## RESEARCH MEMORANDUM

VAPOR PRESSURES OF CONCENTRATED NITRIC ACID SOLUTIONS IN THE COMPOSITION RANGE 83 TO 97 PERCENT NITRIC ACID 0 TO 6 PERGENT NITROGEN DIOXIDE, 0 TO 15 PERCENT WATER, AND IN THE TEMPERATURE RANGE $20^{\circ}$ TO $80^{\circ} \mathrm{C}$

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## SUMMARY

Total vapor pressures were measured for 28 acid mixtures of the ternary system nitric acid, nitrogen dioxide, and water within the temperature range $20^{\circ}$ to $80^{\circ} \mathrm{C}$ and within the composition range $83-97$ percent nitric acid, 0-6 percent nitrogen dioxide, and 0-15 percent water. The ullage of the apparatus used for the measurements was 0.65 .

Ternary diagrams showing isobars as a function of composition of the system, $\mathrm{NO}_{2}-\mathrm{H}_{2} \mathrm{O}-\mathrm{HNO}_{3}$, were constructed from experimental and interpolated data for the temperatures $25^{\circ}, 40^{\circ}$, and $60^{\circ} \mathrm{C}$ and are presented herein.

## INTRODUCTION

Concentrated solutions of nitric acid containing oxides of nitrogen are commonly used in many propellant and chemical applications. Certain properties, such as vapor pressures and boiling points, are therefore of considerable interest. A recent literature survey made at this laboratory indicated that data are lacking on vapor pressures of ternary systems of nitric acid, water, and nitrogen dioxide at temperatures greater than $25^{\circ} \mathrm{C}$.

Vapor pressures of binary systems of nitric acid and water have been determined experimentally for the temperature range $0^{\circ}$ to $125^{\circ} \mathrm{C}$ (refs. 1, 2, and 3). The vapor pressure of pure nitric acid has been calculated from thermodynamic data on the assumption that the fugacity and vapor pressure are equal (ref. 4). Total vapor pressures for the ternary system nitric acid, water, and nitrogen dioxide have been measured at the temperatures $0^{\circ}$, $12.5^{\circ}$, and $25^{\circ} \mathrm{C}$ for anhydrous, i9 N ( 82 weight percent), and 16 N ( 71 weight percent) nitric acid diluted with varying amounts of nitrogen dioxide (ref. 5).

To obtain more complete vapor pressure data, an investigation was made at the NACA Lewis laboratory to determine the total vapor pressures of the ternary system nitric acid, water, and nitrogen dioxide within the temperature range $20^{\circ}$ to $80^{\circ} \mathrm{C}$ and within the composition range 83 to 97 percent nitric acid, 0 to 15 percent water, and 0 to 6 percent nitrogen aloxide. The experiments were planned with a view toward establishing a relation between total vapor pressure and composition of the acid solution.

The total vapor pressures of 28 acid mixtures are presented herein. The data were obtained by use of an isoteniscope.

## APPARAIUS

A diagrammatic sketch of the equipment is shown in figure 1 . The apparatus consisted of an isoteniscope, a mercury manometer, a thermometer, a vacuum system, and a heat control unit.

Isoteniscope. - An isoteniscope was used for the vapor pressure measurements in arder to separate the acid vapors from the corrodible parts of the vacuum system. The instrument was a Smith and Menzies type, modified by the addition of a reservoir, to contain the separating fluid during the degasification procedure (ref. 6, p. 439). The isoteniscope was made of pyrex glass and was attached to the vacuum system by means of a ground-glass sphericsl joint. The acid chamber of the isoteniscope (A in fig. 1) was attached to the U-tube by means of a groundglass taper joint, lubricated with Halocarbon stopcock grease, which resisted attack by the acids. The acid chamber was filled with approximately 5 milliliters of acid during operation of the apparatus. The reservolr ( $B$ in fig. 1) was filled with approximately 10 milliliters of fluorocarbon (Fluorolube 8), the separating fluid. The ullage of the isoteniscope, that is, the ratio of the vapor volume to vapor volume plus Iiquid sample volume, was approximately 0.65 under operating conditions.

Temperature control system. - The isoteniscope was maintained at specified temperatures by inmersion in a 4000 -milililiter transparent Dewar flask filled with water at a predetermined temperature. The water was heated in a separate constant-temperature bath and was circulated through the Dewar Plask by a pump during experimental runs. The constanttemperature bath was heated by two 750 -watt immersion-type heaters connected in series with an immersion-type thermoswitch, which controlled the temperature of the bath to $\pm 0.5^{\circ} \mathrm{C}$. The temperature of the Iiquid in the Dewar flask was measured by a calibrated thermometer that could be read to $\pm 0.2^{\circ} \mathrm{C}$.

## PROCEDURE

Preparation of acid samples. - Acid samples were prepared by mixing aliquot portions of 99.8 percent $\mathrm{HNO}_{3}$, distilled $\mathrm{H}_{2} \mathrm{O}$, and a 33 . 1 percent by weight solution of $\mathrm{HO}_{2}$ in $\mathrm{HHO}_{3}$. The 99.8 percent $\mathrm{HFO}_{3}$ was prepared by the vacuum distillation of a mixture comprising two parts of concentrated sulfuric acid and three parts of commercial white fuming nitric acid (approximately 98 percent $\mathrm{HNO}_{3}$ ) at a temperature of $10^{\circ}$ to $15^{\circ} \mathrm{C}$. The 33.1 percent solution of $\mathrm{NO}_{2}$ in $\mathrm{HFO}_{3}$ was prepared by passing gaseous $\mathrm{HO}_{2}$ into 99.8 percent $\mathrm{HNO}_{3}$.

Degasification of acid sample. - Acid samples were degassed in the isoteniscope to remove absorbed carbon dioxide and air. Degasification was accomplished prior to the determination of vapor pressures by several repetitions of the following procedure: (1) the acid sample was frozen with Iiquid nitrogen; (2) air wes evacuated from the 1soteniscope; (3) the vacuum tap to the isoteniscope was closed; and (4) the sample was allowed to melt. In order to avoid the possibility of carbon dioxide being retained in the acid sample in the frozen state, an ethanol-water solution at a temperature of $-95^{\circ}$ to $-100^{\circ} \mathrm{C}$ was used as a cooling medium in the finsl repetition of the degasification procedure.

Measurement of vepor pressures. - Following degasification, the vacuum tap was closed and the isoteniscope was removed from the vacuum system. With the sample still frozen, the fluorocarbon separating fluid was allowed to flow into the U-tube to approximately one-half the height of the U-tube. The liquid levels were mariked as reference points for essentially equal pressures in both arms of the U-tube. The instrument was reattached to the vacuum system and vapor pressures were measured as follows: (I) water was circulated through the Dewar flask from the constant-temperature bath until the temperature was reached at which the first vapor pressure reading was to be taken; (2) as the pressure of the vapors in the acid chamber increased with rising temperature, the liquid in the arms of the U-tube was maintained at the reference levels by controlled admission of air into the vacuum system; (3) when no further pressure changes were observed, temperature and pressure readings were recorded. The air pressure required to balance the vapor pressure of the acid sample was read on an absolute manometer.

Pressure measurements were made in the same mamer at successively higher temperatures. After the pressure reading at the highest temperature was taken, the acia sample was cooled to the initial temperature and another reading was taken to detect any pressure increase that might have occurred during the run due to the decomposition of the acid.

Pressure measurements were made at all temperatures within the time interval 20 to 30 minutes.

Acid analysis. - The acid samples were analyzed by the method of U. S. Air Force Spectification No. 14104 with the exception that total acidity was determined by direct titration of the acid sample in water with NaOH solution. The $\mathrm{NO}_{2}$ was determined by back-titration of the sample in $\mathrm{Ce}\left(\mathrm{NH}_{4}\right)_{2}\left(\mathrm{SO}_{4}\right)_{3}$ solution with $\mathrm{FeSO}_{4}$. Water content was determined by the subtraction of the sum of the $\mathrm{NO}_{2}$ content and $\mathrm{HNO}_{3}$ content from 100 percent.

Acid analyses were made both on stock solutions and on samples taken from the isoteniscope after experimental runs. The acid analyses reported in table I are for stock solutions, inasmuch as fresh samples from stock solutions were used for each experimental run. The analyses in table I represent the average of two determinations for each sample.

## RELTABIIJTIY OF MEASUREMENIS

Accuracy of the apparatus. - The inherent accuracy of the apparatus was checked by comparison of the measured vapor pressures of benzene and distilled water with their values as reported in the literature. The experimental data and the literature values for the same temperature are presented in the following table:

${ }^{2}$ Values for water are from ref. 7 (table 9, p. 391); values for benzene, from ref. 8.

From this table it appears that the experimental error associated with this apparatus is of the order of 1 to 1.5 percent.

Ullage effects. - The ullage of the isoteniscope used in this investigation was approximately 0.65 under operating conditions. For several samples the ullage was varied approximately 20 percent between the first run and the check run without measurable change in vapor pressure.

The vapor pressures measured by this apparatus are essentially due to the transfer of varying proportions of the constituents from the liquid to the vapor phase, which produces changes in the composition of the liquid remaining. Inasmuch as it is necessary to report vapor pressures as those in equilibrium with samples of composition determined by prior analysis, calculations were made by means of the ideal gas law to determine the maximum change in liquid composition that could take place by the transfer of components from the liquid to the vapor phase. As an extreme case, these calculations were based on the assumption that the vapor space was entirely occupied by the least abundant component of the liquid phase. For most of the samples, these calculations showed that the maximum amount of the component that could be transferred to the vapor phase was generally less than 5 percent of the total quantity of this component present in the original liquid sample. For samples containing 0.15 to 0.21 percent $\mathrm{NO}_{2}$, the calculations showed changes of approximately 50 percent of the $\mathrm{NO}_{2}$ present in the Iiquid sample; however, the condition of these calculations was more severe than the condition encountered in actual practice, since vapor pressure is not due solely to one constituent of the mixture.

From the experimental evidence and the calculations just described, it was therefore concluded that ullage is not a significant source of error in these measurements. However, inasmich as the effects of wide variations in ullage were not experimentally determined, the reader is cautioned against the indiscriminate application of the results to systems with ullage differing from 0.65.

Effects of decomposition and degasification. - As described earlier, the vapor pressure of each sample was measured twice at the initial temperature of the experimental run, once at the beginning of the run and once at the conclusion. Invariably, the second pressure was higher than the first, indicating that a certain amount of decomposition had taken place during the experimental run. The largest pressure increase experfenced for all runs between the initial and final readings was 16.5 millimeters of mercury, and the average increase for all the experimental runs was 4.5 millifineters of mercury. Inasmuch as the amount of decomposition increases with both temperature and time, it is reasonable to expect that errors due to decomposition affect chiefly the higher vaporpressure measurements, corresponding to higher temperatures and longer time intervals. By comparison of the pressure increases with the vapor pressures at the higher temperatures, it appears that errors in pressure measurements due to decomposition were on the average less than 3 percent of the measured pressures at the higher temperatures.

Further evidence, given in the following table, shows that change in composition of the acid due to decomposition and degasification is
small. The data in this table were obtained by analysis of two acid samples both before and after experimental runs.

| Sample number | Anslysis, percent by weight |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{HNO}_{3}$ | $\mathrm{NO}_{2}$ | $\mathrm{H}_{2} \mathrm{O}$ |
| 17 | Stock solution <br> After experimental run number 1 <br> After experimental run number 2 | $\left.\begin{aligned} & 91.10 \\ & 90.81 \\ & 91.19 \end{aligned} \right\rvert\,$ | $\begin{aligned} & 2.60 \\ & 2.75 \\ & 2.58 \end{aligned}$ | $\begin{aligned} & 6.30 \\ & 6.44 \\ & 6.23 \end{aligned}$ |
| 12 | Stock solution <br> After experimental run number 1 <br> After experimental run number 2 | $\begin{aligned} & 95.10 \\ & 95.16 \\ & 95.03 \end{aligned}$ | 2.16 2.09 2.03 | 2.74 2.75 2.94 |

## RESULIS AND DISCUSSION

The measured vapor pressures for 28 acid samples are presented in table I. Vapor pressures were not measured for some of the acids at temperatures above $70^{\circ} \mathrm{C}$ since limiting features of the apparatus made it impossible to measure vapor pressures above 1 atmosphere.

Figure 2 is a logarithmic plot of total vapor pressure of the acid versus vapor pressure of water (ref. 7) at equal temperatures (methods from refs. 9 and 10). This figure is a plot of the raw data for all the acid samples. No special significance is attached to the way the samples are grouped in the figure. When great accuracy is not needed, the vapor pressures of the various acids above $70^{\circ} \mathrm{C}$ may be obtained by extrapolation of the curves in this figure.

Figure 3 is presented to show the effect of variation of composition of the acia sample on vapor pressure at temperatures of $25^{\circ} \mathrm{C}, 40^{\circ} \mathrm{C}$, and $60^{\circ} \mathrm{C}$, respectively. An attempt was made to prepare samples in sets of approximately constant $\mathrm{NO}_{2}$ concentration for the purpose of relating composition of the acid with vapor pressure at spectific temperatures. These concentrations were $0.15-0.21$, 1.07-1.24, $2.02-2.28,2.48-2.70$, 3.48-3.60, and 5.30-5.63 percent $\mathrm{NO}_{2}$, with varying amounts of $\mathrm{HNO}_{3}$ and $\mathrm{H}_{2} \mathrm{O}$. In figure 3 vapor pressure is plotted against weight percent $\mathrm{HNO}_{3}$ for the $\mathrm{NO}_{2}$ concentrations mentioned. Vapor pressure values were obtained from the smoothed curves of the pressure-temperature data of table I for each acid composition. These data indicate that, within the composition range studied, an increase in total vapor pressure is produced by a
decrease in $\mathrm{HNO}_{3}$ content for acids containing 2.0 percent $\mathrm{NO}_{2}$ or more. For acids containing less than 1.25 percent $\mathrm{NO}_{2}$ an opposite effect is shown.

Ternary diagrams showing isobars as a function of the composition of the system $\mathrm{NO}_{2}-\mathrm{H}_{2} \mathrm{O}-\mathrm{HNO}_{3}$ are presented for the temperatures $25^{\circ}, 40^{\circ}$, and $60^{\circ} \mathrm{C}$ in Pigure 4. These diagrams were constructed both from interpolated vapor pressure values taken from Iigure 3 and from experimental data points. While subject to minor inaccuracies due to the manner of their construction, these diagrams can be used to estimate the vapor pressure, at $25^{\circ}, 40^{\circ}$, and $60^{\circ} \mathrm{C}$, of any sample within the range of composition covered by the ternary plots. Such estimates at two different temperatures may then be plotted as the logarithm of the vapor pressure of the acid against the logarithm of the vapor pressure of water at equal temperature. A straight line drawn through these two points gives good predictions of the vapor pressures at other temperatures in the range $20^{\circ}$ to $80^{\circ} \mathrm{C}$.

Vapor pressures of 62.1 millimeters of mercury and 100.5 millimeters of mercury have been reported for anhydrous nitric acids containing 0 and 6 weight percent $\mathrm{NO}_{2}$, reapectively, at $25^{\circ} \mathrm{C}$ (ref. 5). These data correspond closely to the vapor pressures predicted by figure 4 ( a ) ( $65 \mathrm{~nm} \mathrm{Hg}_{\mathrm{g}}$ and 89 mmg ) for these compositions at $25^{\circ} \mathrm{C}$.

The calculated vapor pressures of pure $\mathrm{HNO}_{3}$ are reported in reference 4 as 62.5 millimeters of mercury, 133 millifmeters of mercury, and 317 millimeters of mercury at the termperatures, $25^{\circ}, 40^{\circ}$, and $60^{\circ} \mathrm{C}$, respectively. These data are shown in figure 3 for the purpose of comparison with the values obtained by extrapolation of the 0.15-0.21 percent $\mathrm{NO}_{2}$ curve to 100 percent $\mathrm{HNO}_{3}$. Vapor pressures obtained by this extrapolation were 65.5 millimeters of mercury at $25^{\circ} \mathrm{C}$, 141 millimeters of mercury at $40^{\circ} \mathrm{C}$, and 344 millimeters of mercury at $60^{\circ} \mathrm{C}$.

## SUMMARY OF RESUHTS

Total vapor pressures were measured for concentrated acids of the system, $\mathrm{NO}_{2}-\mathrm{H}_{2} \mathrm{O}-\mathrm{HNO}_{3}$ within the temperature range $20^{\circ}$ to $80^{\circ} \mathrm{C}$. Results of the investigation may be summarized as follows:

1. F'or acids containing 2.0 percent $\mathrm{NO}_{2}$ or more, an increase in $\mathrm{HNO}_{3}$ content resulted in a decreased total pressure. For acids containing 1.2 percent $\mathrm{NO}_{2}$ or less, an increase in $\mathrm{HNO}_{3}$ content resulted in an increased total pressure.
2. A straight line was obtained throughout the temperature range $20^{\circ}$ to $80^{\circ} \mathrm{C}$ for the logarithmic plot of vapor pressure of the acid versus vapor pressure of water at equal temperature.
Lewls Flight Propulsion Laboratory
National Advisory Committee for Aeronautics Cleveland, Ohio, July 10, 1953

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| Saxple | Analyais | or atock | colution | Hum nurber 1 |  |  |  |  |  |  | Run number 2 |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\begin{gathered} \mathrm{HMO}_{3}, \\ \text { percent } \end{gathered}$ | $\mathrm{KO}_{2}$, percent | $\begin{gathered} \text { 耳pO, } \\ \text { perant } \end{gathered}$ |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 1 | 94.40 | 0.18 | B. 42 | Temperature yapor presaure | $\begin{aligned} & 21.0 \\ & 43.1 \end{aligned}$ | $\begin{aligned} & 24.0 \\ & 50.1 \end{aligned}$ | $\begin{aligned} & 32.3 \\ & 75.0 \end{aligned}$ | 12.0 121.0 | $\begin{array}{r} 64.1 \\ 310.0 \end{array}$ | $\begin{array}{r} 75.8 \\ 488.8 \\ \hline \end{array}$ | $\begin{aligned} & 27.7 \\ & 64 . .5 \\ & \hline \end{aligned}$ | $\begin{aligned} & 34.0 \\ & 87.0 \end{aligned}$ | $\begin{array}{r} 40.8 \\ 116.3 \\ \hline \end{array}$ | 53.6 195.0 | $\begin{array}{r} 73.9 \\ 454.0 \\ \hline \end{array}$ | -- |
| 2 | 92.07 | 0.15 | 7.78 | Tamperaturo vapor pressure | $\begin{array}{r} 21.0 \\ 37.8 \\ \hline \end{array}$ | $\begin{aligned} & 27.0 \\ & 51.0 \\ & \hline \end{aligned}$ | $\begin{aligned} & 37.0 \\ & 83.0 \end{aligned}$ | 49.0 149.5 | $\begin{array}{r} 61.0 \\ 289.5 \end{array}$ | ---- | $\begin{array}{r} 24.4 \\ \hline 5.5 \\ \hline \end{array}$ | $\begin{array}{r} 31.0 \\ 61.5 \\ \hline \end{array}$ | $\begin{array}{r} 38.3 \\ 88.0 \\ \hline \end{array}$ | 61.2 | $\begin{array}{r} 76.4 \\ \mathbf{4 3 0 . 0} \\ \hline \end{array}$ | ----- |
| 3 | 89.32 | 0.21 | 10.47 | Tamporature <br> Vapor presture | $\begin{aligned} & 23.8 \\ & 36.5 \end{aligned}$ | $\begin{aligned} & 55.0 \\ & 63.2 \end{aligned}$ | $\begin{aligned} & 64.0 \\ & 97.0 \end{aligned}$ | $\begin{array}{r} 54.9 \\ 189.0 \end{array}$ | $\begin{array}{r} 64.4 \\ 235.8 \\ \hline \end{array}$ | $\begin{array}{r} 77.8 \\ 384.0 \\ \hline \end{array}$ | $\begin{array}{r} 24.9 \\ 30.6 \\ \hline \end{array}$ | $\begin{array}{r} 30.1 \\ 51.0 \\ \hline \end{array}$ | $\begin{aligned} & 40.5 \\ & 80.0 \end{aligned}$ | $\begin{array}{r} 50.5 \\ 135.0 \\ \hline \end{array}$ | $\begin{array}{r} 61.4 \\ 212.0 \\ \hline \end{array}$ | $\begin{array}{r} 72.2 \\ 328.8 \\ \hline \end{array}$ |
| 4 | 98.83 | 0.16 | 5.01 | Tanperature <br> vapor presbure | $\begin{aligned} & 18.0 \\ & 39.6 \end{aligned}$ | $\begin{aligned} & 25.0 \\ & 58.1 \end{aligned}$ | $\begin{aligned} & 32.1 \\ & 84.0 \\ & \hline \end{aligned}$ | $\begin{aligned} & 41.3 \\ & 531.8 \end{aligned}$ | 51.4 210.2 | 88.0 281.3 | $\begin{array}{r} 17.9 \\ 40.1 \end{array}$ | $\begin{aligned} & 25.0 \\ & 58.0 \end{aligned}$ | $\begin{aligned} & 30.0 \\ & 76.8 \end{aligned}$ | 34.0 99.5 | $\begin{array}{r} 69.0 \\ 434.9 \\ \hline \end{array}$ |  |
| 5 | 85.47 | 0.74 | 5.79 | Teuporeture vapor presiare | $\begin{aligned} & 20.8 \\ & 48.8 \end{aligned}$ | $\begin{aligned} & 25.9 \\ & 57.0 \end{aligned}$ | $\begin{aligned} & 34.4 \\ & 98.5 \end{aligned}$ | 144.9 | $\begin{array}{r} 54.0 \\ 285.0 \\ \hline \end{array}$ | $\begin{array}{r} 64.2 \\ 48.0 \end{array}$ | $\begin{aligned} & 21.3 \\ & 52.6 \end{aligned}$ | $\begin{aligned} & 26.0 \\ & 67.0 \end{aligned}$ | $\begin{array}{r} 35.2 .2 \\ 107.8 \end{array}$ | $\begin{array}{r} 75.6 \\ 844.0 \\ \hline \end{array}$ | -- | ------ |
| 6 | 84.38 | 1.20 | 14.42 | Tampirature <br> Fapor preanure | $\begin{array}{r} 18.9 \\ -44.0 \\ \hline \end{array}$ | $\begin{aligned} & 25.2 \\ & 65.0 \\ & \hline \end{aligned}$ | $\begin{aligned} & 29.9 \\ & 62.1 \\ & \hline \end{aligned}$ | $\begin{array}{r} 36.7 \\ 126.6 \\ \hline \end{array}$ | $\begin{array}{r} 57.1 \\ 302.5 \end{array}$ | $\begin{array}{r} 75.5 \\ 654.6 \end{array}$ | $\begin{aligned} & 25.2 \\ & 64.5 \end{aligned}$ | $\begin{aligned} & 32.8 \\ & 96.2 \end{aligned}$ | $\begin{array}{r} 43.0 \\ 159.0 \\ \hline \end{array}$ | $\begin{array}{r} 83.5 \\ 257.8 \\ \hline \end{array}$ | $\begin{array}{r} 63.9 \\ 401.5 \\ \hline \end{array}$ | $\begin{array}{r} 72.8 \\ 574.5 \\ \hline \end{array}$ |
| 7 | 89.62 | 1.24 | 9.14 | Temperatur. vapor pressure | $\begin{aligned} & 18.7 \\ & 44.6 \end{aligned}$ | $\begin{aligned} & 25.0 \\ & 57.3 \end{aligned}$ | $\begin{aligned} & 29.0 \\ & 78.1 \end{aligned}$ | ${ }_{129.1}$ | $\begin{array}{r} 48.8 \\ 208.2 \\ \hline \end{array}$ | $\begin{array}{r} 76.4 \\ 668.9 \end{array}$ | $\begin{aligned} & 25.1 \\ & 69.0 \end{aligned}$ | $\begin{array}{r} 55.4 \\ 106.5 \end{array}$ | $\begin{array}{r} 46.0 \\ 279.9 \\ \hline \end{array}$ | 57.1 503.7 | $\begin{array}{r} 63.8 \\ 401.7 \\ \hline \end{array}$ | $\begin{array}{r} 71.7 \\ 535.3 \\ \hline \end{array}$ |
| 8 | 92.14 | 1.07 | 6.79 | Temparature <br> vaper presaure | $\begin{aligned} & 19.3 \\ & 48.3 \end{aligned}$ | $\begin{aligned} & 23.7 \\ & 82.4 \end{aligned}$ | $\begin{array}{r} 39.0 \\ 185.0 \end{array}$ | 218.4 | $\begin{array}{r} 89.8 \\ 535.6 \end{array}$ | $\begin{gathered} 78.5 \\ 687.5 \end{gathered}$ | $\begin{aligned} & 19.4 \\ & \hline 18.1 \end{aligned}$ | $\begin{array}{r} 25.2 \\ -67.9 \\ \hline \end{array}$ | $\begin{array}{r} 34.1 \\ 105.5 \\ \hline \end{array}$ | $\begin{array}{r} 42.9 \\ 184.5 \end{array}$ | [49.0 | $\begin{array}{r} 60.8 \\ 518.2 \\ \hline \end{array}$ |
| 9 | 91.75 | 1.32 | 6.95 | Temperature <br> Fapor pressure | $\begin{aligned} & 24.0 \\ & 61.1 \end{aligned}$ | $\begin{aligned} & 29.9 \\ & 83.2 \end{aligned}$ | $\begin{array}{r} 39.5 \\ 136.2 \\ \hline \end{array}$ | $\begin{array}{r} 54.9 \\ 286.1 \end{array}$ | $\begin{array}{r} 85.2 \\ 142.0 \\ \hline \end{array}$ | $852.0$ | $\begin{array}{\|l\|} \hline 19.5 \\ 47.5 \\ \hline \end{array}$ | $\begin{aligned} & 30.0 \\ & 85.8 \end{aligned}$ | $\begin{array}{r} 40.9 \\ 148.1 \\ \hline \end{array}$ | $\begin{array}{r} 47.0 \\ 199.0 \\ \hline \end{array}$ | $\begin{array}{r} 72.5 \\ 600.8 \\ \hline \end{array}$ | ----- |
| 10 | 89.50 | 2.22 | 8.28 | Temperature Vapor pressure | $\begin{array}{r} 22.0 \\ 67.5 \end{array}$ | $\begin{array}{r} 29.1 \\ 100.0 \\ \hline \end{array}$ | $\begin{array}{r} 39.0 \\ 160.0 \\ \hline \end{array}$ | [ 485.8 | $\begin{array}{r} 58.2 \\ 395.8 \\ \hline \end{array}$ | [ $\begin{array}{r}68.3 \\ \hline 89.9\end{array}$ | $\begin{array}{r} 19.0 \\ 87.8 \\ \hline \end{array}$ | $\begin{aligned} & 23.0 \\ & 7 I .8 \\ & \hline \end{aligned}$ | $\begin{aligned} & 28.8 \\ & 95.3 \\ & \hline \end{aligned}$ | $\begin{aligned} 34.1 \\ 129.8 \end{aligned}$ | $\begin{array}{r} 43.7 \\ \hline 14.2 \\ \hline \end{array}$ | $\begin{array}{r} 62.0 \\ 449.8 \end{array}$ |
| 11 | 95.96 | 2.02 | 12.02 | 5emperature <br> Vapor pressure | $\begin{array}{r} 24.1 \\ 75.0 \\ \hline \end{array}$ | $\begin{aligned} & 29.4 \\ & 98.4 \end{aligned}$ | 43.9 210.8 | $\left[\begin{array}{r} 50.8 \\ 298.0 \end{array}\right.$ | $\begin{array}{r} 59.4 \\ 432.9 \\ \hline \end{array}$ | $\begin{array}{r} 70.5 \\ 679.1 \\ \hline \end{array}$ | $\begin{array}{r} 15.1 \\ 85.5 \\ \hline \end{array}$ | $\begin{aligned} & 23.0 \\ & 70.0 \end{aligned}$ | 23.8 | $\begin{array}{r} 40.9 \\ 176.7 \end{array}$ | 285.0 | $\begin{array}{r} 67.0 \\ 585.2 \end{array}$ |
| 12 | 85.10 | 2.16 | 2.74 | Temperature Fapor pries aure | $\begin{aligned} & 24.5 \\ & 71.5 \end{aligned}$ | $\begin{aligned} & 29.3 \\ & 91.5 \\ & \hline \end{aligned}$ | $\begin{array}{r}39.0 \\ 151.5 \\ \hline\end{array}$ | $\begin{array}{r} 49.1 \\ 252.0 \\ \hline \end{array}$ | $\begin{array}{r} 59.4 \\ \hline \end{array}$ | $\begin{array}{r} 68.4 \\ \hline 595.7 \\ \hline \end{array}$ | $\begin{array}{\|l} 18.8 \\ 51.3 \end{array}$ | $\begin{aligned} & 29.5 \\ & 92.2 \\ & \hline \end{aligned}$ | $\begin{array}{r} 38.0 \\ 124.8 \\ \hline \end{array}$ | 200.3 | $\begin{array}{r} 59.1 \\ \hline 00.8 \\ \hline \end{array}$ | $\begin{array}{r} 66.3 \\ 547.4 \\ \hline \end{array}$ |
| 13 | 91.00 | 2.28 | 6.72 | Terperature <br> Vapor preseure | $\begin{array}{r} 25.9 \\ 85.4 \\ \hline \end{array}$ | 32.4 119.0 | 39.0 187.2 | 45.8 <br> 276.5 | $\begin{array}{r} 69.5 \\ 452.52 \\ \hline \end{array}$ | 69.4 854 | $\begin{aligned} & 19.0 \\ & 69.7 \end{aligned}$ | $\begin{array}{r} 23.0 \\ 73.9 \\ \hline \end{array}$ | $\begin{array}{r} 29.4 \\ 103.2 \\ \hline \end{array}$ | $\begin{array}{r} 44.0 \\ 212.3 \\ \hline \end{array}$ | 54.0 | $\begin{array}{r} 64.2 \\ 524.8 \end{array}$ |
| 14 | 93.96 | 2.48 | 3.58 | Tenperature <br> Vafor presime | $\begin{aligned} & 19.0 \\ & 52.0 \end{aligned}$ | $\begin{aligned} & 25.5 \\ & 67.0 \end{aligned}$ | $\begin{array}{r} 33.9 \\ 118.9 \\ \hline \end{array}$ | $\begin{array}{r} 51.4 \\ 209.0 \\ \hline \end{array}$ | [503.2 | $\begin{array}{r} 72.4 \\ \hline \end{array}$ | $\begin{aligned} & 16.0 \\ & 44.8 \end{aligned}$ | $\begin{aligned} & 18.0 \\ & 52.8 \end{aligned}$ | $\begin{aligned} & 27.0 \\ & 82.3 \end{aligned}$ | $\begin{array}{r} 35.9 \\ 128.0 \\ \hline \end{array}$ | 40.8 <br> 169.5 | $\begin{array}{r} 71.5 \\ 704.3 \end{array}$ |
| 15 | 84.31 | 2.60 | 3.09 | Tenperthure Vapor praseure | $\begin{aligned} & 24.0 \\ & 75.0 \end{aligned}$ | $\begin{aligned} & 29.2 \\ & 80.4 \end{aligned}$ | $\begin{array}{r} 38.5 \\ 158.0 \\ \hline \end{array}$ | 49.8 275.7 | $\begin{array}{r} 58.9 \\ 428.9 \\ \hline \end{array}$ | $\begin{array}{r} 69.3 \\ 654.8 \end{array}$ | $\begin{array}{\|l\|l\|} 20.3 \\ 60.8 \end{array}$ | $\begin{aligned} & 29.5 \\ & 99.5 \end{aligned}$ | $\begin{array}{r} 54.0 \\ 185.0 \\ \hline \end{array}$ | $\begin{array}{r} 43.0 \\ 198.7 \end{array}$ | 299.5 | $\begin{array}{r} 84.3 \\ 634.7 \end{array}$ |
| 16 | 85.03 | 2.70 | 12.27 | Teaperetiure Vapor presaure | $\begin{aligned} & 24.0 \\ & 77.8 \\ & \hline \end{aligned}$ | $\begin{array}{r} 29.0 \\ 102.8 \\ \hline \end{array}$ | $\begin{array}{r} 41.0 \\ 190.5 \\ \hline \end{array}$ | $\begin{array}{r} 49.0 \\ 288.0 \\ \hline \end{array}$ | $\begin{array}{r} 59.2 \\ 467.0 \\ \hline \end{array}$ | $\begin{array}{r} 70.7 \\ 713.8 \\ \hline \end{array}$ | $\begin{array}{r} 18.9 \\ 55.8 \\ \hline \end{array}$ | $\begin{aligned} & 24.2 \\ & 75.2 \end{aligned}$ | $\begin{array}{r} 30.2 \\ 106.5 \\ \hline \end{array}$ | $\begin{array}{r} 57.8 \\ 159.4 \\ \hline \end{array}$ | 289.7 | $\begin{array}{r} 68.4 \\ 888.0 \\ \hline \end{array}$ |
| 17 | 91.10 | 2.60 | 6.30 | Feryereture Vapor pres sure | $\begin{aligned} & 19.5 \\ & 57.0 \\ & \hline \end{aligned}$ | 25.5 72.5 | 29.1 98.8 | $\begin{array}{r}36.5 \\ 144.7 \\ \hline\end{array}$ | 48.7 <br> 288.6 | $\begin{array}{r} 60.2 \\ 44.0 \\ \hline \end{array}$ | $\begin{array}{r} 25.0 \\ 71.0 \\ \hline \end{array}$ | 29.1 98.5 | 175.2 | 278.1 | [ $\begin{array}{r}88.8 \\ 388.8\end{array}$ | $\begin{array}{r}67.3 \\ 809.4 \\ \hline\end{array}$ |
| IB | 93.45 | 3.58 | 2.98 | Twinperature <br> Yapor presempe | $\begin{aligned} & 22.1 \\ & 73.0 \end{aligned}$ | $\begin{aligned} & 25.5 \\ & 88.8 \\ & \hline \end{aligned}$ | $\begin{array}{r} 35.9 \\ 149.8 \\ \hline \end{array}$ | $\begin{array}{r} 48.2 \\ 238.0 \\ \hline \end{array}$ | $\begin{array}{r} 83.1 \\ 351.0 \\ \hline \end{array}$ | $\begin{array}{r} 86.4 \\ 629.2 \end{array}$ | $\begin{aligned} & 18.7 \\ & 62.4 \end{aligned}$ | 121.0 | $\begin{array}{r} 11.3 \\ 199.5 \\ \hline \end{array}$ | $\begin{array}{r} 49.9 \\ 305.8 \end{array}$ | $\begin{array}{r} 66.8 \\ 418.5 \\ \hline \end{array}$ | $\begin{array}{r} 70.0 \\ 755.1 \\ \hline \end{array}$ |
| 19 | 86.59 | 3.54 | 9.87 | Temperature Vapor pressure | $\begin{aligned} & 18.8 \\ & 75.6 \end{aligned}$ | 107.7 | $\begin{array}{r} 39.1 \\ 199.8 \end{array}$ | 47.5 298.1 | $\begin{array}{r} 55.0 \\ 423.0 \end{array}$ | $\begin{array}{r} 68.1 \\ 726.0 \end{array}$ | $\begin{aligned} & 20.9 \\ & 82.7 \\ & \hline \end{aligned}$ | [ $\begin{array}{r}32.2 \\ 143.8\end{array}$ | 36.9 179.7 | $\begin{array}{r} 50.5 \\ 342.8 \\ \hline \end{array}$ | [60.3 | $\begin{gathered} 67.4 \\ 703.4 \end{gathered}$ |
| 20 | 91.05 | 3.48 | 5.49 | Twaperature Vapor pressure | 56.0 85.8 | 18.2 87.9 | $\begin{array}{r} 30.5 \\ 119.0 \\ \hline \end{array}$ | $\begin{array}{r} 39.0 \\ 179.0 \\ \hline \end{array}$ | $\begin{array}{r} 49.2 \\ 298.6 \end{array}$ | $\begin{array}{r} 69.2 \\ 463.4 \\ \hline \end{array}$ | $\begin{array}{\|l\|l\|} 19.6 \\ 87.1 \end{array}$ | $\begin{aligned} & 25.8 \\ & 92.2 \\ & \hline \end{aligned}$ | $\begin{array}{r} 34.5 \\ 144.0 \\ \hline \end{array}$ | $\begin{array}{r} 44.7 \\ 239.4 \\ \hline \end{array}$ | $\begin{array}{r} 58.2 \\ 898.0 \\ \hline \end{array}$ | $\begin{array}{r} 69.3^{\circ} \\ \hline 894.7 \\ \hline \end{array}$ |
| 21 | 83.68 | 5.60 | 12.74 | Teapernture <br> Vaper pressure | $\begin{aligned} & 19.0 \\ & 68.8 \end{aligned}$ | $\begin{array}{r} 50.9 \\ 130.5 \\ \hline \end{array}$ | $\begin{array}{r}39.0 \\ 200.0 \\ \hline\end{array}$ | $\begin{array}{r}46.0 \\ 283.9 \\ \hline\end{array}$ | $\begin{array}{r} 57.3 \\ 479.4 \\ \hline \end{array}$ | $\begin{gathered} 82.2 \\ 592.5 \end{gathered}$ | $\begin{array}{\|l\|} 18.8 \\ 68.7 \\ \hline \end{array}$ | 23.7 <br> 1.6 | 30.2 129.8 | $\begin{array}{r} 37.0 \\ 184.7 \\ \hline \end{array}$ | $\begin{array}{r} 51.6 \\ 574.3 \\ \hline \end{array}$ | $\begin{array}{r} 83.5 \\ 825.1 \end{array}$ |
| 22 | 84.26 | 5.32 | 10.42 | Twiperaturs <br> Tapor preasure | $\begin{aligned} & 22.7 \\ & 91.2 \end{aligned}$ | $\begin{array}{r} 26.6 \\ 118.0 \\ \hline \end{array}$ | $\begin{array}{r} 37.3 \\ 208.8 \end{array}$ | $\begin{array}{r} 47.2 \\ 546.5 \\ \hline \end{array}$ | $\begin{array}{r} 58.2 \\ 695.0 \\ \hline \end{array}$ | $\begin{array}{r} 83.2 \\ 715.0 \\ \hline \end{array}$ | $\begin{aligned} & 19.9 \\ & 81.9 \end{aligned}$ | $\begin{array}{r} 27.2 \\ 123.5 \\ \hline \end{array}$ | $\begin{array}{r} 33.2 \\ 17 I .5 \\ \hline \end{array}$ | $269.0$ | $\begin{array}{r} 52.2 \\ 44.5 \end{array}$ | $\begin{array}{r} 81.9 \\ 682.0 \\ \hline \end{array}$ |
| 23 | 89.80 | 5.50 | 4.70 | Tempraturo Vepor prasifure | $\begin{aligned} & 21.8 \\ & 78.2 \end{aligned}$ | $\begin{array}{r} 29.9 \\ 181.0 \end{array}$ | $\begin{array}{r} 39.1 \\ 202.8 \\ \hline \end{array}$ | $323.0$ | $\begin{array}{r} 56.0 \\ 480.5 \\ \hline \end{array}$ | $\begin{array}{r} 85-5 \\ 700.5 \\ \hline \end{array}$ | $\begin{aligned} & 20.0 \\ & 72.5 \end{aligned}$ | $\begin{array}{r} 28.9 \\ 104.0 \\ \hline \end{array}$ | $\begin{array}{r} 55.9 \\ 168.4 \\ \hline \end{array}$ | $\begin{array}{\|c} 46.0 \\ \hline \end{array}$ | $\begin{array}{r} 52.8 \\ 401.0 \\ \hline \end{array}$ | $\begin{array}{\|r} 88.3 \\ 737.7 \\ \hline \end{array}$ |
| 24 | 81.00 | 5.63 | 3.37 | Teaperature Vapor preacure | $\begin{aligned} & 22.1 \\ & 75.4 \end{aligned}$ | $\begin{array}{r} 27.1 \\ 104.4 \end{array}$ | $\begin{array}{r} 35.0 \\ 155.7 \\ \hline \end{array}$ | $\begin{array}{r} 39.8 \\ 200.0 \end{array}$ | $\begin{array}{r} 55.0 \\ 395.8 \\ \hline \end{array}$ | $\begin{array}{r} 60.7 \\ 559.1 \\ \hline \end{array}$ | $\begin{array}{\|l\|l} 17.5 \\ 60.3 \end{array}$ | $\begin{aligned} & 20.7 \\ & 71 . \end{aligned}$ | $\begin{aligned} & 33.0 \\ & 142.8 \end{aligned}$ | $\begin{array}{r} 35.8 \\ 174.2 \end{array}$ | $\begin{array}{r} 43.0 \\ 241.5 \\ \hline \end{array}$ | $\begin{array}{r} 62.3 \\ 005.1 \end{array}$ |
| 88 | 86.57 | 5.30 | 7.73 | Twaperature Vapor pressure | $\begin{aligned} & 23.1 \\ & 93.0 \end{aligned}$ | $\begin{array}{r} 30.0 \\ 138.7 \\ \hline \end{array}$ | $\begin{array}{r} 34.3 \\ 274.2 \\ \hline \end{array}$ | $\begin{array}{r} 40.8 \\ 240.2 \end{array}$ | $\begin{array}{r} 55.2 \\ 488.8 \end{array}$ | $\begin{array}{r} 64.0 \\ 715.0 \end{array}$ | $87.1$ | $\begin{array}{r} 29.0 \\ 130.5 \end{array}$ | $\begin{array}{r} 37.6 \\ 205.5 \end{array}$ | $\begin{array}{r} 50.2 \\ 586.2 \end{array}$ | $\begin{array}{\|l\|} \hline 68.9 \\ 878.0 \end{array}$ | ---- |
| 28 | 92.70 | 5.46 | 2.84 | Temperature 7apor prefsure | 24.5 89.7 | $\begin{array}{r}29.4 \\ \hline 18.0\end{array}$ | 35.1 160.1 | $\begin{array}{r} 44.7 \\ 282.9 \end{array}$ | $\begin{array}{r} 54.9 \\ 430.3 \\ \hline \end{array}$ | $\begin{array}{r} 63.9 \\ 658.7 \\ \hline \end{array}$ | $\begin{aligned} & 19.2 \\ & 67.5 \end{aligned}$ | $\begin{aligned} & 24.0 \\ & 88.6 \end{aligned}$ | $\begin{array}{r} 29.7 \\ 120.8 \end{array}$ | +34.8 | $\begin{array}{r} 40.7 \\ 213.8 \\ \hline \end{array}$ | $\begin{array}{r} 66.3 \\ 721.0 \end{array}$ |
| 27 | 83.82 | 5.61 | 10.57 | Tenterature Vapor pressure | $\begin{array}{r} 24.8 \\ 114.2 \\ \hline \end{array}$ | $\begin{array}{r} 28.5 \\ 140.0 \\ \hline \end{array}$ | $\begin{array}{r} 34.0 \\ 186.0 \\ \hline \end{array}$ | $\begin{array}{r} 47.0 \\ 359.2 \\ \hline \end{array}$ | $\begin{array}{r} 54.0 \\ 508.1 \\ \hline \end{array}$ | $\begin{array}{r} 62.1 \\ 76.3 \\ \hline \end{array}$ | $\begin{aligned} & 19.0 \\ & 75.8 \end{aligned}$ | $\begin{array}{r} 32.8 \\ 168.3 \\ \hline \end{array}$ | $\begin{array}{r} 39.0 \\ \mathbf{2 3 7 . 7} \\ \hline \end{array}$ | $\begin{array}{r} 49.0 \\ 391.7 \\ \hline \end{array}$ | $\begin{array}{r} 53.99 \\ 481.8 \\ \hline \end{array}$ | $\begin{array}{r} 69.1 \\ 621.8 \\ \hline \end{array}$ |
| 28 | 90.50 | 6.12 | 3.53 | Tanperature Yapor presture | $\begin{aligned} & 22.6 \\ & 91.8 \end{aligned}$ | $\begin{array}{r} 34.4 \\ 169.1 \end{array}$ | $\begin{array}{r} 41.0 \\ 232.8 \end{array}$ | $310.5$ | $\begin{array}{r} 54.5 \\ 450.0 \end{array}$ | ---- | $\begin{aligned} & 20.1 \\ & 78.2 \end{aligned}$ | 23.9 96.4 | $\begin{array}{r} 29.8 \\ 124.5 \end{array}$ | $\begin{array}{r} 38.0 \\ 158.2 \end{array}$ | $283.7$ | $895.4$ |



(a) Sample numbers 1, 9, 10, 21, and 25.

Figure 2. - Cox-Othmer plot of totel vapor pressures of nitric acid solutions. Ullage, 0.65.

(b) Sample numbers $2,6,22,13,18$, and 26 .

Figure 2. E Continued. Cox-Othmer plot of total vapor pressures of nitric acid solutions. Ullage, 0.65.

(c) Sample numbers $4,8,11,22$, and 24 .

Figure 2. - Continued. Cox-Othmer plot of totel vapor pressures of nitric acid solutions. Ullege, 0.65 .

(d) Sample numbers 3, 7, 14, 20, and 27.

Figure 2. - Contimued. Cox-Othmer plot of total vapor pressures of nitric acid solutions. Ullage, 0.65 .

(e) Sample numbers $15,16,23$, and 28.

Figure 2. - Continued. Cox-Othmer plot of total vapor pressures of nitric acid solutions. Ullage, 0.65.

(f) Sample numbers 5, 17, and 19.

Figure 2. - Concluded. Cox-Othmer plot of total vapor pressures of nitric acid solutions. Ullage, 0.65 .


Figure 3. - Variation of total vapor pressure of nitric acid solutions with composition. Ullage, 0.65.

(b) Temperature, $40^{\circ} \mathrm{C}$.

Figure 3. - Continued. Variation of total vapor pressure of nitric acid solutions with composition. Ullage, 0.65 .

(c) Temperature, $60^{\circ} \mathrm{C}$.

Figure 3. - Concluded. Variation of total vapor pressure of nitric acid solutions with composition. Ullage, 0.65 .


Figure 4. - Total vapor preasures of the system, nftric ecid, nitrogen dioxide, and water. ullage, 0.65 .


Figure 4. - Contimued. Total vapor presbures of the system, nitric acid, pitrogea doxide, and water. tilage, 0.65.


Figure 4. - Concluded. Total vapor pressures of the system, nitric acid, nitrogen dioxide, and water.
Ullage, 0.85 .

