COMPOSITION OF VAPORS FROM BOILING NITRIC ACID SOLUTIONS

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COMPOSITION OF VAPORS FROM BOILING NITRIC ACID SOLUTIONS

by

R. C. Crooks
R. Q. Wilson
A. E. Bearse
R. B. Filbert, Jr.

February 9, 1955
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COMPOSITION OF VAPORS FROM BOILING NITRIC ACID SOLUTIONS


The composition of vapors from aqueous nitric acid solutions boiling at 200 mm mercury total pressure is established for solutions containing between 0 and 67.5 w/o nitric acid. The volatility characteristics of low concentrations of chloride in the same concentration range of nitric acid have been measured in solutions boiling at 200 mm mercury. The effects of chloride concentration and pressure of boiling are evaluated. A spectrophotometric method for the determination of chloride in nitric acid solutions is described.

INTRODUCTION

The current technology of materials processing has resulted in increased use of nitric acid as a solubilizing agent in the processing of nuclear-fuel materials. Recovery of nitric acid for recycling to materials-processing operations has become increasingly important. The present investigation was undertaken as a part of the program of plant assistance to the Feed Materials Production Center operated by the National Lead Company of Ohio.

The technology of nitric acid processing is somewhat determined by the corrosion resistance of available materials of construction. Although the recovered nitric acid is usually concentrated by rectification at atmospheric pressure, advantages of lower corrosion rates in equipment are found in the lower temperatures of distillation at subatmospheric pressures. Therefore, the objective of this work was to examine the existing values (1) of the vapor composition in boiling nitric acid solutions and to extend the experimental data to lower concentrations of nitric acid for solutions boiling at 200 mm of mercury total pressure.

In the concentration of nitric acid solutions which contain some chloride, the chloride tends to accumulate in the fractionation column and sometimes presents a severe corrosion problem. Although several nickel-containing alloys are practically inert to attack by nitric acid solutions, they are often rapidly corroded by nitric acid solutions in which chloride is present. Chloride materials tend to accumulate in fractionating equipment because hydrogen chloride is rapidly stripped from solutions which are high in nitric acid concentration, and is quickly absorbed in the reflux liquid which is low in acid concentration.

* References at end of this report.
Haggerty and Hixon (2) have measured the volatility characteristics of chloride in nitric acid solutions boiling at atmospheric pressure. This report presents work on the determination of chloride-distribution ratios in nitric acid solutions boiling at 200 mm mercury total pressure.

In the course of this work, a spectrophotometric procedure was developed for the determination of small concentrations of chloride in nitric acid solutions.

PART I. COMPOSITION OF VAPORS FROM AQUEOUS SOLUTIONS OF NITRIC ACID BOILING AT 200 MM MERCURY PRESSURE

The liquid-vapor equilibrium compositions of aqueous nitric acid solutions were measured in solutions boiling at 200 mm mercury total pressure. The compositions and boiling temperatures were determined in solutions which contained between 0.0165 and 0.385 mole fraction HNO₃. Published data (1) on partial pressures of nitric acid over aqueous solutions show values for nitric acid concentrations for 20 w/o (0.0665 mole fraction) nitric acid and above. Since dilute nitric acid solutions do not follow Henry's law, the liquid-vapor equilibrium relationship for the more dilute nitric acid solutions was uncertain. Therefore, the aims of this work were (1) to measure the liquid-vapor equilibrium compositions for dilute nitric acid solutions, and (2) to test the experimental data for thermodynamic consistency.

The equilibrium-composition values obtained in this work are in agreement with those of Taylor (1), but slightly lower boiling temperatures were observed. Both this work and Taylor's values were checked by thermodynamic consistency by graphical integration of the Gibbs-Duhem equation. The equilibrium relationships for the nitric acid-water system are readily extrapolated to zero acid concentration when the data are plotted as ratios of the vapor and liquid compositions. The extrapolation provides the information necessary for the construction of liquid-vapor equilibrium diagrams in the dilute-acid region as used in the engineering design of nitric acid distillation columns.

Experimental Work

Apparatus

The compositions of liquid and vapor from nitric acid solutions boiling at 200 mm mercury total pressure were obtained by use of an Othmer-type still (3) of improved design. Vacuum was provided by a water aspirator; a Cartesian manostat controlled the system pressure to within about 0.5 mm
of the 200 mercury operating pressure. A tower filled with soda lime and a 1.5-liter flask were connected between the manostat and the equilibrium still to absorb nitric acid vapors and reduce the pressure fluctuations in the still system. A capillary tube drawn to a very fine diameter at the tip provided a minute stream of air to promote smooth boiling action at the 200 mm mercury pressure. Without such a boiling aid, severe bumping was unavoidable. A resistance wire of 25 ohms, wrapped about an external reboiler U-tube at the bottom of the still, supplied the heat for boiling. The upper surfaces of the still unit were insulated by asbestos and a cloth wrapping.

A thermometer with its bulb located in the vapor tube of the still measured the vapor temperature. The thermometer was graduated in 0.2°C divisions, was calibrated against another thermometer which had been calibrated by the National Bureau of Standards, and was checked in the still against the boiling temperature of distilled water at various pressures. Corrections for the exposed thermometer stem were applied to all readings. A U-tube mercury-filled absolute manometer was used to measure the absolute pressure in the equilibrium still.

**Analytical Method**

Samples of the liquid and condensed vapor were analyzed for total acidity by titration with carbonate-free 0.1487 N NaOH to a phenolphthalein end point. The sodium hydroxide solution was standardized against potassium acid phthalate.

**Procedure**

Approximately 250 ml of a solution of nitric acid in water was charged to the still and the system evacuated to an absolute pressure of 200 mm mercury. With the desired pressure in the system, the by-pass stopcock on the manostat pressure controller was closed to maintain the pressure at that value. Power was then applied to the heater winding of the still to heat the solution to boiling, and the boiling action was continued for 1.5 hr to bring the compositions of the still liquid and vapor condensate to steady-state values. Steady temperature readings were obtained within 0.75 hr after the boiling started. During the boiling period, approximately 5 volumes of condensate flowed through the condensate receiver, thereby assuring steady-state compositions in both the receiver and the still.

Samples were taken from the draw-off connections on the still and the condensate receiver directly into 60-ml glass-stoppered dropper bottles. Check experiments showed that no significant change in composition by selective vaporization occurred with this method of sampling.

The heating rate of 160 w was selected as providing the best rate of boiling for this particular equilibrium still. Lower heating rates resulted
in some fractionation of the vapor, and higher heating rates led to entrainment of particles of liquid in the vapor. The effect of heating rate on the condensation temperature of the vapor while boiling a 20 w/o nitric acid solution is shown in Figure 1. The temperature curve shows that the fractionation effect becomes negligible at heating rates over 140 w.

System pressures were recorded to within 0.1 mm mercury. Temperature readings after stem correction were further adjusted to a pressure of 200.0 mm mercury.

Results and Discussion

Liquid-Vapor Equilibrium Data

The observed values for the liquid-vapor equilibrium compositions of nitric acid solutions boiling at 200 mm mercury pressure are shown in Table 1 and on the temperature-composition graph for the HNO₃-H₂O system in Figure 2. In the temperature-composition diagram of Figure 2, the compositions of liquid and vapor obtained in this work agree well with those of Taylor, but the observed boiling temperatures are somewhat lower. The activity coefficients of nitric acid vary over an exceedingly wide range, from a minimum of 0.00272 in a dilute solution to a maximum of 0.287 near the azeotrope.

The observed activity coefficients of nitric acid and water are plotted in Figure 3, as

\[ \gamma_1 = \frac{y_1 P}{x_1 P^*}, \text{ and } \gamma_2 = \frac{y_2 P}{x_2 P^*}, \]

where

- \( \gamma \) = activity coefficient
- \( x \) = mole fraction in liquid
- \( y \) = mole fraction in vapor
- \( P \) = total pressure
- \( P^* \) = vapor pressure of pure component

Subscript 1 = H₂O
Subscript 2 = HNO₃.

The partial pressures for 100 per cent HNO₃ from Taylor were plotted against temperature to obtain values for nitric acid vapor pressure, \( P_2^* \).

Smoothed values are shown in Table 2 for the boiling temperatures, the liquid and vapor compositions, the activity coefficients, and the nitric acid distribution ratio. The nitric acid distribution ratio, \( K = y/x \), is plotted
FIGURE 1. EFFECT OF HEATING RATE ON VAPOR TEMPERATURE IN THE RE-CIRCULATING STILL

Composition of boiling liquid: 20 w/o HNO₃ in H₂O
Pressure: 200 mm mercury
<table>
<thead>
<tr>
<th>Temperature, C</th>
<th>Concentration of HNO₃</th>
<th>Activity Coefficient</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x₂, Mole Fraction in Liquid</td>
<td>y₂, Mole Fraction in Vapor</td>
<td>γ₁ for H₂O</td>
</tr>
<tr>
<td>66.46</td>
<td>0</td>
<td>0</td>
<td>1.000</td>
</tr>
<tr>
<td>67.13</td>
<td>0.0166</td>
<td>0.000095</td>
<td>0.986</td>
</tr>
<tr>
<td>67.96</td>
<td>0.0315</td>
<td>0.000228</td>
<td>0.966</td>
</tr>
<tr>
<td>68.76</td>
<td>0.0466</td>
<td>0.000699</td>
<td>0.947</td>
</tr>
<tr>
<td>68.84</td>
<td>0.0488</td>
<td>0.000940</td>
<td>0.941</td>
</tr>
<tr>
<td>69.77</td>
<td>0.0631</td>
<td>0.001061</td>
<td>0.922</td>
</tr>
<tr>
<td>70.98</td>
<td>0.0820</td>
<td>0.002180</td>
<td>0.892</td>
</tr>
<tr>
<td>72.69</td>
<td>0.1075</td>
<td>0.00540</td>
<td>0.850</td>
</tr>
<tr>
<td>74.91</td>
<td>0.1374</td>
<td>0.01167</td>
<td>0.796</td>
</tr>
<tr>
<td>76.62</td>
<td>0.1606</td>
<td>0.0201</td>
<td>0.755</td>
</tr>
<tr>
<td>77.88</td>
<td>0.1830</td>
<td>0.0335</td>
<td>0.726</td>
</tr>
<tr>
<td>80.88</td>
<td>0.2212</td>
<td>0.0644</td>
<td>0.653</td>
</tr>
<tr>
<td>82.95</td>
<td>0.2554</td>
<td>0.1082</td>
<td>0.599</td>
</tr>
<tr>
<td>84.73</td>
<td>0.2979</td>
<td>0.1831</td>
<td>0.542</td>
</tr>
<tr>
<td>86.18</td>
<td>0.3440</td>
<td>0.2928</td>
<td>0.475</td>
</tr>
<tr>
<td>86.38</td>
<td>0.3850</td>
<td>0.4122</td>
<td>0.418</td>
</tr>
</tbody>
</table>
FIGURE 2. TEMPERATURE-COMPOSITION DIAGRAM FOR THE SYSTEM HNO₃-H₂O AT 200 MM MERCURY

- ○ Experimental data from this work
- △ Vapor compositions from Taylor
- □ Liquid compositions from Taylor
FIGURE 3. ACTIVITY COEFFICIENTS OF HNO₃ AND H₂O IN SOLUTIONS BOILING AT 200 MM MERCURY
TABLE 2. SMOOTHED VALUES FOR LIQUID-VAPOR EQUILIBRIA BETWEEN NITRIC ACID AND WATER AT 200 MM MERCURY PRESSURE

<table>
<thead>
<tr>
<th>Temperature, C</th>
<th>Concentration of HNO₃</th>
<th>Activity Coefficient</th>
<th>Molar Distribution Ratio, K, for HNO₃, (K = y₂/x₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>x₂, Mole Fraction in Liquid</td>
<td>y₂, Mole Fraction in Vapor</td>
<td>γ₁, for H₂O</td>
</tr>
<tr>
<td>66.46</td>
<td>0.000</td>
<td>0.00000</td>
<td>1.000</td>
</tr>
<tr>
<td>67.4</td>
<td>0.020</td>
<td>0.000128</td>
<td>0.981</td>
</tr>
<tr>
<td>68.4</td>
<td>0.040</td>
<td>0.000433</td>
<td>0.956</td>
</tr>
<tr>
<td>69.6</td>
<td>0.060</td>
<td>0.00105</td>
<td>0.927</td>
</tr>
<tr>
<td>70.8</td>
<td>0.080</td>
<td>0.00221</td>
<td>0.894</td>
</tr>
<tr>
<td>72.2</td>
<td>0.100</td>
<td>0.00421</td>
<td>0.863</td>
</tr>
<tr>
<td>73.6</td>
<td>0.120</td>
<td>0.00752</td>
<td>0.829</td>
</tr>
<tr>
<td>75.1</td>
<td>0.140</td>
<td>0.01273</td>
<td>0.795</td>
</tr>
<tr>
<td>76.6</td>
<td>0.160</td>
<td>0.02023</td>
<td>0.761</td>
</tr>
<tr>
<td>78.0</td>
<td>0.180</td>
<td>0.03098</td>
<td>0.727</td>
</tr>
<tr>
<td>79.5</td>
<td>0.200</td>
<td>0.04529</td>
<td>0.693</td>
</tr>
<tr>
<td>82.6</td>
<td>0.250</td>
<td>0.0998</td>
<td>0.611</td>
</tr>
<tr>
<td>85.0</td>
<td>0.300</td>
<td>0.1881</td>
<td>0.534</td>
</tr>
<tr>
<td>85.6</td>
<td>0.320</td>
<td>0.2337</td>
<td>0.504</td>
</tr>
<tr>
<td>86.15</td>
<td>0.340</td>
<td>0.2841</td>
<td>0.475</td>
</tr>
<tr>
<td>86.35</td>
<td>0.350</td>
<td>0.3103</td>
<td>0.461</td>
</tr>
<tr>
<td>86.45</td>
<td>0.360</td>
<td>0.3393</td>
<td>0.448</td>
</tr>
<tr>
<td>86.5</td>
<td>0.3726</td>
<td>0.3758</td>
<td>0.431</td>
</tr>
<tr>
<td>86.4</td>
<td>0.380</td>
<td>0.3982</td>
<td>0.420</td>
</tr>
<tr>
<td>86.1</td>
<td>0.400</td>
<td>0.4595</td>
<td>0.394</td>
</tr>
</tbody>
</table>
in Figure 4 as a function of nitric acid concentration. The smooth curve for
the distribution ratio is readily extrapolated to zero nitric acid concentration
and should be particularly useful in distillation calculations on dilute solu-
tions of nitric acid.

Figure 5 shows the liquid-vapor equilibrium curve for solutions of
nitric acid in water at 200 mm mercury. The curvature of the equilibrium
curve in dilute nitric acid solutions is illustrated in Figure 6, which was
computed from the extrapolated values for the K distribution ratio.

The boiling temperatures were read from the temperature-composition
plot. Smoothed values for the activity coefficients were taken from the
activity function curves shown in Figure 7. Since the activity of nitric acid
varies over a large range, the data were plotted in the form of

\[ \beta_1 = \frac{\log \gamma_1}{1 - x_1} , \]

as suggested by Darken and Gurry.\(^{(4)}\) From the smoothed values of \(\beta\) were
calculated the corresponding smoothed values for the activity coefficients
and the vapor compositions for the chosen liquid compositions.

**Evaluation of Data**

Both the equilibrium data of this work and those of Taylor were found
to be thermodynamically consistent when checked by the Gibbs-Duhem equa-
tion. The usual form of the equation,

\[ \ln \gamma_1 = - \int_{x_1}^{x_2} \frac{x_2}{x_1} \, d \ln \gamma_2 , \quad x_1 = 1 \]

describes the manner in which the activity coefficients of the water (sub-
script 1) and nitric acid (subscript 2) are related under equilibrium condi-
tions. For example, the Gibbs-Duhem relation requires, for equilibrium
conditions, that each increase in the activity coefficient of nitric acid result-
ing from a change in the acid concentration be accompanied by a correspond-
ing decrease in the activity coefficient of the water. Though this equation is
strictly true only for conditions of constant pressure and temperature, the
unavoidable errors are not great over small changes of pressure or tempera-
ture. In a binary system, such as nitric acid and water, boiling under con-
stant pressure, the changes in composition cause changes in the boiling
temperature.

The thermodynamically consistent curve for the activity coefficient of
water as computed from smoothed values of the nitric acid activity
FIGURE 4. DISTRIBUTION RATIO OF HNO₃ IN BOILING AQUEOUS NITRIC ACID SOLUTIONS AT 200 MM MERCURY
FIGURE 5. VAPOR COMPOSITIONS OVER BOILING AQUEOUS NITRIC ACID SOLUTIONS AT 200 MM MERCURY
FIGURE 6: EQUILIBRIUM DIAGRAM FOR DILUTE SOLUTIONS OF NITRIC ACID IN WATER AT 200 MM MERCURY
FIGURE 7. $\beta$ ACTIVITY FUNCTIONS FOR $H_2O$ AND $HNO_3$
coefficient is shown in Figure 8. For these calculations, the activity coefficients were obtained by graphically integrating the Gibbs-Duhem equation, starting at the azeotropic composition and integrating toward the composition pure H$_2$O. Similar computations were made to test the thermodynamic consistency of the nitric acid-water values compiled by Taylor, and the results are shown in Figure 9. Both the data of this work and the values of Taylor compare favorably with the computed thermodynamically consistent curves for water activities. The maximum deviation in the computed water activity for the data of this work is 5.8 per cent, occurring at 8 mole per cent nitric acid. The similar maximum deviation for the Taylor data is 4.3 per cent, occurring at about 19 mole per cent nitric acid. In both cases, the graphical integrations from the nitric acid-water azeotrope composition give calculated activity coefficients for pure water which are within 2 per cent of the true activity coefficient of 1 for pure water.

To facilitate the integration of the Gibbs-Duhem equation, the method described by Darken and Gurry\(^{(4)}\) was used. In this method, the activity coefficient $\gamma$ is incorporated in a new function $\alpha$, defined as

$$\alpha_2 = \frac{\ln \gamma_2}{(1 - \gamma_2)^2}.$$  

Upon substituting $\alpha_2$ in the Gibbs-Duhem equation, the activity coefficient $\gamma_1$ of water was then expressed in the equation

$$\log \left( \frac{\gamma_1^\prime\prime}{\gamma_1^\prime} \right) = - \left[ \alpha_2^\prime x_1^\prime x_2^\prime - \alpha_1^\prime x_1^\prime x_2^\prime \right] - \int_{x_1^\prime}^{x_1^\prime\prime} \alpha_2^\prime dx_1.$$  

In this work, the "prime" quantities refer to the azeotrope composition, and the "double-prime" quantities refer to nitric acid concentrations between the azeotrope and pure water.

**Conclusions**

The liquid-vapor equilibrium compositions of nitric acid solutions boiling at 200-mm mercury pressure have been established for all concentrations of nitric acid between pure water and the azeotrope (37 mole per cent HNO$_3$). This has been done by extrapolation of the experimentally determined distribution ratios, $K$, for nitric acid to zero acid concentrations on a semilogarithmic chart.

The data of this work and the values reported by Taylor are both fairly consistent from a thermodynamic standpoint as shown by comparison of the data with the values computed from the Gibbs-Duhem equation.
Thermodynamically consistent activity coefficient of water obtained by graphical integration of Gibbs-Duhem equation from composition of azeotrope

Experimental water activity coefficient curve from smoothed data

FIGURE 8. ACTIVITY COEFFICIENT OF H₂O IN NITRIC ACID SOLUTIONS AT 200 MM MERCURY
FIGURE 9. ACTIVITY COEFFICIENT OF H₂O IN NITRIC ACID SOLUTIONS AT 200 MM MERCURY, FROM DATA OF TAYLOR(1)

Values obtained by interpolation of Taylor data

Thermodynamically consistent activity coefficient of water obtained by graphical integration of Gibbs-Duhem equation from composition of azeotrope

Azeotrope
Chlorides in the nitric acid solution feeds to nitric acid distillation columns under certain operating conditions sometimes result in serious corrosion problems. Chlorides tend to accumulate in the column rather than to pass through in a straightforward path.

Operating conditions which favor the build-up of chloride concentration in a column can occur when dilute nitric acid is concentrated toward the higher boiling azeotropic composition (67 w/o HNO₃) and the lower boiling water is rectified from the top of the column. Under these circumstances, the chloride is rapidly vaporized from the solutions in the lower part of the column, and quickly absorbed by the dilute nitric acid reflux in the upper part of the column. Chlorides originally present in low concentrations in the feed accumulate to much higher concentrations within the column. At this point, the particular corrosive properties of chlorides become evident.

Aqueous solutions of strong inorganic acids are highly nonideal in behavior, and their vaporization characteristics are difficult to predict. In concentrated nitric acid solutions, chloride is oxidized to free chlorine. Haggerty and Hixon (2) investigated the volatility of chloride in nitric acid solutions boiling under atmospheric pressure. In this work, the effects of pressure and concentration level of chloride on the vaporization characteristics of chloride in nitric acid solution were studied.

Experimental Work

Apparatus

A recirculation still constructed according to the specifications of Othmer(3) was used to obtain equilibrium liquid and vapor samples of nitric acid solutions of chloride. A Cartesian manostat in the vacuum line was used to control the pressure in the system. Part I of this report gives additional details on the construction and arrangement of the apparatus.

Analytical Methods

Chlorides were determined from the absorbance of light by the silver chloride suspensions formed upon reaction with silver nitrate. A Beckman Model DU spectrophotometer with 1-cm-wide Corex cells was used to measure the light absorbance of the silver chloride suspensions at a wavelength of 450 mμ. Since the silver chloride suspensions were not stable, they were prepared and examined under controlled conditions. The suspensions were prepared in an aqueous media which contained 25 volume per cent
ethyl alcohol* and nitric acid in the range between 0.5 and 2.0 N HNO₃. Absorbance readings were taken at 20 min after the silver chloride was precipitated. Chloride concentrations in the suspensions were then obtained from a calibration curve.

To prepare a sample for chloride analysis, a sample of known volume and containing between 0.05 and 1.5 mg of chloride was pipetted into a 50-ml volumetric flask. Then 2.5 ml of 13 N HNO₃, 12 ml of 200-proof ethyl alcohol, and sufficient distilled water to bring the total volume to about 40 ml were added to the flask and the contents mixed. Following this, 2.5 ml of 0.05 N AgNO₃ was added dropwise to the flask while swirling the contents, then distilled water was added to the 50-ml mark and the suspension thoroughly mixed. A portion of the suspension was poured directly into the Corex cell, and the covered cell positioned in the spectrophotometer compartment. Twenty min after the suspension was formed, the light absorbance of the suspension at 450 nm was measured. Distilled water in a similar Corex cell was used as a reference at 100 per cent transmission. Additional information on the spectrophotometric method for the determination is presented in Part III.

The acid contents of the liquid and vapor were determined by titration with 0.1487 N NaOH to a phenolphthalein end point. Since comparatively small quantities of HCl were present in the samples, the total acidities were recorded as nitric acid concentrations.

**Procedure**

Approximately 250 ml of a solution of nitric acid containing a measured quantity of hydrochloric acid was charged to the equilibrium still. Known volumes of a standardized hydrochloric acid solution provided the desired chloride concentrations. After evacuation to a subatmospheric pressure of 200 mm mercury, the still was heated at a rate of 160 w to give a boiling period of about 1 hr. During the boiling period, about three receiver volumes of condensate flowed through the condensate receiver to provide steady-state compositions in the still pot and the receiver. Samples were taken at atmospheric pressure, from draw-off connections on the still and condensate receiver, directly into 60-ml glass-stoppered dropper bottles.

* Caution: Concentrated nitric acid may react with ethanol to form ethyl nitrate which is highly explosive.
Results and Discussion

Data on Vaporization of Chloride

The vaporization characteristics of chloride in aqueous solutions containing between 0 and 67.5 w/o of nitric acid were measured. In these solutions, chloride was present in concentrations between 17 and 2180 ppm as chloride. The measured relative volatilities of chloride varied widely in magnitude, from very low values in nitric acid-free solutions to exceedingly high values in concentrated nitric acid. For example, in a nitric acid-free solution of dilute hydrochloric acid, the measured molar distribution ratio between the vapor and the liquid for chloride was \( K = 0.0046 \). In a solution containing 58 w/o nitric acid, the distribution ratio was \( K = 91.9 \).

The experimental results on the vaporization of chloride from nitric acid solutions are shown in Table 3. Acidities of the liquid and vapor phases are expressed as total acidity in terms of mole fraction of nitric acid, because the hydrochloric acid concentrations are comparatively very low. The tendency for the chloride to vaporize is expressed as the molar distribution ratio

\[
K = \frac{y_{Cl^-}}{x_{Cl^-}},
\]

where

\( y_{Cl^-} \) = mole fraction of chloride (Cl\(^-\)) in the vapor

\( x_{Cl^-} \) = mole fraction of chloride (Cl\(^-\)) in the liquid.

Since the presence of nitric acid resulted in the loss of chloride from the distillation system, the durations of boiling and amounts of chloride recovered are reported in the data. In the solution which contained 68.5 w/o nitric acid (Run 8), the chloride was rapidly oxidized to free chlorine as the solution was heated to its boiling temperature. Over 99 per cent of the chloride was lost from the concentrated nitric acid solution during the 1-hr boiling period. The presence of a small quantity of free chlorine was noted in the vapors from a solution containing 58.15 w/o nitric acid (Run 10), but no free chlorine was observed during distillation of solutions containing less than 50 w/o nitric acid.

The chloride concentrations reported in Table 3 represent the total chlorine content of the liquid and vapor samples. Analyses in which sodium nitrite was used to reduce free chlorine that may have been present gave the same results as when the samples were not treated with sodium nitrite.
### TABLE 3. VAPORIZATION OF CHLORIDE FROM NITRIC ACID SOLUTIONS

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature, C</th>
<th>Pressure, mm Hg</th>
<th>Concentration of HNO₃ in Liquid</th>
<th>Concentration of HNO₃ in Vapor</th>
<th>Concentration of Chloride in Liquid (x \text{Cl}^-)</th>
<th>Concentration of Chloride in Vapor (y \text{Cl}^-)</th>
<th>Molar Distribution Ratio of (\frac{y \text{Cl}^-}{x \text{Cl}^-})</th>
<th>Duration of Boiling, hr</th>
<th>Total Chloride in Distillation Apparatus Charged Before Boiling, mg</th>
<th>Total Chloride in Distillation Apparatus Found After Boiling, mg</th>
<th>Chloride Recovered Per Cent of (\text{Cl}^-) in Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>66.2</td>
<td>199.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>181.4</td>
<td>0.83</td>
<td>0.0046</td>
<td>2.2</td>
<td>75.0</td>
<td>75.7</td>
<td>101</td>
</tr>
<tr>
<td>2</td>
<td>66.9</td>
<td>200.0</td>
<td>0.0292</td>
<td>0.000273</td>
<td>193.4</td>
<td>1.08</td>
<td>0.0056</td>
<td>1.3</td>
<td>75.6</td>
<td>79.5</td>
<td>101</td>
</tr>
<tr>
<td>3</td>
<td>68.6</td>
<td>198.7</td>
<td>0.0588</td>
<td>0.000945</td>
<td>187.6</td>
<td>5.50</td>
<td>0.0294</td>
<td>1.0</td>
<td>82.3</td>
<td>76.9</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>72.3</td>
<td>198.5</td>
<td>0.1038</td>
<td>0.00312</td>
<td>198.3</td>
<td>32.2</td>
<td>0.167</td>
<td>1.0</td>
<td>86.5</td>
<td>81.0</td>
<td>94</td>
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<tr>
<td>5</td>
<td>75.9</td>
<td>200.2</td>
<td>0.1528</td>
<td>0.01860</td>
<td>184.2</td>
<td>21.5</td>
<td>0.17</td>
<td>0.8</td>
<td>91.1</td>
<td>85.1</td>
<td>93</td>
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<tr>
<td>6</td>
<td>79.0</td>
<td>197.0</td>
<td>0.2020</td>
<td>0.0489</td>
<td>98.5</td>
<td>563.2</td>
<td>0.52</td>
<td>0.9</td>
<td>96.0</td>
<td>77.2</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>83.6</td>
<td>198.0</td>
<td>0.283</td>
<td>0.1580</td>
<td>15.2</td>
<td>746.1</td>
<td>49.1</td>
<td>1.0</td>
<td>102.0</td>
<td>56.2</td>
<td>55</td>
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<tr>
<td>8</td>
<td>85.6</td>
<td>199.0</td>
<td>0.362</td>
<td>0.394</td>
<td>2.6(a)</td>
<td>1.6(a)</td>
<td>--</td>
<td>(a)</td>
<td>105.0</td>
<td>0.96</td>
<td>0.9</td>
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<tr>
<td>9</td>
<td>72.0</td>
<td>197.0</td>
<td>0.1083</td>
<td>0.00515</td>
<td>212.2</td>
<td>32.2</td>
<td>0.152</td>
<td>0.8</td>
<td>86.4</td>
<td>84.9</td>
<td>98</td>
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<tr>
<td>10</td>
<td>83.1</td>
<td>199.0</td>
<td>0.284</td>
<td>0.1670</td>
<td>54.3</td>
<td>4990.0</td>
<td>91.9</td>
<td>0.5</td>
<td>678.1</td>
<td>347.1</td>
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<td>11</td>
<td>83.7</td>
<td>198.0</td>
<td>0.285</td>
<td>0.1620</td>
<td>6.84</td>
<td>312.0</td>
<td>45.6</td>
<td>0.5</td>
<td>20.4</td>
<td>23.7</td>
<td>116(b)</td>
</tr>
<tr>
<td>12</td>
<td>76.3</td>
<td>202.0</td>
<td>0.1585</td>
<td>0.0211</td>
<td>1270.2</td>
<td>1052.0</td>
<td>0.829</td>
<td>0.8</td>
<td>607.8</td>
<td>550.9</td>
<td>90</td>
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<tr>
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<td>200.0</td>
<td>0.1528</td>
<td>0.0173</td>
<td>29.4</td>
<td>40.0</td>
<td>1.36</td>
<td>0.9</td>
<td>6.08</td>
<td>14.0</td>
<td>230(b)</td>
</tr>
<tr>
<td>14</td>
<td>75.9</td>
<td>200.0</td>
<td>0.1510</td>
<td>0.0204</td>
<td>12.3</td>
<td>16.6</td>
<td>1.35</td>
<td>1.5</td>
<td>6.0</td>
<td>5.8</td>
<td>97</td>
</tr>
<tr>
<td>15</td>
<td>69.0</td>
<td>200.0</td>
<td>0.0545</td>
<td>0.00069</td>
<td>1160.2</td>
<td>25.6</td>
<td>0.0222</td>
<td>0.8</td>
<td>550.2</td>
<td>477.2</td>
<td>87</td>
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<tr>
<td>16</td>
<td>66.4</td>
<td>200.4</td>
<td>0.0011</td>
<td>0.000005</td>
<td>1110.0</td>
<td>5.48</td>
<td>0.0049</td>
<td>0.8</td>
<td>507.6</td>
<td>462.9</td>
<td>91</td>
</tr>
</tbody>
</table>

(a) Chloride was rapidly oxidized to free chlorine.

(b) High chloride recovery due to presence of some chloride in the still from a previous run.
Evidently the oxidation-reduction reaction between concentrated nitric acid and the chloride, as

$$3\text{HCl} + \text{HNO}_3 = \text{Cl}_2 + \text{NOCl} + 2\text{H}_2\text{O},$$

may have been reversed upon dilution of the samples for analysis. Although there is the possibility that the ethyl alcohol used to stabilize the silver chloride suspension may have reduced some free chlorine to the chloride, other experiments show that such a reduction was not likely. For example, chloric acid, $\text{HClO}_3$, tested by the same analytical procedure showed practically no reduction by the ethyl alcohol to the chloride, but was rapidly reduced by sodium nitrite.

**Distribution Ratio of Chloride in Boiling Acid Solutions**

The volatility of chloride in boiling nitric acid solutions was found to depend primarily upon the total acidity. Values for the molar-distribution ratios for chlorides observed in the boiling nitric acid solutions are plotted as a function of the nitric acid acidity in Figure 10. Over the range of chloride concentrations investigated, the distribution ratio was independent of the chloride concentration. The curve drawn on the chart probably represents all the data within the range of experimental accuracy. Since some chloride was slowly lost from the distillation system, most likely through oxidation to free chlorine by the nitric acid, it was not possible to obtain a true physical equilibrium in some of the experiments.

The chloride volatility is determined primarily by the acidity of the solution. To a smaller extent the chloride volatility is altered by changes in the chloride concentration and by the pressure a temperature at which boiling takes place. As seen in Figure 10, the distribution ratio, $K$, for chloride varies from a value of 0.002 in very dilute acid solutions to values over 70 in solutions containing over 0.30 mole fraction (60 w/o) nitric acid. Therefore a range of over 35,000 to 1 in the value of $K$ may occur in a distillation process for concentrating nitric acid.

When the boiling pressure is increased from 200 mm mercury total pressure to atmospheric pressure, the distribution ratio, $K$, for chloride in boiling nitric acid solutions increases by a factor of from 2 to 4. The chloride distribution ratios calculated from the data of Haggerty and Hixon are plotted against nitric acid acidity in Figure 11. The smooth curve drawn through the atmospheric-pressure $K$ values lies about 300 per cent above the 200-mm curve for $K$.

In nitric acid solutions which contain less than about 2 w/o of chloride, the chloride-distribution ratio, $K$, is essentially independent of the chloride concentration. Figure 12 shows the $K$ values for chloride in boiling hydrochloric acid plotted as a function of the HCl acidity, as computed from
FIGURE 10. DISTRIBUTION RATIO OF CHLORIDE IN NITRIC ACID SOLUTIONS BOILING AT 200 MM MERCURY

Figures indicate concentration of chloride in liquid phase, as mole fraction chloride x 10^6.
FIGURE II. EFFECT OF PRESSURE ON THE DISTRIBUTION RATIO OF CHLORIDE IN BOILING NITRIC ACID SOLUTIONS
**FIGURE 12. DISTRIBUTION RATIO OF CHLORIDE AS HCl IN BOILING AQUEOUS HYDROCHLORIC ACID SOLUTIONS AT SELECTED BOILING TEMPERATURES**

Boiling temperature has same value as for nitric acid solutions of equivalent acidity and boiling under 200 mm mercury total pressure.

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published values on partial pressures over hydrochloric acid solutions. In the calculation of the K values, the boiling temperatures of the hydrochloric acid solutions were selected to match the boiling temperatures of nitric acid solutions of equivalent acidity and boiling under 200 mm mercury total pressure. A comparison of the values for the distribution ratio, K, of chlorine in hydrochloric acid solutions with the chlorine K values at equivalent acidities in nitric acid solutions shows that they do not differ greatly over a wide range of acidity. In solutions containing less than 0.2 mole fraction of HCl or HNO₃, the largest deviation is about 300 per cent between the nitric acid solutions and the hydrochloric acid solutions. Therefore, the K values for chloride should vary not more than about plus or minus 15 per cent in nitric acid solutions which have an HCl:HNO₃ mole ratio of less than 0.1. However, high concentrations of nitric acid no doubt would increase the volatility of chloride by oxidation of the chloride to free chlorine.

The decrease in value of the distribution ratio of chloride in concentrated hydrochloric acid solutions occurs because HCl and H₂O constitute a binary system, in which the distribution ratio, K, must approach unity as the system composition approaches pure HCl. In aqueous nitric acid solutions of HCl, a ternary system HNO₃-HCl-H₂O is formed, therefore, there is no theoretical limit to the values which K may assume.

Conclusions

The molar distribution ratio, K, of chloride in boiling nitric acid solutions is determined primarily by the total acidity of the solutions, and varies over an extremely wide range. In the range between 0.00 and 0.30 mole fraction (60 w/o) of HNO₃, the values for K increase from 0.002 to 70, or a range of 35,000 to 1.

Lowering of the boiling pressure results in a lower volatility of chloride. At 200 mm mercury pressure, the volatility of chloride is about one-third that of chloride in nitric acid solutions boiling at atmospheric pressure.

In dilute solutions of chloride in nitric acid, the distribution ratio of chloride is nearly independent of the chloride concentration.

In nitric acid solutions of chloride boiling at 200 mm mercury pressure, chloride is rapidly oxidized by 67.5 w/o HNO₃, but only slowly oxidized by 58 w/o HNO₃.
PART III PHOTOMETRIC DETERMINATION OF CHLORIDE IN AQUEOUS NITRIC ACID SOLUTIONS

The very low solubility of silver chloride in aqueous solutions has been for several years a convenient basis for the determination of chloride in the parts per million range of concentrations. By the formation of a precipitate of silver chloride under controlled conditions, the turbidity of the resulting suspension can be measured by one of several optical methods and the chloride concentration then obtained from a calibration curve. However, the silver chloride suspensions are not completely stable and their stability characteristics are often affected by interfering materials present in solution. In the determination of small amounts of chloride in nitric acid solutions, comparatively large quantities of nitric acid are present in the silver chloride suspensions and adversely affect the stability of the suspensions.

By adding ethanol to the sample as suggested by the work of Lamb, Carlton, and Meldrum the stability of the silver chloride suspension was greatly increased. Within a certain range of nitric acid concentrations, the optical density of silver chloride suspensions was found to be substantially independent of the acid concentration. By using alcohol as a stabilizing agent, and controlling the acidity of the sample, the silver chloride suspensions were sufficiently stable and reproducible to permit the determination of chloride in dilute or concentrated nitric acid solutions.

Kolthoff and Yutzy describe the stabilizing action of ethanol upon silver chloride suspensions, and discuss the effects of other factors in the preparation of samples. Luce, Denice, and Akerlund describe a turbidimetric method for the determination of chloride in which the sample is first neutralized by addition of alkali (or acid) and the suspension stabilized by the use of ethanol.

Apparatus and Reagents

A Beckman Model DU spectrophotometer was used to measure the absorbance of the silver chloride suspension. Corex sample cells having a light-path length of 1.0 cm contained the samples of silver chloride suspension and distilled water, which was used as a reference material. Light at a wavelength of 450 μm was used in the measurement of absorbance for the determination of chloride.

The silver nitrate solution was 0.05 N AgNO₃ and 0.2 N HNO₃, containing 8.5 g of silver nitrate and 12.5 ml concentrated nitric acid per liter of solution in distilled water. The nitric acid reagent was 13 N HNO₃, prepared by dilution of concentrated nitric acid with distilled water.
ethanol used in the preparation of samples was 200 proof. A stock solution
of hydrochloric acid which contained 100 mg chloride per liter of solution
was used in the preparation of the calibration curve.

**Determination of Chloride**

**Calibration Curve**

A calibration curve was prepared by measuring the absorbancies of
suspensions containing known quantities of chloride. Aliquot quantities of
the hydrochloric acid stock solution to give concentrations of 1, 2, 5, 10,
20, 30, 40, and 60 mg of chloride per liter of dilution were used in the prep­
aration of the calibration curve. The silver chloride suspensions were pre­
pared by the procedure described in the following section for the determi­
nation of chloride. The suspensions were 0.65 N HNO₃, contained 25 volume
per cent ethanol, and were measured at 450 m/μ at 20 min after the formation
of the silver chloride precipitate.

The calibration curve in Figure 13 shows the absorbancies of the sus­
pensions plotted against the chloride concentrations. A straight line passes
through the calibration points for chloride concentrations between 2 and 30
mg chloride per liter concentrations. At concentrations below 2 mg per liter
chloride the curve is no longer straight. Above 30 mg per liter chloride,
the suspensions were too unstable and erratic readings were obtained.

The optical properties of the suspension deviated slightly from the
Lambert-Beer relationship, which requires in normal solutions that the
absorbancy be directly proportional to the first power of the concentration.
In the silver chloride suspensions containing between 2 and 30 mg per liter
chloride, the absorbance curve for the 1-cm light path length is described
by the equation

\[
A = \log \frac{I_0}{I} = 0.418 C^{0.847},
\]

where,

- \(A\) = absorbance
- \(I_0\) = intensity of incident light (450 m/μ)
- \(I\) = intensity of transmitted light
- \(C\) = concentration of chloride in mg per liter.

The absorbance of the reagents in the sample was very small, amount­
ing to an absorbance value of 0.004 when no chloride was added to the sample
in blank determinations. Therefore the absorbance of the reagent was in­
cluded in the values used for the calibration curve.
FIGURE 13. CALIBRATION CURVE FOR CHLORIDE IN SUSPENSION OF SILVER CHLORIDE

- Age of suspension: 20 min
- Concentration of ethanol: 25 volume per cent
- Concentration of HNO₃: 0.65 N
- Light wavelength: 450 mμ
- Slit width: 0.28 mm
- Reference at 100 per cent transmission: Distilled water

Concentration of Chloride, mg chloride per liter

Absorbance
Analytical Procedure

A known volume of sample containing between 0.05 and 1.5 mg of chloride was transferred to a 50-ml volumetric flask by use of a pipette. To the sample were added 2.5 ml of 13 N HNO₃, 12 ml of ethanol, and sufficient distilled water to bring the total volume to about 40 ml, and the contents mixed. With samples which contained over about 20 w/o HNO₃, a portion of the distilled water was added before the ethanol to avoid exposure of ethanol to high concentrations of nitric acid.* Then 2.5 ml of 0.05 N AgNO₃ reagent was added dropwise to the flask while swirling the contents, distilled water added to the 50-ml mark, and the suspension thoroughly mixed. A portion of the suspension was poured into the Corex sample cell, the cell cover replaced, and the sample cell positioned in the spectrophotometer compartment. The light absorbance of the suspension was measured at 450 mₜ at a time 20 min after the silver chloride was precipitated. Distilled water was used as a reference at 100 per cent transmission. The concentration of chloride in the suspension was then read from the calibration curve, and the chloride concentration in the original sample calculated from the dilution factor and density of the sample, as

\[
\text{\text{mg Cl}^-/\text{kg sample}} = \frac{\text{\text{mg Cl}^-/\text{liter suspension}}}{\text{density of sample}} \cdot \frac{\text{50}}{\text{ml sample}}
\]

Characteristics of Silver Chloride Suspensions

Spectral Transmission

Silver chloride suspensions in water have their greatest light absorbances at the lower wavelengths. Figure 14 shows that there are no peaks in a spectral-absorbance curve between 350 and 900 mₜ but the absorbance decreases rapidly as the wavelength is increased. The absorbance of the silver chloride suspension is probably more a characteristic of the size of particles rather than the spectral color of the individual particles.

Stability of Silver Chloride Suspensions

In Aqueous Nitric Acid Solutions. Suspensions of silver chloride were found to be much more stable in extremely dilute or very concentrated solutions of nitric acid than they were in acid solutions of intermediate concentration. Figure 15 shows the effect of nitric acid concentration upon the stability of the silver chloride suspensions. The stability is seen to be at a minimum at an acid concentration of 0.20 N HNO₃. However, the stability

---

*Caution: Concentrated nitric acid may react with ethanol to form ethyl nitrate which is highly explosive.
Chloride, 9.6 mg per liter
Acidity, 0.0064 N HNO₃

FIGURE 14. EFFECT OF WAVELENGTH UPON ABSORBANCE OF A SILVER CHLORIDE SUSPENSION
FIGURE 15. EFFECT OF NITRIC ACID CONCENTRATION UPON THE AGING CHARACTERISTICS OF SILVER CHLORIDE SUSPENSIONS IN AQUEOUS NITRIC ACID SOLUTIONS
of the silver chloride suspension was relatively independent of the actual acid concentration in the range between about 0.20 and 2.0 N HNO₃.

The similarity of stability characteristic over a comparatively wide range of acid concentrations becomes a useful feature in a method for the determination of chloride in nitric acid solutions. By adjusting the nitric acid concentration to within a suitable range, by either dilution with water or addition of concentrated nitric acid, it was possible to form silver chloride precipitates of reproducible stability characteristics.

During the formation of the precipitate the particles first grow in size and number, and the optical absorbance of the suspension increases. Upon aging, the individual particles tend to agglomerate and settle out of suspension. Either action results in lower absorbance.

In Alcoholic Nitric Acid Solutions. Ethanol in the suspending medium was quite effective in stabilizing the silver chloride suspensions for a short period of time. In aqueous solutions containing nitric acid, the optical absorbance of the suspension decreased rapidly with time from the earliest reading, which was about 4 min after the silver chloride was precipitated. The presence of ethanol resulted in a gradual initial increase in the absorbance, which reached a maximum within 20 to 30 min after the suspension was formed. Figure 16 shows the effect of ethanol upon the stability of the suspension in solutions with 0.50 N and 0.65 N HNO₃ acidities. Lower initial optical absorbancies were obtained with suspensions in which ethanol was present.

The presence of ethanol greatly improved the stability of the silver chloride suspensions in the presence of nitric acid. Figure 17 shows that suspensions which contained 25 volume per cent ethanol gradually increased to a maximum in absorbance. For the acidity range between 0.65 and 2.5 N HNO₃, it is seen that a variation in acidity would result in no more than a 4 per cent change in the optical absorbancy. The stabilization effect of ethanol and the very small variation in absorbance over a range of nitric acid acidity provided a basis for spectrophotometric determination of chloride in nitric acid solutions.

Conclusions

By using ethanol to stabilize the silver chloride suspension and controlling the nitric acid acidity, low concentrations of chloride in nitric acid solutions can readily be determined by a spectrophotometric procedure.
FIGURE 16. EFFECT OF ETHYL ALCOHOL UPON THE AGING CHARACTERISTICS OF SILVER CHLORIDE SUSPENSIONS IN DILUTE NITRIC ACID SOLUTIONS
Chloride content, 20 mg per liter
Ethanol, 25 volume per cent
450 mµ

FIGURE 17. EFFECT OF NITRIC ACID CONCENTRATION UPON THE AGING CHARACTERISTICS OF SILVER CHLORIDE SUSPENSIONS IN DILUTE ETHYL ALCOHOL SOLUTIONS

A - I 3 7 0 4
SUMMARY

The compositions of liquid and vapor in aqueous solutions of nitric acid boiling at 200 mm mercury total pressure have been established for the range of concentrations between pure water and the nitric acid-water azeotrope (67.5 w/o HNO₃). The molar distribution ratio of nitric acid concentrations in the vapor and liquid phases reaches a minimum of about 0.004 in very dilute solutions of nitric acid.

The liquid-vapor equilibrium measurements are in agreement with partial-pressure data published for nitric acid concentrations over 20 w/o. The thermodynamic activities of the water component are shown to be thermodynamically consistent with the nitric acid activities, using the Gibbs-Duhem equation as a criterion.

The vaporization characteristics of chloride in boiling nitric acid solutions vary over a wide range and are determined primarily by the total acidity of the solutions. Over a nitric acid concentration range between 0 and 60 w/o HNO₃, the chloride molar distribution ratio increases from 0.002 to 70, a range of 35,000 to 1, in nitric acid solutions boiling at 200 mm mercury. The data of Haggerty and Hixon indicate that the relative volatility of chloride is about 300 per cent greater in similar solutions at atmospheric pressure. In nitric acid solutions which contain less than about 2 or 3 per cent of chloride, the chloride distribution ratio is practically independent of the chloride concentration.

Chloride in a 58 w/o nitric acid solution boiling at 200-mm mercury is slowly oxidized to free chlorine, and rapidly oxidized in a 67.5 w/o nitric acid solution.

Chloride concentrations as low as 1 part per million were determined in nitric acid solutions by measurement of the light absorbance of silver chloride suspensions at 450 mμ. The suspensions were stabilized by the addition of ethanol to the diluted nitric acid solutions prior to the addition of a silver nitrate reagent. Consistent measurements were obtained by adjusting the acidity and reading the light absorbance of the suspensions at a definite time after precipitation.

REFERENCES


I-III AND