New Modeling of Nitric Acid Dissociation Function of Acidity and Temperature

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ABSTRACT: Nitric acid is widely used for many applications. However, because of the large number of nitrogen species and the fact that for concentrations greater than $10^{-2}$ mol·L$^{-1}$, its dissociation is incomplete in an aqueous medium, nitric media are very complex to describe especially in temperature. Using data from the literature and some nitrous acid analyses, it was possible to determine the balance sheet of all different aqueous nitrogen species for a total nitric acidity ranging from 1.5 to 8.5 mol·L$^{-1}$ and for temperature ranging from 50 to 95°C with the assumption that the use of a refrigerant column makes gaseous species negligible. For this, it was necessary to determine the ionic, molecular, and solvent activity coefficients and then solve an eight equation system with nine unknowns by determining one unknown experimentally.

1. INTRODUCTION

Nitric acid has been the subject of many studies since its industrialization in the 19th century because of its reactivity with metals (at that time it was one of the only acids capable of dissolving gold and platinum). The large number of nitrogen species present at the different degrees of oxidation makes the chemistry of this acid extremely complex. Nitric acid, from a concentration greater than $10^{-2}$ mol·L$^{-1}$, behaves as a weak acid, which means that its dissociation is incomplete in an aqueous medium. The purpose of this publication is to determine the different dissociation constants of the nitric acid in a range of acidity varying from 1.5 to 8.5 mol·L$^{-1}$ and in a range of temperature varying from 50 to 95°C. The data collected in the scientific literature show that the higher the acidity and the temperature of the medium, the less the dissociation is advanced. Davis and De Bruin studied for the first time, in 1964, the behavior of the equilibrium water–acid mixtures varying from 0 to 100%. These authors had, however, taken into account the presence of only three species in solution which are HNO₃, H⁺, and NO₃⁻. Later, Nichols and Taylor, based on data collected in the scientific literature, simulated the evolution of the various ionic and molecular activity coefficients, the osmotic coefficients but also the dissociation of nitric acid in aqueous medium with the evolution of the acidity and the temperature of the medium at equilibrium. These results show considerable differences in comparison with the results of the previous authors at room temperature. It is therefore not excluded that similar differences are observed at higher temperatures. To conclude, there are currently no reliable and valid data on the concentrations of species in solution as a function of temperature and acidity. This work deals with the understanding of the nitric medium and more particularly with the calculation of the concentrations and real activities of the ions in solution for large ranges of total nitric concentrations and temperatures from thermodynamic data listed in the literature.

2. EXPERIMENTAL SECTION

2.1. Experimental Setup. The tests are carried out in a batch of 60 mL containing 15 mL of nitric acid. Solutions were stirred at 300 rpm and maintained 1 h at each temperature. The different nitrous concentrations were recorded using UV–visible spectroscopy. The device used was Varian Cary 50 from Agilent Technologies. The nitric gases are recombined via a cooling column thermostated at 6°C. Thus, only the species in solution were taken into consideration in the determination of the concentrations of the nitrogen species of the system.

2.2. Griess Analysis. The concentration of the nitrous acid HNO₂ in solution was determined by a colorimetric method derived from the Griess method. Samplings were first stabilized by dilution in a sodium hydroxide solution to form NaNO₂. Then, the colored compound (absorption coefficient

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close to 47 000 at 530 nm) is obtained by diazotization of the nitrous acid with sulphanilic acid, followed by coupling with α-naphthylamine. Reactions occur at pH 2.4. Samples from the solution were immediately diluted in a solution of sodium hydroxide at 10 mol L\(^{-1}\). The dilutions were carried out by weighing. More precisely, to perform this analysis, several additions to the aliquot of the solution to be characterized are needed:

- Concentrated sodium hydroxide solution (100 μL, 10 mol L\(^{-1}\)) (Merck reference 480648) was added to an aliquot of the sample to characterize to freeze the nitrous acid contained into the sample as NaNO\(_2\).
- Then, 500 μL of a solution of sulfanilic acid (Sigma-Aldrich reference 251917) at a concentration of 3.4 × 10\(^{-2}\) mol kg\(^{-1}\), solubilized in nitric acid (Sigma-Aldrich CAS number 7697-37-2) concentrated at 3 mol kg\(^{-1}\) was added.
- Then, 500 μL of a solution composed of a mixture of sodium acetate (Merck reference 106267) and chloroacetic acid (Sigma-Aldrich CAS number 79-11-8), respectively, concentrated at 0.8 and 3.2 mol kg\(^{-1}\) was introduced. After 5 min of rest, an addition of 1.5 mL of a solution composed of α-naphthylamine (Sigma-Aldrich CAS number 134-32-7) at a concentration of 4.15 × 10\(^{-2}\) mol kg\(^{-1}\), solubilized in nitric acid (3 mol kg\(^{-1}\)) was proceeded.
- Finally, after 10 min of rest, a new addition of the previous sodium acetate and chloroacetic acid mixture was performed to complete the volume to 5 mL.

At this stage, the colored complex was formed and was ready for the determination of its absorbance using a Varian Cary 50 spectrophotometer from Agilent Technologies. Prior to the determination of nitrous concentrations of the different samples, a calibration has to be done using sodium nitride solutions of known concentrations.

The absorption is measured at 530 nm following a Beer–Lambert law. A 10% error bar has to be applied to experimental concentration data. This error was calculated taking into account uncertainties from the dilution of samples (5%), the weighing (1%), and calibration precision (8%).

### 3. RESULTS AND DISCUSSION

#### 3.1. Nitric Acid Properties

In aqueous solution, nitric acid HNO\(_3\) has a strong oxidizing power and can therefore react with reducing agents, allowing the formation of new species at lower oxidation degrees. Plieth\(^5\) summarized the different gaseous or liquid nitrogen species that may appear during the reduction of the acid as a function of their degrees of oxidation. The species included in this study are identified in Table 1.

**Table 1. Aqueous Species in Solution Considered for This Study**

| oxidation degree | chemical formula | denomination       |
|------------------|------------------|--------------------|
| +V               | HNO\(_3\)        | nitric acid        |
| +IV              | NO\(_3^−\)       | nitrate ion         |
| +II              | NO\(_2^+\)       | nitronium ion       |
| +III             | NO\(_2\)         | nitrogen dioxide    |
| +II              | NO\(^−\)         | nitrosonium ion     |
| +II              | NO               | nitrogen monoxide   |

Many nitrogen species cannot be included in this table because of either their absence in a concentrated environment or the lack of information on chemical equilibria and stabilities in aqueous solution at the temperatures studied. Moreover, in view of the recombination of the gases by means of a cooling column, only species in aqueous form will be considered in this study. Chemical equilibria will be listed in the next section involving the aqueous species listed in the Table 1. Despite its presence in solution has been demonstrated by Schmid and Kirchel\(^6\) in 1964, nitrogen monoxide will not participate at these equations. More recently in 2010, Binnewies et al.\(^7\) explained that nitrous acid cannot be pure in solution and that it would then form equilibrium with HNO\(_3\) and NO.

This article presents concentrations of the species with molarities while most of the scientific articles deal with molalities. Conversion involves the density of the solutions. The density of the nitric acid solution varies not only with the acidity of the solution but also with the temperature of the medium. The data are repertoried in international databases.\(^8\)

#### 3.2. Chemical Equilibria of Aqueous Solutions of Nitric Acid

**3.2.1. HNO\(_3\) Dissociation**

In the case of concentrations above 10\(^{-2}\) mol L\(^{-1}\), the dissociation of nitric acid is incomplete according to equilibrium 3.2.1

\[
\text{HNO}_3(aq) = H^+(aq) + NO_3^−(aq) \quad (3.2.1)
\]

In general, the authors agree that when temperature and acidity increase, the dissociation of nitric acid is favored.
Davis and De Bruin\(^1\) in 1964 studied for the first time this equilibrium for all nitric acid concentrations. These authors had, however, taken into account the presence of only three species in solution appearing in eq 3.2.1. The equilibrium thermodynamic constant of eq 3.2.1 given by the authors at 25 °C is 15.4 ± 2.1.

More recently, the Sicsic model\(^3\) presents the evolution of the concentrations of gaseous and aqueous species function of the acidity of the medium. The equilibrium constant 3.2.1 calculated by Sicsic at 25 °C is 19.5. The author’s model describes the concentration evolution of 14 different nitrogen species (8 gaseous and 6 aqueous) according to the acidity of the system. In the case of same equilibrium in the remainder of this article, the values calculated by Sicsic will be retained because these data are more accurate.

Nichols and Taylor,\(^2\) based on data collected in the scientific literature, simulated the nitric acid dissociation at equilibrium, considering evolution of the various ionic and molecular activity coefficients and the osmotic coefficients. In this modeling, the authors were studying the evolution of nitric acid and temperature in this modeling. However, the authors took into account the “simple” system already studied by Davis and De Bruin. This study at 25 °C is compared with the Sicsic model, and the results are presented in Figure 2. The difference between the data of the different authors, related to the use of a simpler system, was calculated on 12 points and can be fitted by a polynomial function 3.2.2

\[
y = 0.7669x^2 - 0.5177x + 10.604 \quad R^2 = 0.9412
\]

with \(y\) as the difference and \(x\) as the total nitric acid of the system.

The corrected Nichols and Taylor dissociation values are virtually close to those of Sicsic (Figure 2). This deviation, estimated as constant as a function of temperature in the absence of other thermodynamic data, will be used for calculations at temperatures higher than 25 °C.

3.2.2. HNO\(_3\) Self-Ionization. In the mid-twentieth century, some authors\(^9,10\) observed that nitric acid solutions were predominantly exists in the molecular form HNO\(_2\) in dilute nitric acid solutions. However, when the acidity of the solution increases, the equilibrium of the reaction 3.2.5 is shifted in favor of nitrosonium NO\(^+\) formation

\[
\text{HNO}_3 (aq) + H^+ (aq) = NO^+ (aq) + H_2O (l)
\]

3.2.3. Formation of Nitrosonium Ion NO\(^+\). Nitric acid predominantly exists in the molecular form HNO\(_3\) in dilute nitric acid solutions. However, when the acidity of the solution increases, the reaction 3.2.5 is shifted in favor of nitrosonium NO\(^+\) formation

\[
\text{HNO}_3 (aq) + H^+ (aq) = NO^+ (aq) + H_2O (l)
\]

To conclude, the nitric acid molecule partially self-ionizes into NO\(^-\) and NO\(^+\) ions.

3.2.4. Absorption of Nitrogen Dioxide NO\(_2\). Vetter\(^13\) shown in 1949 that in a closed medium, at four different acidities varying from 20 to 100 °C, the dioxide nitrogen is present in solution, and its concentration increases with temperature and acidity according to the following mechanism 3.2.6

\[
2\text{NO}_2 (aq) + H_2O (l) = \text{HNO}_3 (aq) + H^+ (aq) + NO^- (aq)
\]

By circulating an electric current in nitric acid solutions at different concentrations, the author produced known concentrations of nitric acid according to equilibrium 3.2.7

\[
\text{NO}_3^- + 3H^+ + 2e^- = \text{HNO}_2 + H_2O
\]

Using a platinum electrode, the author registered the half-wave potential of the HNO\(_3\)/HNO\(_2\) couple, allowing it to recover to the concentration of nitrous acid in solution. For the study described, the activity coefficients were kept constant for all acidities. The coefficients used were those presented by Davis and De Bruin.\(^1\) More recently in 1999, Lehning\(^14\) validates the 3.2.6 equilibrium between NO\(_3^-\), NO\(_2\), and HNO\(_3\) by NMR on the \(^15\)N spectrum.

3.2.5. Calculations of the Standard Free Enthalpies of the Selected Mechanisms. Table 2 lists the different aqueous species retained for this simulation and the notation used in the rest of this article to present them in a system of equations. Equivalent standard free enthalpies are also indicated. The standard enthalpy of NO(aq) does not have to be determined because this molecule only intervenes in conservation equations of the oxygen and nitrogen atoms.

The different standard free enthalpies of the previous equilibria are listed in the eqs 3.2.8–3.2.11.

\[
\Delta H^\circ_{rxn} = \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}}
\]

\[
\Delta H^\circ_{rxn} (\text{eq} 3.2.1) = \Delta H^\circ_{\text{H}^+\text{H}^+\text{NO}_3^-} - \Delta H^\circ_{\text{H}_2\text{O}}
\]

\[
= 0 - 205.00 + 189.93
\]

\[
= -15.07 \text{kJ} \cdot \text{mol}^{-1}
\]
Table 2. Standard Enthalpies Listed at 1013 ± 3 hPa in the Literature Corresponding to the Chemical Species Studied \(^{a,b}\)

| chemical species X | notation used for \([X]\) | free standard enthalpies (kJ mol\(^{-1}\)) |
|--------------------|-----------------------------|------------------------------------------|
| H\(^+\)(aq)        | \(X_1\)                     | 0\(^{15}\)                                 |
| NO\(_3^−\)(aq)     | \(X_2\)                     | -205.00\(^{16}\)                          |
| H\(_2\)O(l)        | \(X_3\)                     | -285.8\(^{27}\)                           |
| HNO\(_3\)(aq)      | \(X_4\)                     | -189.9\(^{28}\)                           |
| NO\(_2^+\)(aq)     | \(X_5\)                     | -25\(^{19}\)                              |
| NO\(_2\)(aq)       | \(X_6\)                     | 53.6\(^{20}\)                             |
| NO(aq)             | \(X_7\)                     | n.d.                                     |
| NO\(_2\)(aq)       | \(X_8\)                     | -147.4\(^{11}\)                           |
| HNO\(_2\)(aq)      | \(X_9\)                     | -120.1\(^{12}\)                           |

\(^{a}\) All of these data were found in scientific literature, references specific to each value are listed next to the values. \(^{b}\) n.d. not determined.

\[ ΔH^0_{\text{1.2}} \text{ (equation 3.2.4)} = \Delta H^0_{\text{NO}_2^+} + \Delta H^0_{\text{NO}_3^-} + \Delta H^0_{\text{H}_2\text{O}} - 2\Delta H^0_{\text{H}_2\text{NO}_3} = -25 - 205 - 285.8 + 2 \times 189.93 = -135.94 \text{ kJ mol}^{-1} \] (3.2.9)

\[ ΔH^0_{\text{1.3}} \text{ (equation 3.2.5)} = \Delta H^0_{\text{H}_2\text{O}} - \Delta H^0_{\text{NO}_2^-} - \Delta H^0_{\text{H}_2^+} = 53.59 - 285.8 + 120.14 - 0 = -112.07 \text{ kJ mol}^{-1} \] (3.2.10)

\[ ΔH^0_{\text{1.4}} \text{ (equation 3.2.6)} = \Delta H^0_{\text{H}_2\text{NO}_2} + \Delta H^0_{\text{H}_2^+} + \Delta H^0_{\text{NO}_3^-} - 2\Delta H^0_{\text{H}_2\text{O}} = -120.14 + 0 - 205.00 + 2 \times 147.4 + 285.8 = 255.47 \text{ kJ mol}^{-1} \] (3.2.11)

Shock et al.\(^{23,24}\) studied the evolution of the equilibrium constant \(ΔH^0_{\text{1.1}}\) according to the temperature. After calculating, the authors concluded after calculation to a standard enthalpy equal to \(-27\) kJ mol\(^{-1}\). This difference of 55% with the calculated data is important and corresponds to the differences of free enthalpies chosen, thus modifying the standard enthalpy of the equilibrium.

Sicsic also presented the equilibrium 3.2.6 and the standard enthalpy is similar (difference of 3% between both values).

To correlate the evolution of the equilibrium constants with the temperature studied, van’t Hoff’s law is used 3.2.12.

\[
\frac{\text{dln}(K)}{\text{dT}}(K) = \frac{\Delta H^0}{RT^2} \quad \Leftrightarrow \quad \ln K_2 = \ln K_1 + \frac{\Delta H^0}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\] (3.2.12)

The literature data were used to find at least one equilibrium constant value at a precise temperature (shown in bold in Table 3). Once these data were collected, it was then possible to apply the formula 3.2.12 and complete Table 3.

Table 3. Equilibrium Constants According to the Evolution of the Temperature at 1013 ± 3 hPa \(^{a}\)

| equilibrium constant \(K\) | temperature (°C) | value |
|-----------------------------|------------------|-------|
| K1.1                        | 25               | 19.50\(^{24}\) |
|                            | 50               | 12.18 |
|                            | 75               | 8.14  |
|                            | 95               | 6.14  |
| K1.2                        | 25               | 2.80 \times 10^{-60} |
|                            | 50               | 4.02 \times 10^{-8} |
|                            | 75               | 1.06 \times 10^{-8} |
|                            | 95               | 8.29 \times 10^{-11} |
| K1.3                        | 25               | 1.20 \times 10^{-25} |
|                            | 50               | 3.63 \times 10^{-10} |
|                            | 75               | 1.82 \times 10^{-11} |
|                            | 95               | 2.22 \times 10^{-12} |
| K1.4                        | 25               | 8.4 \times 10^{26} |
|                            | 50               | 4.89 \times 10^{11} |
|                            | 75               | 4.51 \times 10^{14} |
|                            | 95               | 5.46 \times 10^{16} |

\(^{a}\) The data at 25 °C were found in scientific literature. Then, the equilibrium constant at the other temperatures were calculated from eq 3.2.12. References specific to each value are listed next to the values.

In addition to the four equilibria mentioned above, it is possible to add four equations concerning the conservation of the charges, oxygen, hydrogen, and nitrogen atoms. All of this leads to a system of eight equations with nine unknowns. The system is presented by eqs 3.2.13–3.2.20 and cannot be solved as it (more unknowns than equations). The unknowns are therefore the concentrations \(X_1\) to \(X_9\).

The terms \(γ\) represent the molecular or ionic activity coefficients. In the same mixture, the activity coefficients are different for the ionic species and the molecular species. In a same mixture, all ionic species of the same charge will have the same activity coefficient.\(^{27}\) The same applies to molecular species. The determinations of the ionic and molecular activity coefficients in each mixture will be presented later in this article (see section 3.2.7). Quantification of the solvent activity coefficient, in this case water, is found from the Nichols and Taylor data via the osmotic coefficient (directly related to the molecular activity coefficient of the solvent), this development is carried out in the section 3.2.8.

Nitric acid dissociation: \(K1.1 = \frac{X_1 \times X_2}{X_3} \times \frac{\gamma_1 \times \gamma_2}{\gamma_4}\) (3.2.13)

Nitric acid self-ionisation: \(K1.2 = \frac{X_1 \times X_3 \times X_4}{X_5^2} \times \frac{\gamma_1 \times \gamma_2 \times \gamma_3}{\gamma_4^2}\) (3.2.14)

Formation of nitrosonium ion: \(K1.3 = \frac{X_6 \times X_3}{X_1 \times X_9} \times \frac{\gamma_1 \times \gamma_5}{\gamma_6}\) (3.2.15)

with \(\gamma_6 = \gamma_1\)
Absorption of nitrogen dioxide: $K_{1.4}$

$$= \frac{X_1 \times X_2 \times X_9}{X_2^0 \times X_3} \times \frac{Y_1 \times Y_2 \times Y_9}{Y_2^0 \times Y_3}$$
$$= \frac{X_1 \times X_2 \times X_9}{X_2^0 \times X_3} \times \frac{Y_1 \times Y_2}{Y_2^0 \times Y_3}$$ (3.2.16)

with $Y_9 = Y_8$

Charges conservation: $X_1 + X_4 + X_6 = X_2$ (3.2.17)

Nitrogen atoms conservation: $X_2 + X_4 + X_5 + X_6 + X_7 + X_8 = C_{\text{acide}}$ (3.2.18)

Oxygen atoms conservation: $3X_2 + X_3 + 3X_4 + 2X_5 + X_6 + X_7 + 2X_8 + 2X_9 = 3C_{\text{acide}} + [\text{H}_2\text{O}]$ (3.2.19)

Hydrogen atoms conservation: $X_1 + 2X_4 + X_5 + X_9 = C_{\text{acide}} + 2[\text{H}_2\text{O}]$ (3.2.20)

To solve this system of eight equations with nine unknowns, it is necessary to be able to determine at different acidities and temperatures the evolution of the concentration of at least one of the species intervening in the previous mechanisms. This will reduce the number of unknowns, and it will then be possible to calculate the concentrations of all nitrogen species in solution. The nitrous acid HNO$_2$ has been chosen because there are many available protocols to determine its concentration in nitric solution by UV–visible spectroscopy.$^{28}$

3.2.6. Evolution of Nitrous Acid Concentration in Concentrated Nitric Medium. Nitric acid is the nitrogen species (excluding HNO$_3$) most studied in the literature.$^{29,30}$ Its dosage can be carried out from an absorbent titration by the Griess reagent. In her work, Fournier$^{31}$ describes a concentration of nitrous acid of about $10^{-5}$ mol·L$^{-1}$ when the total acidity of the medium is 10 mol·L$^{-1}$ and the temperature is set at 80 °C.

Similar experiments were carried out, and the Griess method was also used to determine the concentration of nitrous acid required for solving the system of equations at the acidities and temperatures of interest. The results of the UV spectrophotometry demonstrate that the concentrations of nitric acid for the same total acidity (in molarity) were identical whatever the temperature in the range [50–95 °C]. The results of this study are presented in Figure 3, and the graph shows a linear decrease of the nitrous acid concentrations while the total acidity of the system increases according to the formula 3.2.21

At all temperatures: $[\text{HNO}_2]_{aq}$

$$= -3 \times 10^{-6} \times [\text{HNO}_3]_{\text{total}} + 6 \times 10^{-5}$$ (3.2.21)

The values presented are on the same order of magnitude ($10^{-5}$ mol·L$^{-1}$) as those of Fournier study.$^{30}$

3.2.7. Calculations of the Ionic and Molecular Activity Coefficients in HNO$_3$/$\text{H}_2\text{O}$ Mixtures. Some authors assimilate the activities to ionic or molecular concentrations. This choice, which is appropriate in the case of an ideal solution, is justified by the very low concentrations of the species studied. In such a case, the difference between the ionic and molecular activity coefficients is reduced. For this study in a concentrated nitric medium, it is necessary to consider the activity coefficients for ionic, molecular, and water species. Nichols and Taylor$^2$ presented in their study the modeling of the evolution of the ionic and molecular activities according to the evolution of the molality and the temperature of the system. Modeling is based on experimental data collected by Clegg and Brimblecombe.$^{32}$ Thus, while the temperature increases, the activity coefficients decrease and vice versa (for acidities >1 mol/kg). Table 4 lists the ionic and molecular activity coefficients according to the acidities and temperatures of interest.

| temperature (°C) | acidity (mol·L$^{-1}$) | acidity (mol·kg$^{-1}$) | $\gamma_i$ | $\gamma_{\text{HNO}_3}$ |
|----------------|----------------------|-----------------------|----------|---------------------|
| 50             | 8.5                  | 10.23                 | 1.21     | 2.48                |
| 7.5            | 7.5                  | 8.83                  | 1.15     | 2.22                |
| 6.5            | 6.5                  | 7.49                  | 1.08     | 2.04                |
| 5              | 5.5                  | 5.56                  | 0.97     | 1.63                |
| 3              | 3.18                 | 5.56                  | 0.83     | 1.31                |
| 1.5            | 1.5                  | 3.18                  | 0.73     | 1.18                |
| 75             | 8.5                  | 10.03                 | 1.04     | 1.94                |
| 7.5            | 7.5                  | 8.67                  | 1.01     | 1.81                |
| 6.5            | 6.5                  | 7.35                  | 0.96     | 1.68                |
| 5              | 5.5                  | 5.47                  | 0.89     | 1.50                |
| 3              | 3.13                 | 5.56                  | 0.78     | 1.29                |
| 1.5            | 1.5                  | 3.13                  | 0.70     | 1.11                |
| 95             | 8.5                  | 9.84                  | 0.90     | 1.58                |
| 7.5            | 7.5                  | 8.51                  | 0.88     | 1.47                |
| 6.5            | 6.5                  | 7.22                  | 0.85     | 1.40                |
| 5              | 5.5                  | 5.38                  | 0.81     | 1.27                |
| 3              | 3.09                 | 5.38                  | 0.73     | 1.13                |
| 1.5            | 1.49                 | 3.09                  | 0.68     | 1.00                |

*Values represented here are found from the authors’ graph. With $\gamma_i$ and $\gamma_{\text{HNO}_3}$, respectively, the ionic and molecular activity coefficients.

3.2.8. Coefficient of Water Activity in HNO$_3$/$\text{H}_2\text{O}$ Mixtures. In the case of the solvent, here distilled water, its properties are defined with the osmotic coefficient. Thus, Nichols and Taylor$^3$ quantified this coefficient with the evolution of the temperature and the acidity of the medium. Then, a formula introduced by Butler and James$^{33}$ in 1998 converts the osmotic coefficient into water activity 3.2.22

![Figure 3. Linear evolution of the concentration of nitrous acid as a function of the total acidity of the system at all temperatures in the range [50–95 °C]. Concentrations of nitrous acid were extrapolated from spectroscopic results by the Griess method.](image-url)
\[ \gamma_{\text{H}_2\text{O}} = \times = \frac{a}{m \ln([\text{H}_2\text{O}])} \] (3.2.22)

with:
- \( a \) the activity of water (product of the molecular activity coefficient and the concentration),
- \( \phi \) the osmotic coefficient,
- \( \nu \) the number of ions produced during the dissociation of a molecule of HNO₃ (in this case equivalent to the dissociation coefficient multiplied by 2),
- \( m \) the nitric molality,
- \( 55.51 \) the water molality.

Table 5 shows the osmotic coefficients of water in HNO₃/H₂O mixtures modeled by Nichols and Taylor² and the values of calculated activity coefficients. There is a significant variation of the osmotic coefficient depending on acidity or temperature; the effect on water coefficient values remains low because the difference between the lowest value and the largest does not exceed 20%, whatever the acidity or temperature of the medium.

### 3.2.9. Calculation of Concentrations of Nitric Species in Equilibrium Solution

Using the nitrous acid concentrations previously determined, it is then possible to solve the system of equations relating to the dissociation of HNO₃:

\[
\begin{align*}
K_{1.1} &= \frac{X_1 \times X_2}{X_4} \times \frac{Y_1 \times Y_2}{Y_4} \quad (3.2.23) \\
K_{1.2} &= \frac{X_3 \times X_2 \times X_3}{X_4^2} \times \frac{Y_3 \times Y_2 \times Y_3}{Y_4^2} \quad (3.2.24) \\
K_{1.3} \times X_8 \times Y_9 &= \frac{X_6 \times X_3}{X_1 \times X_9} \times \frac{Y_6 \times Y_3}{Y_1} = \frac{X_6 \times X_3}{X_1} \times \frac{Y_3}{Y_6} \quad (3.2.25) \\
K_{1.4} &= \frac{X_5 \times Y_9}{X_6 \times X_3} \times \frac{Y_2 \times Y_3}{Y_8} \Rightarrow K_{1.4} = \frac{X_5 \times X_2}{X_6 \times X_3} \times \frac{Y_2 \times Y_3}{Y_8} \\
&= \frac{X_5 \times X_2}{X_6 \times X_3} \times \frac{Y_2 \times Y_3}{Y_8} \quad (3.2.26)
\end{align*}
\]

Charges conservation: \( X_1 + X_5 + X_6 = X_2 \) (3.2.27)

Table 5. Osmotic Coefficients and Water Activity Coefficients Modeled at 1013 ± 3 hPa by Nichols and Taylor² as a Function of the Temperature of the Medium and Its Acidity

| Temperature (°C) | Acidity (mol·L⁻¹) | Acidity (mol·kg⁻¹) | Osmotic Coefficient | \( \nu \) | \( a_{\text{H}_2\text{O}} \) (mol·L⁻¹) | [H₂O] (mol·L⁻¹) | γ₇₅[H₂O] |
|-----------------|------------------|-------------------|-------------------|-------|----------------|----------------|------------|
| 50              | 8.5              | 10.23             | 1.27              | 1.13  | 0.76           | 40.19          | 0.019      |
|                 | 7.5              | 8.83              | 1.25              | 1.28  | 0.80           | 42.23          | 0.019      |
|                 | 6.5              | 7.49              | 1.22              | 1.42  | 0.80           | 44.21          | 0.018      |
|                 | 5                | 5.56              | 1.17              | 1.60  | 0.85           | 47.04          | 0.018      |
|                 | 3                | 3.18              | 1.1               | 1.77  | 0.91           | 50.57          | 0.018      |
|                 | 1.5              | 1.53              | 1.01              | 1.90  | 0.95           | 53.03          | 0.018      |
| 75              | 8.5              | 10.03             | 1.19              | 0.92  | 0.80           | 40.19          | 0.020      |
|                 | 7.5              | 8.67              | 1.18              | 1.07  | 0.80           | 42.23          | 0.019      |
|                 | 6.5              | 7.35              | 1.16              | 1.22  | 0.84           | 44.21          | 0.019      |
|                 | 5                | 5.47              | 1.13              | 1.44  | 0.85           | 47.04          | 0.018      |
|                 | 3                | 3.13              | 1.06              | 1.68  | 0.91           | 50.57          | 0.018      |
|                 | 1.5              | 1.51              | 0.99              | 1.77  | 0.95           | 53.03          | 0.018      |
| 95              | 8.5              | 9.84              | 1.12              | 0.85  | 0.84           | 40.19          | 0.021      |
|                 | 7.5              | 8.51              | 1.11              | 0.99  | 0.84           | 42.23          | 0.020      |
|                 | 6.5              | 7.22              | 1.1               | 1.14  | 0.84           | 44.21          | 0.019      |
|                 | 5                | 5.38              | 1.08              | 1.35  | 0.89           | 47.04          | 0.019      |
|                 | 3                | 3.09              | 1.04              | 1.62  | 0.96           | 50.57          | 0.019      |
|                 | 1.5              | 1.49              | 0.97              | 1.76  | 0.95           | 53.03          | 0.018      |

Values represented here are found from the authors’ graph. \( \nu \) is the number of ions produced during the dissociation of a molecule of HNO₃. \( a_{\text{H}_2\text{O}}, [\text{H}_2\text{O}] \) and \( \gamma_{\text{H}_2\text{O}} \) are, respectively, the activity, the concentration and the coefficient activity of water.

Figure 4. Evolution of the concentrations modeled of HNO₃, NO₃⁻, and H⁺ according to the variation of the acidity of the system at three different temperatures.
Nitrogen atoms conservation: \( X_2 + X_4 + X_5 + X_6 + X_7 + X_8 = C_{\text{acide}} - X_9 \)  

(3.2.28)

Oxygen atoms conservation: \( 3X_1 + X_3 + 3X_4 + 2X_5 + X_6 + X_7 + 2X_8 = 3C_{\text{acide}} + [H_2O] - 2X_9 \)  

(3.2.29)

Hydrogen atoms conservation: \( X_4 + 2X_5 + X_4 = C_{\text{acide}} + 2[H_2O] - X_9 \)  

(3.2.30)

The Scilab software was used to solve this system using an iterative method. Equilibrium constants or standard enthalpy calculations present uncertainties. However, because of a lack of information on uncertainties on thermodynamic data of reaction (equilibrium constants) and compound (standard enthalpies), unfortunately not always associated with the data found in the literature, it was impossible to determine uncertainties on our modeled values. The system of equations presented is therefore not strictly correct. The use of about 500 iterations allows getting close to the resolution of the system of equations.

The evolution of the concentrations of \( \text{HNO}_3 \), \( \text{NO}_3^- \), and \( \text{H}^+ \) according to the variation of the temperature and the acidity of the nitric solution is presented in Figure 4. In the same way as presented in the literature, the more the acidity and the temperature increase, the more the dissociation of the nitric acid is partial. The clearest example appears at 95 °C for a total nitric acidity of 8.5 mol·L\(^{-1}\): one-third of the nitric acid is not dissociated (i.e., \( 2.74 \) mol·L\(^{-1}\)). Conversely, in the less aggressive conditions selected, at a concentration of 1.5 mol·L\(^{-1}\) at 50 °C, the entire nitric acid molecule seems dissociated.

Evolutions of concentrations of the major species \( \text{HNO}_3 \), \( \text{NO}_3^- \), and \( \text{H}^+ \) follow linear regressions. The equations of the lines as a function of the overall acidity of the system and the temperature are as follows:

- For the nondissociated \( \text{HNO}_3 \) molecule 3.2.31

\[
\begin{align*}
95^\circ \text{C}: & \quad [\text{HNO}_3]_{\text{in.d.}} = 0.3779 \times [\text{HNO}_3]_h - 0.5619 \quad R^2 = 0.9904 \\
75^\circ \text{C}: & \quad [\text{HNO}_3]_{\text{in.d.}} = 0.3450 \times [\text{HNO}_3]_h - 0.5603 \quad R^2 = 0.9848 \\
50^\circ \text{C}: & \quad [\text{HNO}_3]_{\text{in.d.}} = 0.2813 \times [\text{HNO}_3]_h - 0.4708 \quad R^2 = 0.9791
\end{align*}
\]

(3.2.31)

- For \( \text{NO}_3^- \) and \( \text{H}^+ \) ions 3.2.32

\[
\begin{align*}
95^\circ \text{C}: & \quad [\text{NO}_3^-] = [\text{H}^+] = 0.6222 \times [\text{HNO}_3]_h + 0.5618 \quad R^2 = 0.9964 \\
75^\circ \text{C}: & \quad [\text{NO}_3^-] = [\text{H}^+] = 0.6550 \times [\text{HNO}_3]_h + 0.5602 \quad R^2 = 0.9957 \\
50^\circ \text{C}: & \quad [\text{NO}_3^-] = [\text{H}^+] = 0.7189 \times [\text{HNO}_3]_h + 0.4676 \quad R^2 = 0.9968
\end{align*}
\]

(3.2.32)

The precision of the concentrations presented in this section concerning the concentrations of minor species is in the order of magnitude (because of inaccuracies in the determinations of thermodynamic equilibrium constants or enthalpies of the species present in solution). The following paragraphs present the effects of temperature and acidity changes on concentrations of minority nitrogen species (concentration below to \( 10^{-5} \) mol·L\(^{-1}\)) in solution, by descending order. The logarithmic scale was applied in the following figures to visualize the evolution of the concentrations at the three temperatures as a function of the acidity.

3.2.9.1. For Nitrogen Monoxide \( \text{NO} \). It is the most concentrated minority species. This species is the only one that does not fit into the equilibria mentioned in the previous sections. However, it has been considered in the system of equations for the conservation of nitrogen and oxygen atoms. The results are presented in Figure 5 and the resolution of the system of equations at all temperatures and acidities leads to an independent temperature evolution for nitrogen monoxide in the same way as it was measured for nitrous acid. Concentrations decrease linearly while the acidity increases according to eq 3.2.33. The point modeled at 95 °C for the lower acidity is abnormally high, probably resulting from an error related to the determination of a thermodynamic data under these operating conditions.

\[
[\text{NO}] = -8.6 \times 10^{-6} \times [\text{HNO}_3]_h + 1.5 \times 10^{-4} \\
R^2 = 0.9957
\]

(3.2.33)

3.2.9.2. For Nitrous Acid \( \text{HNO}_2 \). The second most concentrated minority species in solution is nitrous acid \( \text{HNO}_2 \). The evolution of its concentration, solely dependent on the acidity of the medium, was mentioned earlier (Figure 3) in this article.

3.2.9.3. For Nitrogen Dioxide \( \text{NO}_2 \). The modeling of evolution of nitrogen dioxide concentrations is shown in Figure 6. Concentrations increase with the total acidity of the system. On the other hand, an increase in temperature induces a decrease in the concentrations of nitrogen dioxide in solution. The concentrations modeled for each temperature lead to lines whose regressions are expressed in eq 3.2.34.

Figure 5. Evolution of the concentration modeled of the nitrogen monoxide in solution according to the variation of temperature and acidity of the system.
Figure 6. Evolution of the concentration modeled of the nitrogen dioxide in solution according to the variation of temperature and acidity of the system.

\begin{align*}
95 °C: [NO_2] &= 1.1 \times 10^{-11} \times [\text{HNO}_3] + 1.9 \times 10^{-11} \\
R^2 &= 0.9882 \\
75 °C: [NO_2] &= 1.3 \times 10^{-10} \times [\text{HNO}_3] + 1.9 \times 10^{-10} \\
R^2 &= 0.9992 \\
50 °C: [NO_2] &= 4.4 \times 10^{-9} \times [\text{HNO}_3] + 5.3 \times 10^{-9} \\
R^2 &= 0.9751
\end{align*}

(3.2.34)

3.2.9.4. For the Nitronium Ion NO^+. Figure 7 presents the evolution of the concentration of the NO_2^+ ion according to the variation of temperature and acidity of the system.

Figure 7. Evolution of the concentration modeled of the NO_2^+ ion in solution according to the variation of temperature and acidity of the system.

The evolution of the temperature and the total acidity of the system. The concentration of this ion increases with the total acidity of the medium. In general, the graph shows an increase in the concentration of the NO_2^+ ion in solution when the acidity decreases, as a function of the temperature according to the laws described by the eq 3.2.35. Under the experimental conditions at 50 °C for acidity of 7.5 mol·L⁻¹, the modeled NO_2^+ concentration appears to be low compared with the concentrations determined for other nitric acidities at the same temperature. This difference can only be explained by an error at this point on the determination of one or more thermodynamic parameters. The correlation coefficient of the linear regression for the temperature at 50 °C is expressed without taking into account the point at 7.5 M. The points at 1.5 M for each temperature were also not considered for eq 3.2.35 because they are too low. The eq 3.2.35 are therefore valid in the acidity interval [3–8.5 M].

95 °C: [NO_2^+] = 6.0 \times 10^{-11} \times [\text{HNO}_3]_t - 8.6 \times 10^{-11} \\
R^2 &= 0.9401 \\
75 °C: [NO_2^+] = 7.0 \times 10^{-10} \times [\text{HNO}_3]_t - 1.1 \times 10^{-9} \\
R^2 &= 0.9291 \\
50 °C: [NO_2^+] = 1.6 \times 10^{-8} \times [\text{HNO}_3]_t - 2.5 \times 10^{-8} \\
R^2 &= 0.9991

(3.2.35)

3.2.9.5. For the Nitrosonium Ion NO^+. The evolution of the concentration of the NO^+ ion is shown in Figure 8. When the temperatures of the medium are equal to 50 and 95 °C, the concentrations obtained increase with the acidity. The points modeled at these temperatures according to the variation of the acidity forms lines that are expressed by eq 3.2.36.

\begin{align*}
95 °C: [NO^+] &= 5.6 \times 10^{-17} \times [\text{HNO}_3]_t + 2.7 \times 10^{-16} \\
R^2 &= 0.9495 \\
50 °C: [NO^+] &= 2.1 \times 10^{-14} \times [\text{HNO}_3]_t + 4.5 \times 10^{-14} \\
R^2 &= 0.9657
\end{align*}

(3.2.36)

Figure 8. Evolution of the concentration modeled of the NO^+ ion in solution according to the variation of temperature and acidity of the system.

For modeling at 75 °C, the solution concentration of the NO^+ ion appears to increase with the acidity of the medium without following a linear regime. Concentrations obtained for the extreme acidity conditions appear to be particularly erroneous because they differ from several orders of magnitude of those found for intermediate nitric concentrations. These deviations can be attributed to inaccuracies in the determinations of certain thermodynamic equilibrium constants. The lesser error at this scale can have repercussions as observed here on concentrations below 10^{-11} mol·L⁻¹. The value retained at 75 °C describing the concentration of the NO^+ ion is therefore 10^{-14} mol·L⁻¹, four points on the six presented are modeled at this order of magnitude.

3.2.9.6. Modeling Balance Sheet. This article deals with the modeling of the concentrations of the nitric species in solution at equilibrium in an acid range between 1.5 and 8.5 mol·L⁻¹ as a function of a temperature ranging from 50 to 95 °C. The set of modeled data is summarized in Table 6. All these data are based on two main assumptions. The first is that the difference between the Sicsic and Taylor data at 25 °C is applicable to the other temperatures and the second is that the medium is only aqueous (recombined gases via a refrigerant column).
On the basis of the data in Table 6, it is possible to express at each acidity the impact of temperature on the concentrations of nitrogenous species in solution. Because the concentrations of nitrogen monoxide and nitrous acid do not vary with temperature, the above eqs 3.2.21 and 3.2.33 stay valid. For the other species with the exception of NO+, the concentration plot is shown Figure 9. Concentrations appear to change with temperature depending on known functions.

The temperature-dependent change in the concentration of NO+ cannot, however, be expressed by a function. This is due to the points at 75 °C having a different tendency from the points obtained at the same acidity at other temperatures.

After quantifying the functions impacting the concentrations of nitrogen species according to acidity and temperature, it is possible to determine a global law, for each species, determining the evolution of its concentration whatever the acidity or the temperature. These laws, presented by the eqs 3.2.37–3.2.42, are valid in an acidity range from 1.5 to 8.5 mol·L⁻¹ and a temperature range from 50 to 95 °C. For the determination of the correlation coefficient of NO₂⁺ in eq 3.2.42, the point at 7.5 M 75 °C was not considered, in the same way as it had not been considered in the eq 3.2.35.

Table 6. Summary of the Different Modeled Concentrations of the Species in Solution at Equilibrium According to the Acidities and Temperatures of the Medium at 1013 ± 3 hPa

| temperature (°C) | acidity | [H⁺] = [NO₃⁻] | [HNO₂] | [NO] × 10⁻³ | [HNO₃] × 10⁻³ | [NO₂⁻] × 10⁻⁵ | [NO₂⁺] × 10⁻¹¹ | [NO⁺] × 10⁻¹⁷ |
|-----------------|---------|----------------|---------|-------------|---------------|----------------|-----------------|----------------|
| 50              | 8.5     | 6.47           | 2.03    | 7.59        | 2.85          | 42.39          | 10 000          | 2036           |
|                 | 7.5     | 5.84           | 1.66    | 8.18        | 3.07          | 36.41          | 320.7           | 1859           |
|                 | 6.5     | 5.22           | 1.28    | 8.99        | 3.37          | 35.45          | 5264            | 1514           |
|                 | 5       | 4.17           | 0.83    | 10.53       | 3.95          | 30.18          | 2074            | 1087           |
|                 | 3       | 2.69           | 0.31    | 12.16       | 4.56          | 19.31          | 383.3           | 768.2          |
|                 | 1.5     | 1.41           | 0.09    | 13.48       | 5.55          | 9.91           | 53.08           | 311.4          |
| 75              | 8.5     | 6.02           | 2.48    | 7.59        | 2.85          | 1.25           | 459.4           | 1206.0         |
|                 | 7.5     | 5.44           | 2.06    | 8.18        | 3.07          | 1.18           | 320.7           | 76.99          |
|                 | 6.5     | 4.89           | 1.61    | 8.99        | 3.37          | 1.09           | 207.5           | 47.08          |
|                 | 5       | 3.97           | 1.03    | 10.53       | 3.95          | 0.93           | 93.41           | 85.30          |
|                 | 3       | 2.61           | 0.39    | 12.16       | 4.56          | 0.61           | 19.02           | 137.1          |
|                 | 1.5     | 1.39           | 0.11    | 13.51       | 5.55          | 0.32           | 2.25            | 38 130         |
| 95              | 8.5     | 5.76           | 2.74    | 7.59        | 2.85          | 0.10           | 40.04           | 6.78           |
|                 | 7.5     | 5.20           | 2.30    | 8.18        | 3.07          | 0.10           | 28.20           | 6.21           |
|                 | 6.5     | 4.67           | 1.83    | 8.99        | 3.37          | 0.09           | 19.01           | 5.76           |
|                 | 5       | 3.78           | 1.22    | 10.53       | 3.95          | 0.08           | 9.12            | 4.84           |
|                 | 3       | 2.51           | 0.49    | 12.16       | 4.56          | 0.05           | 2.07            | 3.18           |
|                 | 1.5     | 1.36           | 0.14    | 14.99       | 5.55          | 0.03           | 0.27            | 1.60           |

Figure 9. Modeled concentrations of nitrogen species in solution as a function of temperature for different acidities.
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