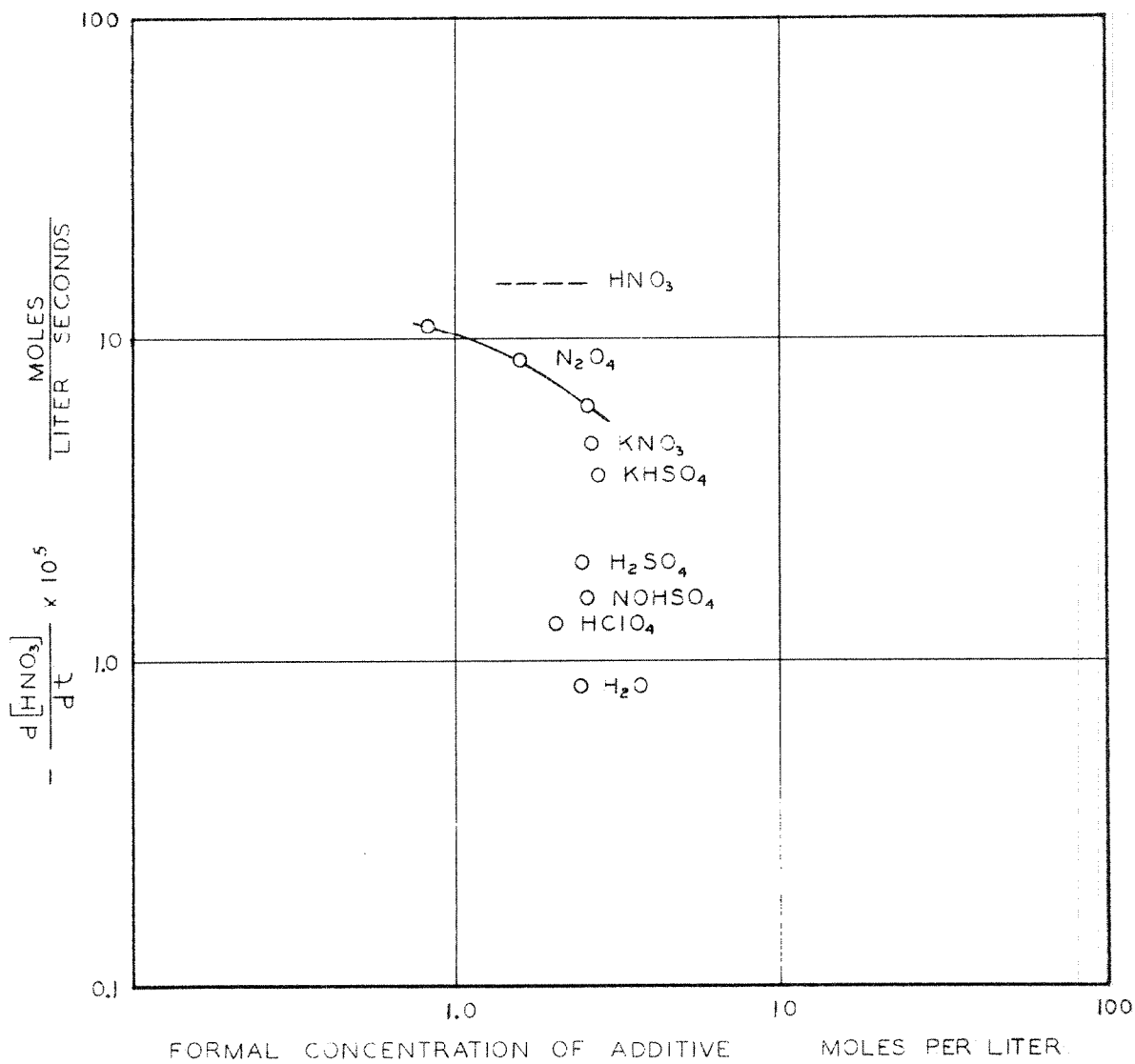


Figure 8. The Effect of Several Additives on the Rate of Decomposition of Nitric Acid at 71.1° C

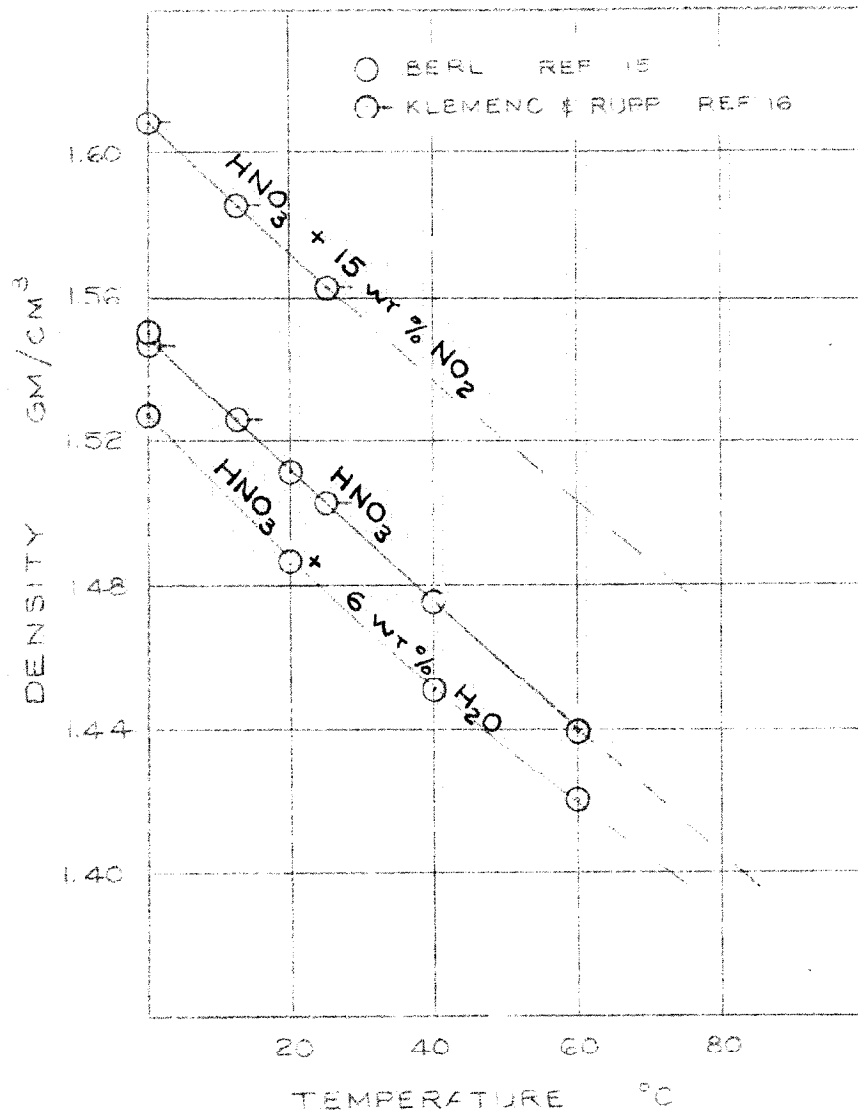


Figure 9. The Effect of Temperature on the Density of Fuming Nitric Acid

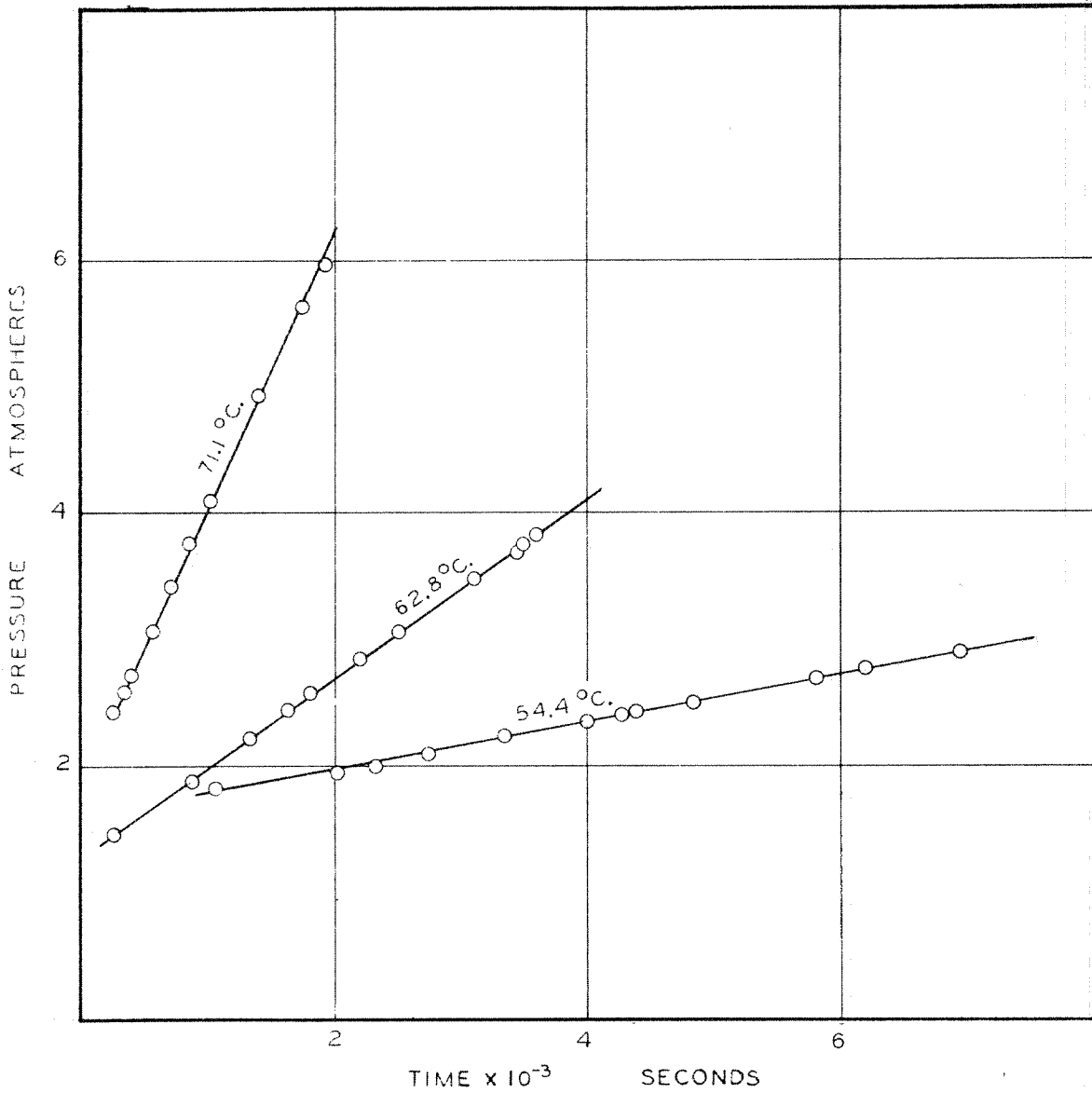


Figure 10. The Effect of Temperature on the Rate of Decomposition of Pure Nitric Acid

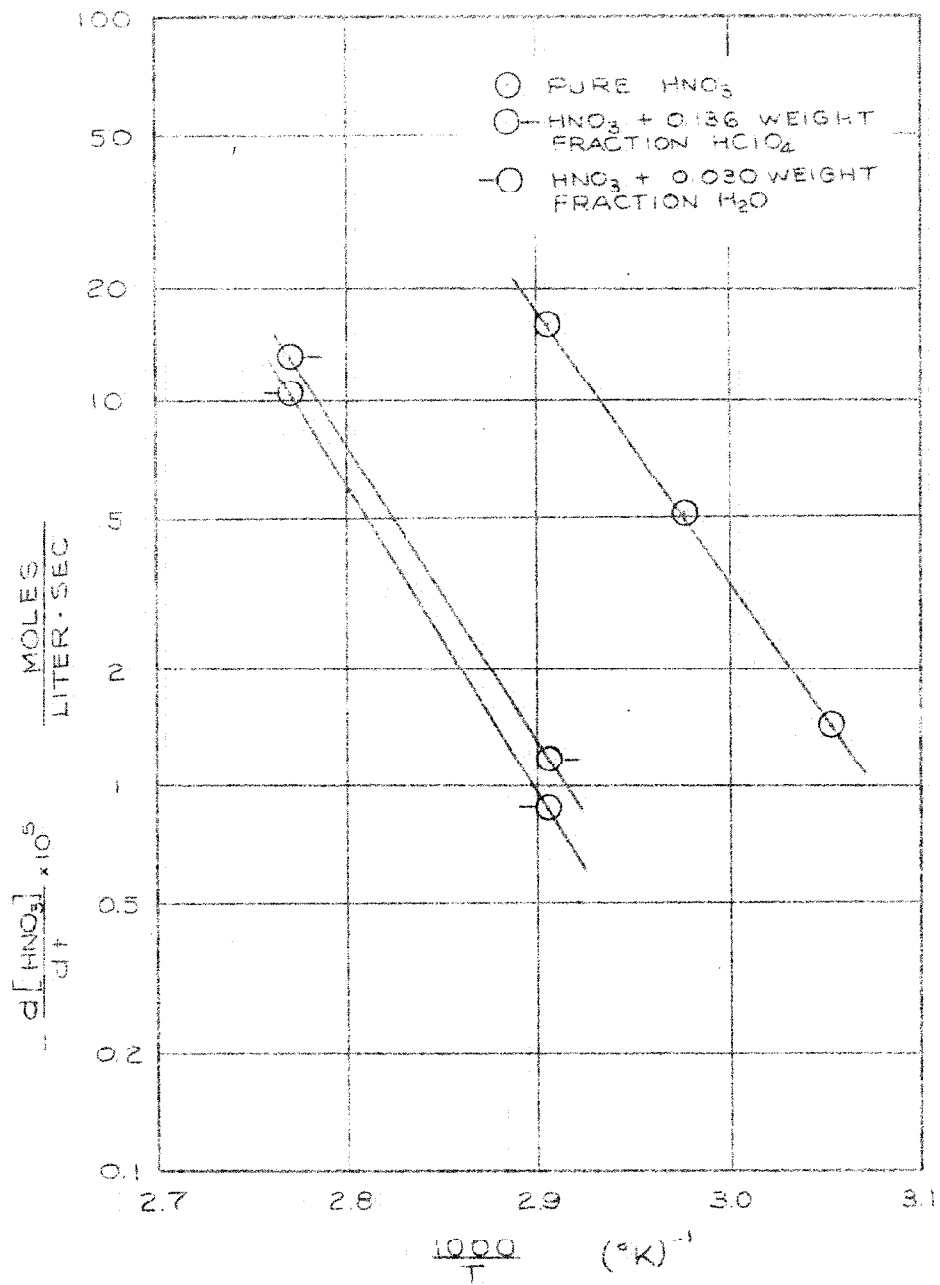


Figure 11. The Variation with Temperature of the Rate of Decomposition of Fuming Nitric Acid

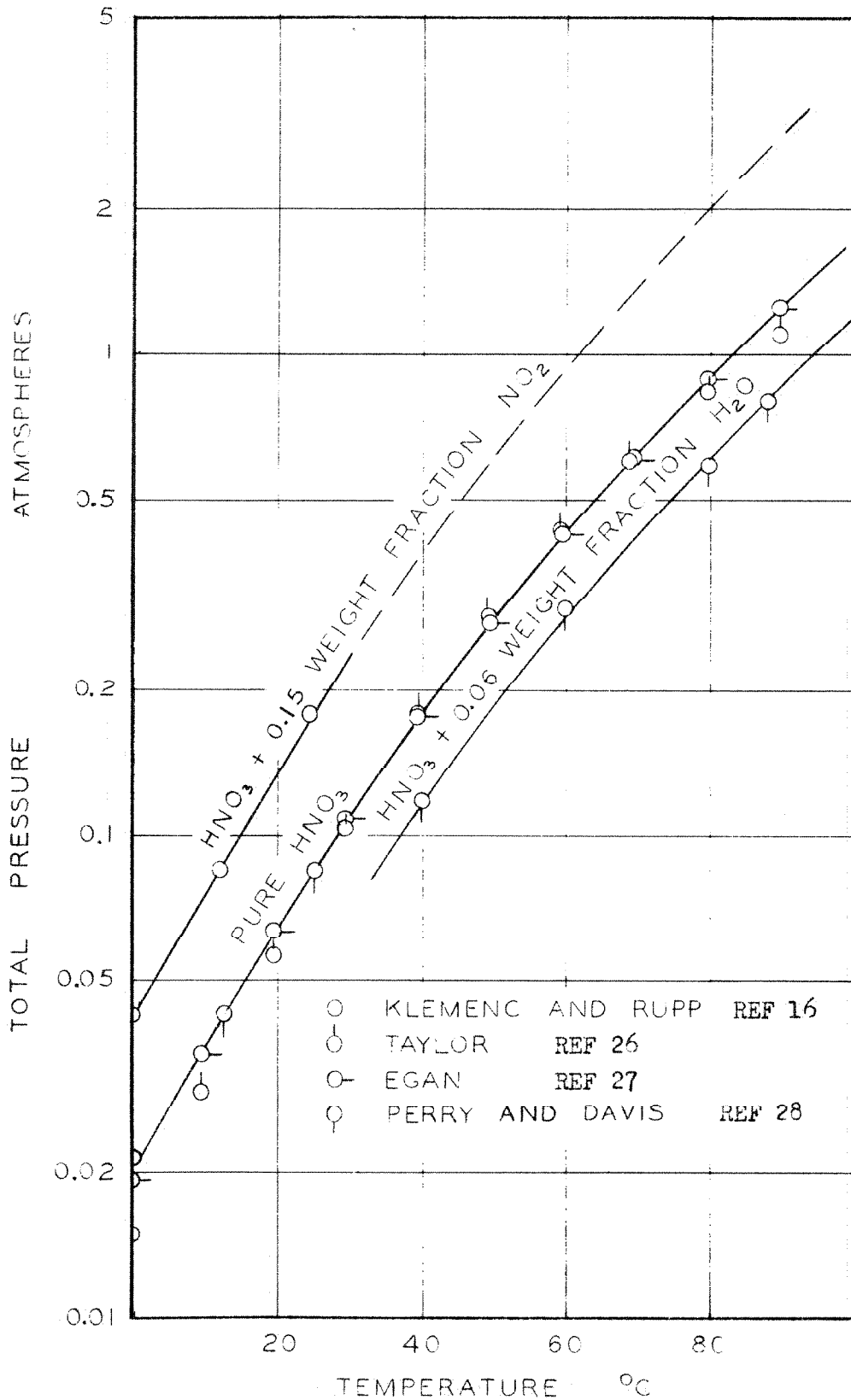


Figure 12. The Effect of Temperature on the Total Pressure of Vapor above Fuming Nitric Acid

APPENDIX

- I. Relationship of Kinetic Rate to Observed Rate of Pressure Increase
- II. Method of Determining Oxygen Solubility from Observed Data
- III. Conversion of Data from Experimental Ullage to a Common Ullage of 25%
- IV. Original Kinetic Data
- V. Original Oxygen Solubility Data



Derivation of Relationship:

From the stoichiometry

$$-\frac{d}{dt} \text{ (moles HNO}_3\text{)} = 4 \frac{d}{dt} \text{ (moles O}_2\text{)} \quad (33)$$

The oxygen formed in equation 1 passes partially into the gas phase and partially remains dissolved in the liquid phase. The solubility of oxygen in fuming nitric acid has been determined, see Figure 6, and has been found to obey Henry's law under the conditions encountered here. Therefore,

$$\frac{n_{O_L}}{V_L} = \alpha \cdot P_O \quad (34)$$

From the perfect gas and Dalton's laws

$$n_{O_G} = \frac{P_O V_G}{RT} \quad (35)$$

The total amount of oxygen in the system at any time as given by the sum of equations 34 and 35 is

$$n_O = n_{O_G} + n_{O_L} = \frac{P_O V_G}{RT} + \alpha P_O V_L \quad (36)$$



The ullage,  $U$ , is defined as

$$U = \frac{V_G}{V_G + V_L} \times 100 \quad (37)$$

from which is obtained

$$V_G = \frac{U}{100 - U} \cdot V_L \quad (38)$$

Substituting the value of  $V_G$  from equation 38 in expression 36, there is obtained

$$n_0 = P_0 V_L \left\{ \frac{U}{(100 - U) RT} + \alpha \right\} \quad (39)$$

Since  $V_L$ ,  $U$ ,  $T$  and  $\alpha$  are effectively constant with respect to time and pressure under the conditions of the experiments, equation 39 can be differentiated to yield

$$\frac{dn_0}{dt} = V_L \left\{ \frac{U}{(100 - U) RT} + \alpha \right\} \frac{dP_0}{dt} \quad (40)$$

By Dalton's law

$$P = P_0 + P_A + P_I = \text{total pressure} \quad (41)$$

$P_A$  is the vapor pressure of the acid sample and depends primarily on the temperature and initial composition. The small change in  $P_A$  that occurs due to the gradual change in composition resulting from the decomposition of the acid is neglected here.  $P_I$  represents the pressure exerted by the inert gas in the air initially dissolved in the sample, and is a constant throughout any particular experiment.

Therefore

$$\frac{dP}{dt} = \frac{dP_0}{dt} \quad (42)$$

A combination of equation 42 with equations 34 and 40 yields

$$\frac{d}{dt} \left( \frac{n_0}{V_L} \right) = \left\{ \frac{U}{(100 - U) RT} + \alpha \right\} \frac{dP}{dt} \quad (43)$$

A consideration of the stoichiometry of equation 1 shows that

$$- \frac{d}{dt} \left( \frac{n_{\text{HNO}_3}}{V_L} \right) = 4 \frac{d}{dt} \left( \frac{n_0}{V_L} \right) \quad (44)$$

The final expression relating the kinetic rate,

$$- \frac{d}{dt} \left( \frac{n_{\text{HNO}_3}}{V_L} \right) = - \frac{d [\text{HNO}_3]}{dt}, \text{ to the observed}$$

pressure rise,  $\frac{dP}{dt}$ , is obtained by combining (43) and (44) to give

$$- \frac{d [\text{HNO}_3]}{dt} = 4 \left\{ \frac{U}{(100 - U) RT} + \alpha \right\} \frac{dP}{dt} \quad (45)$$

## II. Method of Determining Oxygen Solubility From Observed Data

System:           Liquid phase: acid, dissolved oxygen

                  Gas phase: oxygen, acid vapor

Conditions:       Constant temperature

                  Subscript 1 refers to conditions at higher  
                  pressure (22 atm)

                  Subscript 2 refers to conditions at lower  
                  pressure (8 atm)

                  Liquid phase is saturated with oxygen at  
                  conditions 1 and 2

Observed

Quantities:        $V_G, P, V_L$  at conditions 1 and 2

$$V_{L_1} = V_{L_2} = V_L$$

Assumptions:     Gas phase obeys perfect gas and Dalton's laws.

### Derivation of Expression for Solubility Coefficient:

The total number of moles of oxygen in the system at conditions 1 and 2 is given by expressions similar to equation 36, thus

$$n_{O_1} = n_{O_{G_1}} + n_{O_{L_1}} = \frac{P_{O_1} V_{G_1}}{RT} + \alpha V_L P_{O_1} \quad (46)$$

$$n_{O_2} = n_{O_{G_2}} + n_{O_{L_2}} = \frac{P_{O_2} V_{G_2}}{RT} + \alpha V_L P_{O_2} \quad (47)$$

The total number of moles of oxygen does not remain constant throughout any particular experiment but increases slowly because of the small amount of oxygen formed by the decomposition of the acid. Therefore, the total number of moles of oxygen at condition 2 is related to the number present at condition 1 by the equation

$$n_{O_2} = n_{O_1} + n_d \quad (48)$$

in which  $n_d$  represents the number of moles of oxygen formed from decomposition during the time interval between the physical measurements which determined conditions 1 and 2. The magnitude of this corrective term,  $n_d$ , can be determined from kinetic data. For the range of conditions encountered in this investigation,  $n_d$  never exceeded 3% of the oxygen transferred between the phases during the measurements. Substituting the expressions for  $n_{O_1}$  and  $n_{O_2}$  from equations 46 and 47 into equation 48 yields

$$\frac{P_{O_2} V_{G_2}}{RT} + \alpha V_L P_{O_2} = \frac{P_{O_1} V_{G_1}}{RT} + \alpha V_L P_{O_1} + n_d \quad (49)$$

The total pressure,  $P$ , is the sum of the partial pressures of oxygen and acid vapor, thus

$$P_1 = P_{O_1} + P_A \quad \text{or} \quad P_{O_1} = P_1 - P_A \quad (50)$$

and

$$P_2 = P_{O_2} + P_A \quad \text{or} \quad P_{O_2} = P_2 - P_A \quad (51)$$

When the expressions for  $P_{O_1}$  and  $P_{O_2}$  as given by equations 50 and 51 are used, equation 49 becomes

$$\frac{(P_2 - P_A) V_{G2}}{RT} + \alpha V_L (P_2 - P_A) = \frac{(P_1 - P_A) V_{G1}}{RT} + \quad (52)$$

$$\alpha V_L (P_1 - P_A) + n_d$$

Equation 52 can be solved explicitly for the solubility coefficient,

$\alpha$ , to yield the final expression

$$\alpha = \left\{ \frac{(P_2 V_{G2} - P_1 V_{G1}) - P_A (V_{G2} - V_{G1})}{RT} - n_d \right\} \left\{ \frac{1}{V_L (P_1 - P_2)} \right\} \quad (53)$$

$P$ ,  $V_L$ ,  $V_G$ , and  $T$  are all experimentally measured quantities.  $P_A$  has been obtained from several sources in the literature<sup>(16,26,27,28)</sup> and the data used are presented in graphical form in Figure 12.

III. Conversion of Data from Experimental Ullage to a Common Ullage of 25%.

System and Stoichiometry: same as section I

Conditions: Constant temperature

Subscript 1 refers to conditions at experimental ullage

Subscript 2 refers to condition at 25% ullage

$$V_{L1} = V_{L2} = V_L$$

Derivation of Conversion Equation:

When written for conditions 1 and 2, equation 39 for the total number of moles of oxygen becomes

$$n_{O_1} = P_{O_1} V_L \left\{ \frac{U_1}{(100 - U_1) RT} + \alpha \right\} \quad (54)$$

and

$$n_{O_2} = P_{O_2} V_L \left\{ \frac{U_2}{(100 - U_2) RT} + \alpha \right\} \quad (55)$$

It is evident that the total number of moles of oxygen before and after the ullage correction is invariant, i.e.  $n_{O_2} = n_{O_1}$ . Thus, equations 54 and 55 can be equated to give

$$P_{O_1} \left\{ \frac{U_1}{(100 - U_1) RT} + \alpha \right\} = P_{O_2} \left\{ \frac{U_2}{(100 - U_2) RT} + \alpha \right\} \quad (56)$$

Since  $P_A$  is independent of ullage, equation 41 can be written

$$P_1 = P_{O_1} + P_{I_1} + P_A \quad \text{or} \quad P_{O_1} = P_1 - (P_{I_1} + P_A) \quad (57)$$

and

$$P_2 = P_{O_2} + P_{I_2} + P_A \quad \text{or} \quad P_{O_2} = P_2 - (P_{I_2} + P_A) \quad (58)$$

The combination of equations 56, 57, and 58 yields

$$\left\{ P_1 - (P_{I_1} + P_A) \right\} \left\{ \frac{U_1}{(100 - U_1) RT} + \alpha \right\} = \left\{ P_2 - (P_{I_2} + P_A) \right\} \left\{ \frac{U_2}{(100 - U_2) RT} + \alpha \right\} \quad (59)$$

Equation 59 can be solved explicitly for,  $P_2$ , the pressure which would be observed if the sample were confined at 25% ullage, thus

$$P_2 = \left\{ P_1 - (P_{I_1} + P_A) \right\} \frac{\left\{ \frac{U_1}{(100 - U_1) RT} + \alpha \right\}}{\left\{ \frac{U_2}{(100 - U_2) RT} + \alpha \right\}} + P_{I_2} + P_A \quad (60)$$



Equation 60 could be applied directly to pressure data obtained at any ullage to give pressure vs time curves corrected to 25% ullage, similar to those in Figure 5. However, equation 60 is the sum of a term including  $P_1$ , which varies with time, and other terms involving  $P_I$  and  $P_A$ , which are independent of time.

Thus, for any particular experiment,

$$P_2 = P_1 \frac{\left\{ \frac{U_1}{(100 - U_1) RT} + \alpha \right\}}{\left\{ \frac{U_2}{(100 - U_2) RT} + \alpha \right\}} + \text{constant} \quad (61)$$

Since it is the slope of the pressure vs time curve which indicates the rate of reaction, the absolute magnitude of  $P_2$  is relatively unimportant. For this reason, the constant term in equation 61 has been assumed to be zero for the purpose of correcting the original data to appear in Figures 3 and 5.

IV. Original Kinetic Data

Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
Pure HNO <sub>3</sub>	71.1	24.38	2.40	270
			2.57	360
			2.70	420
			3.05	582
			3.40	720
			3.74	864
			4.08	1032
			4.57	1260
			4.92	1410
			5.61	1770
Pure HNO <sub>3</sub>	62.8	24.43	1.46	270
			1.87	900
			2.22	1338
			2.43	1650
			2.57	1830
			2.84	2220
			3.05	2520
			3.46	3120
			3.67	3456
			3.74	3510
Pure HNO <sub>3</sub>	54.4	25.16	1.81	1080
			1.93	2040
			1.98	2340
			2.08	2760
			2.22	3360
			2.33	4020
			2.40	4290
			2.43	4410
			2.50	4860
			2.69	5820
2.77	6210			
2.91	6960			

Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
0.00880 H <sub>2</sub> O 0.99120 HNO <sub>3</sub>	71.1	23.18	1.94	240
			1.97	540
			2.16	840
			2.23	1080
			2.51	1440
			2.81	2220
			3.74	3960
0.00880 H <sub>2</sub> O 0.99120 HNO <sub>3</sub>	87.8	23.56	2.33	60
			3.01	180
			3.35	270
			4.04	360
			5.06	600
			5.74	720
			6.08	780
			6.76	900
			7.57	1140
			8.12	1230
0.03035 H <sub>2</sub> O 0.96965 HNO <sub>3</sub>	71.1	25.67	1.66	360
			1.76	1800
			1.80	1950
			1.90	2700
			1.91	3000
			1.93	3210
			2.05	3540
			2.14	4980
			2.18	5280
			2.25	6000
			2.31	6480

Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
0.03035 H <sub>2</sub> O 0.96965 HNO <sub>3</sub>	87.8	23.71	3.22	570
			3.42	720
			3.90	900
			4.44	1320
			4.78	1500
			5.33	1800
			5.87	2160
			7.30	3120
			7.64	3300
			10.09	5100
0.0600 H <sub>2</sub> O 0.9400 HNO <sub>3</sub>	87.8	23.37	2.67	150
			2.88	300
			3.01	480
			3.22	780
			3.42	1380
			3.63	2100
			3.76	2700
			3.97	3420
			5.74	9480
			6.42	12000
0.0509 NO <sub>2</sub> 0.9491 HNO <sub>3</sub>	71.1	22.91	2.09	222
			2.44	420
			2.74	600
			3.05	780
			3.40	1008
			3.67	1140
			3.90	1320
			4.29	1512
			4.57	1740
			4.85	1950
5.06	2070			
6.10	2880			
6.73	3420			

Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
0.0971 NO <sub>2</sub> 0.9029 HNO <sub>3</sub>	71.1	28.06	2.36	180
			2.59	360
			2.98	660
			3.28	960
			3.55	1170
			3.81	1380
			4.06	1650
			4.53	2100
0.1536 NO <sub>2</sub> 0.8464 HNO <sub>3</sub>	71.1	22.93	5.23	2850
			2.70	240
			2.77	330
			2.91	450
			3.02	600
			3.25	780
			3.53	1050
			3.81	1320
			4.11	1620
			4.36	1860
0.0089 H <sub>2</sub> O 0.0866 NO <sub>2</sub> 0.9045 HNO <sub>3</sub>	71.1	24.51	4.64	2220
			5.26	2670
			5.69	3060
			5.86	3240
			6.02	3420
			6.17	3600
			2.25	120
			2.60	270
			2.63	510
			2.77	840
2.77	900			
2.91	1290			
3.09	1680			
3.26	2100			
3.40	2520			
3.53	2850			
3.71	3300			

Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
0.165 N <sub>2</sub> O <sub>5</sub> 0.835 HNO <sub>3</sub>	71.1	24.38	6.65	210
			8.79	300
			9.96	360
			11.00	420
			12.39	498
			13.07	540
			14.25	600
			14.80	642
			16.88	810
			17.50	852
			17.78	882
			18.47	960
			18.88	990
19.30	1026			
20.27	1140			
21.31	1290			
0.1585 KNO <sub>3</sub> 0.8415 HNO <sub>3</sub>	71.1	26.06	2.36	360
			2.43	510
			2.50	600
			2.61	720
			2.77	960
			2.91	1200
			3.18	1620
			3.29	1800
			3.37	1890
			3.50	2100
			3.91	2940
			3.99	3090
			4.23	3480
4.46	4020			
0.2085 KHSO <sub>4</sub> 0.7915 HNO <sub>3</sub>	71.1	26.85	1.39	420
			1.49	600
			1.52	690
			1.59	840
			1.91	1140
			2.21	2010
			2.40	2400
			2.50	2670
			2.70	3150
			2.87	3540
			3.23	4350
4.05	6420			

Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
0.1836 $\text{NOHSO}_4$ 0.8164 $\text{HNO}_3$	71.1	24.64	1.60	360
			1.63	450
			1.67	540
			1.78	1020
			1.85	1380
			1.94	1680
			2.03	2040
			2.15	2580
			2.26	3120
			2.43	3840
2.91	5940			
0.1584 $\text{H}_2\text{SO}_4$ 0.8416 $\text{HNO}_3$	71.1	24.64	1.87	540
			2.01	1080
			2.15	1530
			2.29	1980
			2.50	2712
			2.57	3000
			2.91	4080
			3.53	6300
0.1363 $\text{HClO}_4$ 0.8637 $\text{HNO}_3$	71.1	24.23	1.63	360
			1.66	840
			1.80	1500
			1.87	1890
			2.00	2502
			2.33	4110
0.1363 $\text{HClO}_4$ 0.8637 $\text{HNO}_3$	87.8	24.90	4.29	120
			4.57	360
			4.92	522
			5.34	720
			5.96	1050
			6.31	1260
			6.66	1410
			7.07	1662
			7.76	2040
			8.03	2172
8.31	2292			

Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
0.0982 NH <sub>4</sub> NO <sub>3</sub> 0.9018 HNO <sub>3</sub>	87.8	23.95	0.97	60
			6.76	240
			10.16	360
			12.88	480
			15.26	600
			17.31	720
			20.71	960
0.1223 KNO <sub>3</sub> 0.8777 HNO <sub>3</sub>	87.8	27.07	3.01	150
			3.70	240
			4.04	300
			5.07	480
			5.40	540
			6.08	660
			7.44	900
			9.00	1320
			10.09	1620
			12.34	2400
Pure HNO <sub>3</sub>	87.8	24.08	5.74	240
			6.76	300
			8.46	420
			10.50	540
			11.18	630
			11.86	660
			12.88	780
			13.90	840
			15.26	960
			17.30	1140



Initial Composition of the System weight fraction	Temperature °C	Ullage %	Pressure atm	Time sec
Pure HNO <sub>3</sub> without agitation	87.8	24.93	3.70	2
			6.08	270
			6.42	300
			7.30	360
			8.46	450
			9.00	480
			9.41	510
			10.02	570
			10.30	600
			11.04	660
			11.59	720
			12.54	810
			14.11	990
			15.40	1140
16.76	1320			
Pure HNO <sub>3</sub> with glass wool, without agitation	87.8	34.5	2.67	90
			3.90	210
			5.06	360
			6.42	480
			11.52	1170
			12.20	1290

V. Original Oxygen Solubility Data

Composition of the System	T	P <sub>1</sub>	P <sub>2</sub>	V <sub>G1</sub>	V <sub>G2</sub>	V <sub>L</sub>	Elapsed* Time
weight fraction	°C	atm		liters x 10 <sup>3</sup>			sec
Pure HNO <sub>3</sub>	37.7	21.73	7.91	0.302	1.048	0.816	600
	54.4	21.73	7.91	0.311	1.122	0.830	600
0.154 NO <sub>2</sub>	37.7	21.73	7.91	0.309	1.007	0.778	540
	37.7	21.73	7.91	0.304	0.999	0.778	540
0.846 HNO <sub>3</sub>	54.4	21.73	7.91	0.315	1.083	0.791	540
	54.4	21.73	7.91	0.311	1.074	0.791	540
0.060 H <sub>2</sub> O	37.7	18.95	14.80	0.348	0.466	0.797	2700
	37.7	14.80	12.73	0.466	0.557	0.797	1500
	37.7	12.73	10.66	0.557	0.683	0.797	1500
	37.7	10.66	8.58	0.683	0.867	0.797	1200
	37.7	21.73	7.91	0.257	0.860	0.786	600
0.940 HNO <sub>3</sub>	37.7	21.73	7.91	0.246	0.825	0.788	900
	54.4	21.73	7.91	0.232	0.814	0.800	600
	71.1	21.73	7.91	0.254	0.936	0.817	900
	87.8	21.73	7.91	0.244	0.994	0.835	420

\* Time elapsed between the measurements which define conditions 1 and 2. This time is used in determining the amount of oxygen formed from the decomposition of the sample.

Part II. Electrolytic Conductance of the  
Ternary System Nitric Acid --  
Nitrogen Dioxide -- Water at  
32° F and Atmospheric Pressure \*

\* B. H. Sage and D. M. Mason are coauthors  
of Part II.

## I. INTRODUCTION AND SUMMARY

The electrolytic conductance of the system nitric acid--nitrogen dioxide<sup>a</sup>--water in the liquid phase was measured at 32°F and a pressure of 1 atmosphere for compositions containing more than 80 weight per cent nitric acid.<sup>b</sup> The conductance of the associated binary systems nitric acid--water and nitric acid--nitrogen dioxide was measured over the entire range of compositions from 0 to 100 weight per cent nitric acid. The conductance of the binary system nitrogen dioxide--water was not measured as a result of the fact that these species undergo chemical reaction and that the rate of attainment of equilibrium is extremely slow at 32°F. The conductance measurements indicate that pure nitrogen dioxide and, as would be expected, water are relatively nonconducting, whereas nitric acid is relatively a good conductor. The addition of small quantities of nitrogen dioxide to nitric acid results in an increase in conductance. The addition of water to nitric acid results in a decrease in conductance in one range of compositions covered by this investigation. The experimental results are presented in both graphical and tabular form.

## II. DESCRIPTION OF EQUIPMENT AND METHODS

Essentially the method of Kohlrausch as described by Ostwald (Cf. Ref. 1), utilizing an alternating-current Wheatstone bridge, was adopted in the present set of conductance measurements. A simplified circuit is shown in Figure 1. The unknown resistance  $R_x$  of the solution is determined when balance in the bridge circuit is obtained by adjustment of the variable resistors  $R_1$ ,  $R_2$ , and  $R_3$ . A state of balance is indicated if no current flows through the current detector  $D$  when a source  $S$  of alternating voltage is applied to the system. A commercial impedance bridge was used for the variable resistors, a cathode-ray oscilloscope was employed as the current detector, and an audio oscillator furnished the source of alternating current at a frequency of 1000 cyc/sec. Direct-current measurements are precluded as a result of polarization at the electrodes.

The conductance equipment was a modified dip cell manufactured by the Central Scientific Company and had a constant of approximately 1.0 ohm-cm. The electrodes were black platinized platinum disks 0.5 inch in diameter, set 1.5 inches apart. The conductance-cell assembly shown in Figure 2 was immersed for temperature control in an ice bath located in a Dewar flask. A sample of liquid was introduced so as to fill the cell to the point  $A$  of the Pyrex receptacle shown in the Figure. The widened top portion of the vessel permitted further addition of material to the system so that a range of compositions could be obtained. As a result of appreciable changes in enthalpy for the solution, it was necessary after the mixing of materials to allow ample time for attainment of thermal equilibrium between the cell and the surrounding ice bath before conductance measurements were made. The liquid was agitated thoroughly to insure complete mixing.

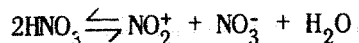
<sup>a</sup>For the sake of brevity, the term nitrogen dioxide, unless otherwise specified, is used throughout this paper to designate the equilibrium mixture of nitrogen dioxide and nitrogen tetroxide.

<sup>b</sup>The term fuming nitric acid will be applied to the ternary system in this composition range.

The nitric acid was prepared by vacuum distillation at room temperature of a mixture of concentrated sulfuric acid and sodium nitrate. The nitric acid was collected in a receptacle at  $-70^{\circ}\text{F}$ . The material collected was at least 99.9 weight per cent nitric acid as determined by an acidimetric titration. The nitric acid was stored at  $-10^{\circ}\text{F}$  to reduce the thermal decomposition rate to a negligible value. Commercial nitrogen dioxide was fractionated and dried over phosphorus pentoxide. Water was redistilled from the commercial laboratory supply.

### III. RESULTS

The results of the conductance measurements are depicted in Figures 3 through 5 and in Tables I through III. In Figure 3 specific conductance at  $32^{\circ}\text{F}$  is shown as a function of the weight fraction nitric acid for the binary system nitric acid--water. For comparison, measurements of conductance for this system by Veley and Manley (Cf. Ref. 2) are included in Figure 3. The experimental data for the nitric acid--water system are presented in Table I. At  $32^{\circ}\text{F}$  these components are completely miscible throughout the entire composition range. The conductance of the system increases with an increase in the weight fraction nitric acid and reaches a maximum at about 0.29 weight fraction nitric acid. Between 0.30 and 0.97 weight fraction the conductance decreases and reaches a minimum at 0.97 weight fraction nitric acid. Below 0.97 weight fraction nitric acid, hydrogen and nitrate ions are the predominant conducting species. In the range 0.97 to 1.00 weight fraction nitric acid, the conductance again increases. In this latter range, studies of the Raman spectra (Cf. Ref. 3) of the system indicate that nitric acid undergoes self-ionization to yield nitronium ions ( $\text{NO}_2^+$ ) and nitrate ions ( $\text{NO}_3^-$ ) according to the expression



It is evident from this expression that the self-ionization of nitric acid is suppressed by the addition of water. Thus the reduction of conductance of pure nitric acid upon the addition of water may be explained.

Figure 4 presents the specific conductance at  $32^{\circ}\text{F}$  for the binary system nitric acid--nitrogen dioxide. The corresponding experimental data are recorded in Table II. At  $32^{\circ}\text{F}$  and atmospheric pressure nitrogen dioxide is miscible with nitric acid only above 0.48 weight fraction nitric acid. Below 0.48 weight fraction nitric acid a second liquid phase appears containing less than 0.1 weight per cent nitric acid. The specific conductance of this latter phase is small, being less than  $7 \times 10^{-6}$  ( $\text{ohm-cm}^{-1}$ ) at  $32^{\circ}\text{F}$ . Between 0.72 and 1.00 weight fraction nitric acid the conductance of the system decreases with increasing concentrations of acid. This behavior is in agreement with studies of Raman spectra of solutions of nitrogen dioxide in nitric acid where nitrosonium ions ( $\text{NO}^+$ ) and nitrate ions ( $\text{NO}_3^-$ ) have been identified (Cf. Ref. 4). The nitrogen dioxide ionizes to give these ionic species according to the expression



This ionization causes the increase in conductance observed when nitrogen dioxide is added to nitric acid. At weight fractions of nitric acid below 0.72, a decrease in nitric acid concentration results in a decrease in conductance until the phase boundary is reached.

In Figure 5 are shown smoothed curves of constant specific conductance as a function of composition for states greater than 0.80 weight fraction nitric acid.

These smoothed data are tabulated in Table III. The mean deviation of the conductance measurements from these data is estimated to be less than 2 per cent. From Figure 5 it is evident that conductance measurements present a possible analytical tool for determining the composition of fuming nitric acid. It is necessary to determine the concentration of only one species in the system by another physicochemical method such as the measurement of transmittance with a spectrophotometer.

The nitrogen dioxide or water concentration can be determined by transmittance measurements in the visible region or the infrared region, respectively. These measurements together with the conductance measurements establish no more than two values of composition in Figure 5. The actual composition of the sample may be determined by adding one of the components to the mixture and noting whether an increase or decrease in conductance occurs.

#### IV. CONCLUSION

The conductance data for a portion of the nitric acid--nitrogen dioxide--water system give additional evidence of the presence of the ionic species, nitronium, nitrosonium, and nitrate, which were indicated earlier by studies of Raman spectra (Cf. Ref. 4). A method of chemical analysis may possibly be based upon such conductance measurements. These measurements are part of an investigation of physicochemical properties which may be of value in understanding the kinetics of the thermal decomposition of fuming nitric acid and the corrosion of metals by this material.

TABLE I  
EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE OF NITRIC  
ACID--WATER AT 32°F AND ATMOSPHERIC PRESSURE

Nitric Acid (wt fraction)	Specific Conductance [(ohm-cm) <sup>-1</sup> x 10 <sup>2</sup> ]	Nitric Acid (wt fraction)	Specific Conductance [(ohm-cm) <sup>-1</sup> x 10 <sup>2</sup> ]
1.000	3.77	0.703	28.4
0.998	3.34	0.674	31.3
0.993	2.53	0.645	34.7
0.988	1.99	0.595	38.5
0.983	1.65	0.497	46.4
0.978	1.44	0.431	52.2
0.973	1.34	0.376	56.3
0.968	1.31	0.362	56.8
0.964	1.35	0.349	56.8
0.959	1.43	0.336	57.8
0.954	1.55	0.325	57.8
0.949	1.72	0.315	58.3
0.945	1.90	0.295	58.3
0.940	2.09	0.279	58.3
0.931	2.48	0.251	58.3
0.922	3.00	0.226	55.5
0.914	3.49	0.207	52.6
0.892	5.15	0.189	50.0
0.872	6.91	0.161	46.1
0.756	21.4	0.132	39.8
0.730	25.3	0.093	31.3

TABLE II

EXPERIMENTAL VALUES OF SPECIFIC CONDUCTANCE OF NITRIC ACID--  
NITROGEN DIOXIDE AT 32°F AND ATMOSPHERIC PRESSURE

Nitric Acid (wt fraction)	Specific Conductance [(ohm-cm) <sup>-1</sup> x 10 <sup>2</sup> ]	Nitric Acid (wt fraction)	Specific Conductance [(ohm-cm) <sup>-1</sup> x 10 <sup>2</sup> ]
1.000	3.41 - .77	0.800	14.6
0.980	5.00	0.751	15.2
0.971	5.83	0.707	15.3
0.962	6.53	0.642	14.7
0.952	7.20	0.581	13.6
0.942	7.91	0.529	12.5
0.916	9.60	0.489	11.7
0.890	11.2	0.451	10.7
0.856	12.9		

TABLE III  
SMOOTHED VALUES OF CONDUCTANCE OF NITRIC ACID--NITROGEN  
DIOXIDE--WATER AT 32°F AND ATMOSPHERIC PRESSURE

Nitric Acid (wt fraction)	Specific Conductance [(ohm-cm) <sup>-1</sup> x 10 <sup>2</sup> ]															
	Nitrogen Dioxide (wt fraction)															
	0	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15
1.00	3.77															
0.99	2.18	4.25														
0.98	1.51	3.2	4.90													
0.97	1.31	2.7	3.9	6.05												
0.96	1.40	2.3	3.4	4.8	6.55											
0.95	1.69	2.3	3.2	4.0	5.7	7.10										
0.94	2.07	2.7	3.2	3.9	5.0	6.4	8.10									
0.93	2.55	2.9	3.4	4.0	4.8	5.9	7.3	8.85								
0.92	3.10	3.3	3.8	4.2	4.9	5.7	6.9	8.1	8.40							
0.91	3.75	3.9	4.2	4.6	5.0	5.7	6.7	7.7	8.8	10.1						
0.90	4.52	4.7	4.8	5.0	5.3	5.9	6.6	7.4	8.3	9.5	10.6					
0.89	5.36	5.3	5.3	5.4	5.7	6.1	6.7	7.3	8.1	9.0	10.0	11.2				
0.88	6.24	6.1	6.0	6.0	6.1	6.4	6.9	7.3	8.0	8.8	9.7	10.7	11.7			
0.87	7.10	6.9	6.7	6.6	6.6	6.8	7.1	7.5	8.0	8.7	9.3	10.2	11.1	12.1		
0.86	8.00	8.0	7.6	7.2	7.1	7.2	7.4	7.7	8.2	8.7	9.2	9.9	10.8	11.7	12.6	
0.85	9.5	9.0	8.6	8.2	8.0	7.9	7.9	8.1	8.3	8.8	9.2	9.8	10.4	11.3	12.1	13.0
0.84	10.7	10.0	9.6	9.1	8.8	8.6	8.4	8.4	8.7	8.9	9.3	9.7	10.3	11.0	11.8	12.6
0.83	11.9	11.1	10.6	10.0	9.7	9.3	9.1	9.0	9.0	9.1	9.4	9.7	10.2	10.8	11.4	12.1
0.82	13.2	12.4	11.7	11.0	10.6	10.1	9.8	9.6	9.4	9.4	9.7	9.9	10.2	10.7	11.2	11.8
0.81	14.7	13.8	13.0	12.1	11.5	11.0	10.6	10.2	10.0	9.9	9.9	10.1	10.3	10.7	11.1	11.7
0.80	15.9	15.0	14.2	13.5	12.8	12.0	11.4	11.0	10.7	10.4	10.3	10.2	10.3	10.7	11.0	11.4



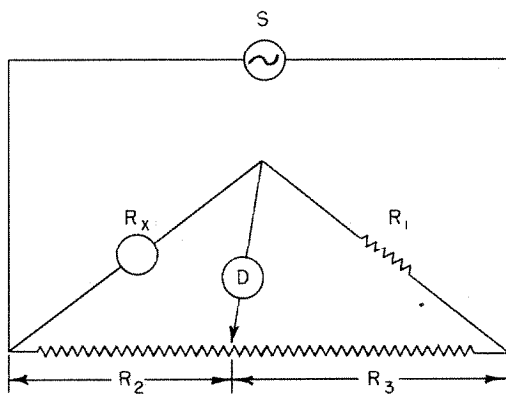


Figure 1  
Wheatstone Bridge for Conductance  
Measurements

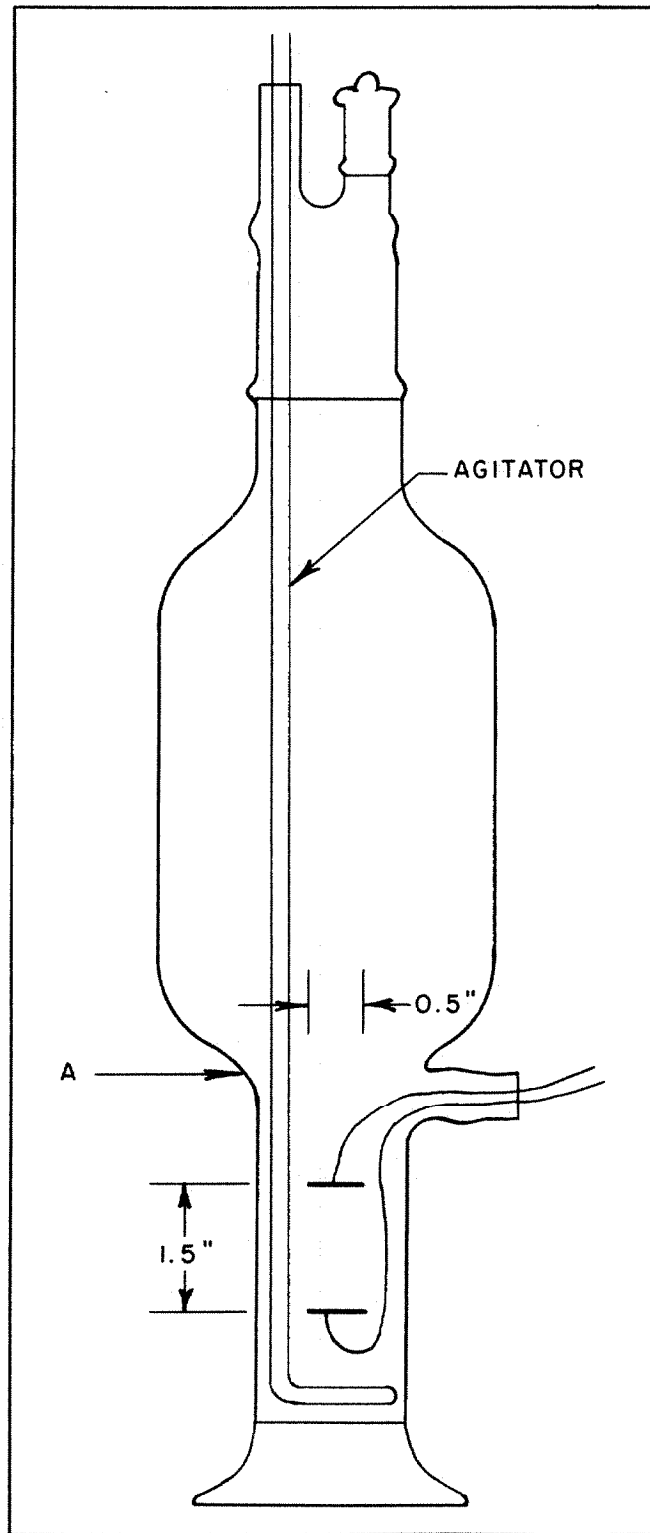


Figure 2  
Conductance-Cell Assembly

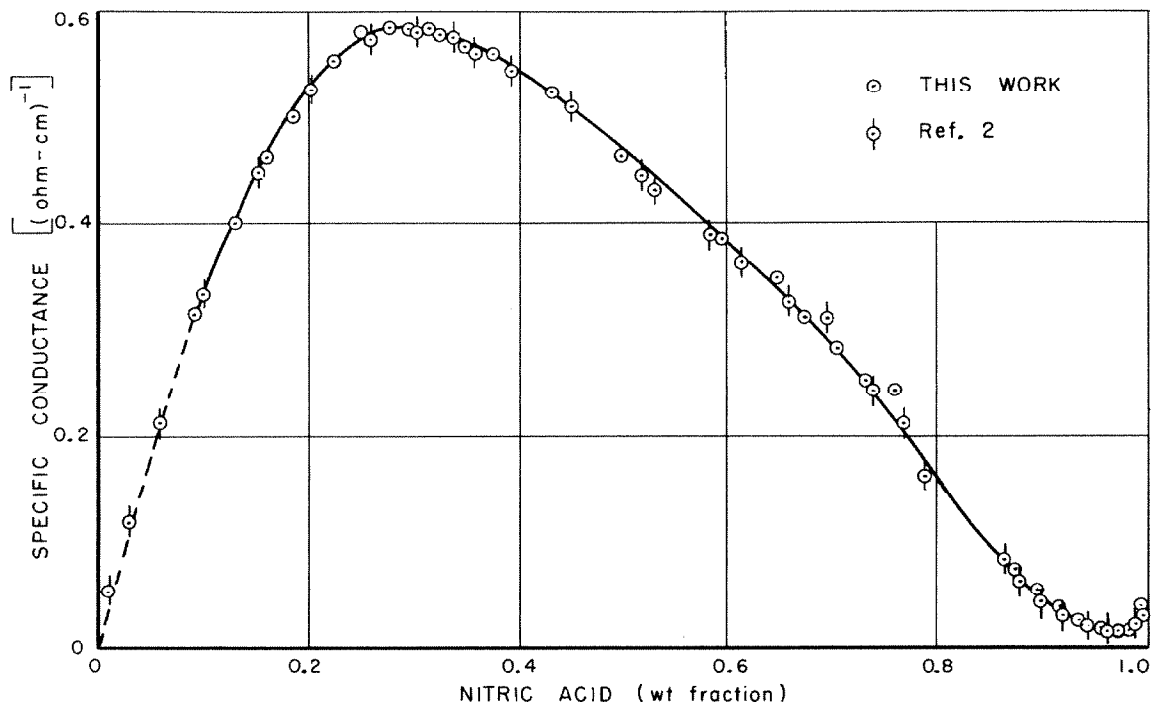


Figure 3. Specific Conductance of Nitric Acid--Water at 32°F and Atmospheric Pressure

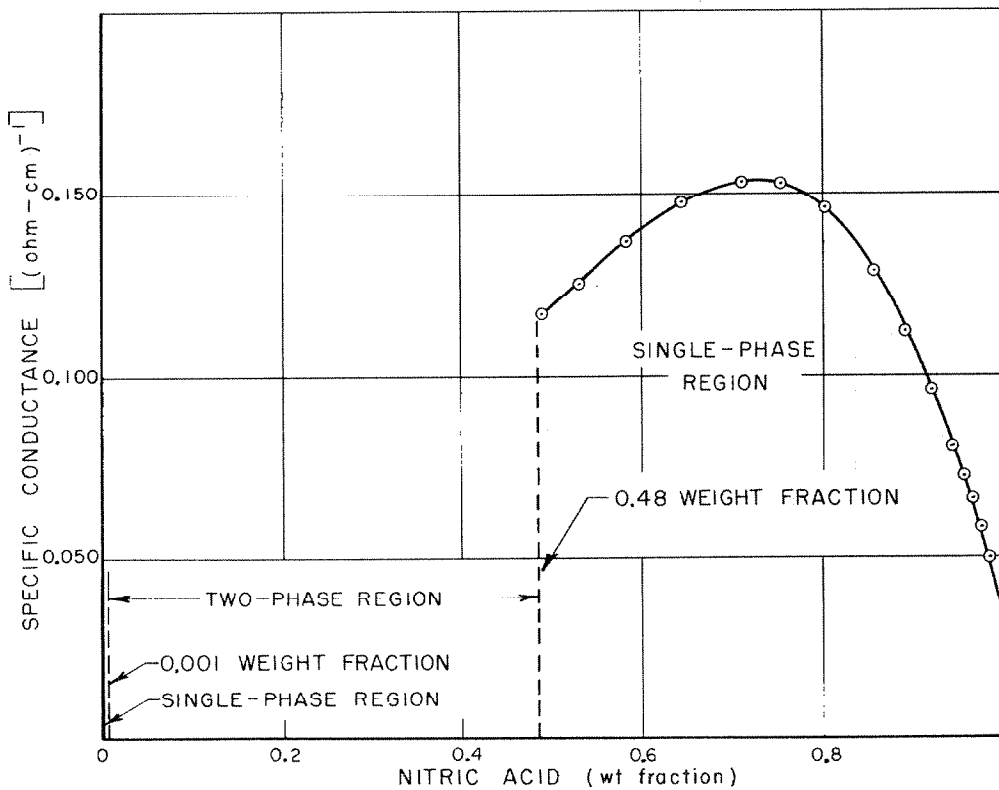


Figure 4. Specific Conductance of Nitric Acid--Nitrogen Dioxide at 32°F and Atmospheric Pressure

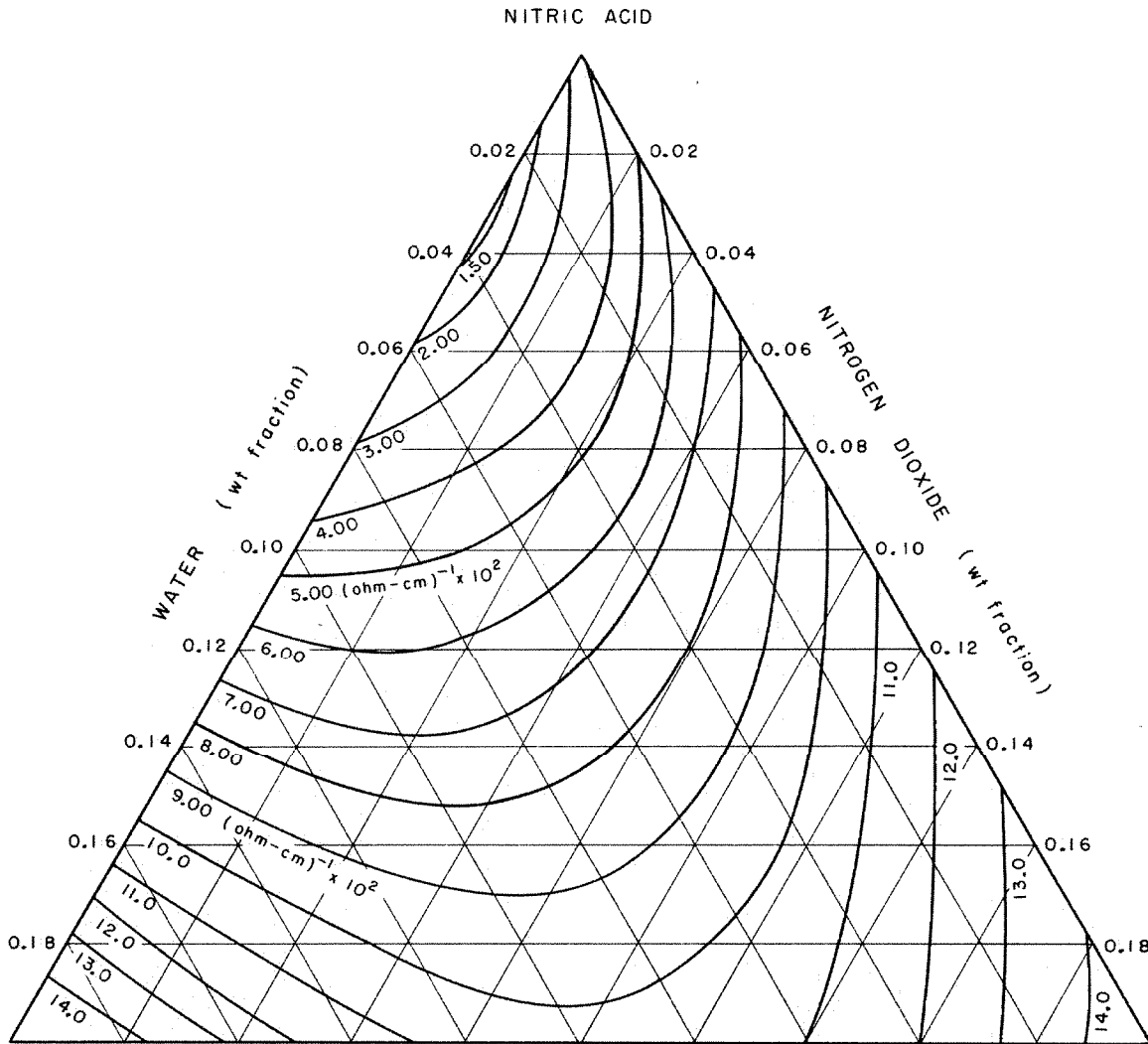


Figure 5. Curves of Constant Specific Conductance for Nitric Acid--Nitrogen Dioxide--Water at 32°F and Atmospheric Pressure

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