MODELING AND STOCHASTIC SIMULATION OF THE REACTIONS AND ABSORPTION OF NO\textsubscript{X} IN WATER

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Absorption of NO\textsubscript{X} in Water

Summary

This work discusses the absorption of NO\textsubscript{X} in an absorption column. This is of relevance to the production of nitric acid and the fertilizer industry. Non-reacted NO\textsubscript{X}, released with stack-gases, plays an important role in environmental pollution problems.

NO\textsubscript{X} absorption characterizes itself as a very complex system that is difficult to describe or to model. Up to forty equilibrium reactions exist and describe the system together with some irreversible kinetic reactions. Mass and heat transport limitation plays an important role in this reaction model.

This complex model results in a complex simulation of a NO\textsubscript{X} absorption column. Simulations have been done with a simplified model (only four reactions) and an enhanced model (with eight reactions and two more components). This enhanced model requires extra parameters to describe the physical and chemical properties of the components and reactions that were added to this model.

The parameters that were needed in the enhanced model were found in literature, calculated with appropriate correlations, or some had to be guessed. Introducing uncertain parameters to the model meant that uncertainties were added to the results. A method of simulation has been evolved, called stochastic simulation, which enables to translate the uncertainties in model parameters to uncertainties in the results.

Several simulations have been done with the flowsheeting program ASPEN PLUS, where different classes of parameters have been varied to study their effects on the results. It is found that uncertainties in reaction parameters are less important then uncertainties in pure component parameters and thermodynamic parameters. If operating parameters are stochastic (like temperatures, pressures and feed compositions) then uncertainties in model parameters have no or little effect, taking realistic estimates for these uncertainties.

In this thesis the modeling of NO\textsubscript{X} absorption and the concept of stochastic simulation is discussed. It is found that stochastic simulation is a useful tool in chemical process engineering. Also, recommendations are made to enhance the simulation model of NO\textsubscript{X} absorption. A good knowledge of the model and its uncertainties gives the possibility to optimize absorption column performance and design.
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Absorption of \( NO_X \) in Water

1 Introduction

Absorption of \( NO_X \) gas in aqueous solutions plays an important role in several processes. First, in the manufacture of nitric acid and secondly, the removal of \( NO_X \) from the flue gases that have received considerable attention due to strict regulations on a clean environment. Absorption of \( NO_X \) gases is probably the most complex case in all absorption operations. Joshi (1985) gives therefore the following reasons:

- The \( NO_X \) gas is a mixture of several components, all nitrogen oxides. The absorption of \( NO_X \) gas in water results in two oxyacids, nitric acid and nitrous acid.
- Several equilibria exist between the nitrogen oxides and oxyacids, both in liquid and gas phase. The number of equilibrium reactions is more then forty.
- Absorption and desorption occur simultaneously. Further the absorption is accompanied by chemical reaction and the desorption is preceded by chemical reaction.
- All kinds of reactions undergo in this system. They occur in both phases and include parallel, reversible and consecutive reactions.
- The knowledge of physical and chemical data such as diffusivity, solubility, equilibrium and rate constants are still incomplete.

In this thesis a mathematical model will be examined for the absorption and reactions of \( NO_X \), based on the current knowledge about the subject in literature. This model will be restricted by the limitations that the simulation program (here ASPEN PLUS) possesses.

Nitric acid is a very common chemical compound and numerous companies produce this acid. Because the model of \( NO_X \) absorption is so complex, there is no adequate simulation model available yet to simulate this process with a commercial flowsheet simulation program. Venkataraman (1990) introduced an ASPEN PLUS simulation model for the absorption of \( NO_X \), but in this model the reactions are simplified and the results of this simulation are difficult to verify with experimental data. With Valentijn de Leeuw from Aspen Technology there is decided to derive a model for the absorption of \( NO_X \) in water and to simulate this with ASPEN PLUS.
Absorption of NOx in Water

In this first chapter some background information will be provided on the subject of NOx absorption. The nitric acid production will be discussed, and finally a problem identification and definition will be given.

Chapter two will describe the reactions and reaction equilibria that the NOx absorption system describes. It also gives some information on the mass transport limitations between the vapor and liquid phase. Three reaction models that can be simulated will be presented here.

Chapter three describes the flowsheet simulation program ASPEN PLUS and how it is used to simulate reactive absorption.

Chapter four will introduce a rather new concept in process simulation, stochastic simulation. The purpose of stochastic simulation and the implementation is described here.

Finally the results of the (stochastic) simulations will be presented, and the last chapter discusses and comments the results and will give some recommendations for further research on this subject.

1.1 What is NOx?

According to the definition given in Ullmann (Thieman, 1991) NOx is defined as the compound of oxygen with nitrogen. Because nitrogen can exist in several oxidation states (+1 to +6) numerous compounds of nitrogen oxide exist. The oxides known are:

(+1) N2O  dinitrogen monoxide (laughing gas),
(+2) NO  nitrogen monoxide,
N2O2  dinitrogen dioxide,
(+3) N2O3  dinitrogen trioxide,
(+4) NO2  nitrogen dioxide,
N2O4  dinitrogen tetroxide,
(+5) N2O5  dinitrogen pentoxide,
(+6) NO3  nitrogen trioxide,
N2O6  dinitrogen hexoxide.

Very little is known of NO3 and its dimeric form N2O6. In the case of NOx absorption not all compounds are of equal importance. In this project only NO, NO2, N2O4 and N2O3 are considered so NOx in this thesis will denote those four compounds.
Absorption of NO$_x$ in Water

For the simulation model more compounds are relevant. These include of course the oxyacids:

\[
\begin{align*}
\text{HNO}_2 & \quad \text{nitrous acid,} \\
\text{HNO}_3 & \quad \text{nitric acid,} \\
\text{NO}_3^- & \quad \text{nitrate,} \\
\text{NO}_2^- & \quad \text{nitrite,} \\
\text{H}_2\text{O}^+ & \quad \text{hydrogen-ion,}
\end{align*}
\]

and further:

\[
\begin{align*}
\text{H}_2\text{O} & \quad \text{water,} \\
\text{O}_2 & \quad \text{oxygen,} \\
\text{N}_2 & \quad \text{nitrogen.}
\end{align*}
\]

Nitric acid is classified as a hazardous substance. It reacts with and causes spontaneous ignition of organic substances. Its MAC value (Maximum Allowable Concentration) is 10 ppm. At room temperature nitrous gases are released from nitric acid. Nitrous acid is toxic because it decomposes to form nitric acid and nitrogen monoxide. Nitrogen monoxide does not have irritating effects. It reacts, however, with hemoglobin and can cause possibly death. Nitrogen dioxide is an irritant gas. Its MAC value is 5 ppm. Inhalation of a lethal dose of 200 ppm of nitrogen dioxide may result in death (Thieman, 1991).

### 1.2 The production of nitric acid

One of the major applications for NO$_x$ absorption is the production of nitric acid. Nitric acid is a very important industrial compound. Figure 1 shows the top ten of industrial important chemicals where nitric acid ranks tenth.

Originally sodium nitrate was used to produce nitric acid. When at the beginning of the 20th century the sodium nitrate reserves were thought to be exhausted, new processes were developed:

- Production of nitrogen monoxide by reacting atmospheric nitrogen and oxygen at temperatures higher than 2000 °C (direct process).
- Production of ammonia by hydrolysis of calcium cyanamide under pressure.
- Production of ammonia from nitrogen and hydrogen.

The last process, ammonia produced from nitrogen and hydrogen (Haber-Bosch process) is still used as a feedstock for nitric acid production.

The most critical part in nitric acid production is the combustion of ammonia with oxygen (Ostwald process). This catalytic oxidation of ammonia, used to produce nitrogen monoxide, is:

\[
4 \text{NH}_3 + 5 \text{O}_2 \rightarrow 4 \text{NO} + 6 \text{H}_2\text{O} .
\]  
(1)
The next step in the acid production is the oxidation of nitrogen monoxide:

$$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 = \text{N}_2\text{O}_4 \ ,$$

and the last step is the absorption of the nitrogen oxides to obtain nitric acid:

$$3 \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{NO} \ .$$

These steps can be implemented in several ways. There are the low pressure, medium pressure, high pressure and dual pressure processes. Although the low pressure plants are not longer built, the other processes still are. The choice between those processes is based on plant capacity, energy costs and environmental aspects. In Europe the dual pressure process is more popular. The combustion process takes place at medium pressure (4-6 bar) and the absorption at high pressure (9-14 bar). Figure 2 shows a simplified flowsheet of a dual pressure nitric acid production plant.

This process combines the favorable economics of medium pressure combustion with the efficiency of high-pressure absorption. Dual pressure processes are used when large capacities are needed. Single train plants can produce up to 2000 ton of nitric acid per day.
Industrially produced nitric acid contains 50-70 wt % HNO₃, which is high enough for fertilizer production. Nitric acid needed for nitration processes in organic chemistry calls for higher HNO₃ concentrations (98-100%). However, it is not possible to distill nitric acid because it forms an azeotrope with water (68.4%, 1 atm). To produce pure nitric acid, nitrous gases can be reacted with azeotropic acid to form a concentrated acid that can be distilled in pure nitric acid and azeotropic acid. The azeotropic acid can be completely recycled.

Waste-water problems will be overcome by appropriate design of the nitric acid plant. A more serious problem is the environmental pollution with NOₓ gases. Some stack gases of older plants contain up to 3000 ppm NOₓ. In the last decade regulations have been issued to restrict the NOₓ concentrations of stack gases. The concentration of NOₓ has to be lower then 240 ppm and further on the stack-gas may be discharged only if colorless. A practical limit used is a NOₓ concentration lower then 200 ppm (Thieman, 1991).

To improve NOₓ absorption and especially to purify tail gases, a number of methods have been developed. Some methods use scrubbing solvents other then water. These include ammonia, hydrogen peroxide or a solution of urea and nitric acid in water. Other methods to reduce the NOₓ content in stack gases are adsorption by molecular sieves and catalytic reduction of NOₓ. All methods reduce the NOₓ content to approximate 50 ppm.
1.3 Modeling absorption columns

Several aspects for NO\textsubscript{X} absorption tower design have to be noted. The tower can be a packed column or a plate column. Most modern absorption towers have sieve plates.

Figure 3 is an example of a packed absorption column. To handle packed columns in a process simulation program, the program uses equivalent tray-heights. The equivalent tray-height is the height of the package with the same results as would be obtained with one equilibrium tray for tray columns.

For sieve tray columns the tray height increases while NO\textsubscript{X} content decreases. This is because the NO\textsubscript{X} reacts slower when its content decreases. Acid formation chiefly takes place at the lower third of the column, while NO\textsubscript{X} is reduced in the upper two-thirds. As a result most of the heat must be withdrawn in the lower third.

The top of the column contains a demister to remove the entrained acid droplets.

1.4 Problem identification for modeling NO\textsubscript{X} absorption

One of the goals of this project is to define a model for the reactions and absorption of NO\textsubscript{X} in water. As a starting point a model has been provided by Aspen Technology (Venkataraman, 1990). Objective for this project was to:

- enhance this model by introducing extra components and adding extra reactions,
- take account for mass transport limitations and use the ASPEN PLUS program RATEFRAC to simulate this model,
- verify the results of the simulations with experimental data and use this data to reconsolidate the NO\textsubscript{X} absorption model,
- optimize column performance by increasing nitric acid concentration and decreasing stack gas NO\textsubscript{X} content.
Absorption of NO\textsubscript{x} in Water

During this project some extra problems appeared. Starting with the first simple model, some components and reactions had to be added. The pure component data for these extra components were difficult or even impossible to find and in some cases had to be estimated. Also kinetic data for these reactions and thermodynamic binary parameters were uncertain.

Therefore additional goals have been defined:

- Try to find pure component data, thermodynamic binary data and reaction data for the components added to the simulation model. If not found use a correlation model to estimate these properties else estimate the properties by comparing them with properties of other components.
- Evolve a method to translate these uncertainties in model parameters to uncertainties in results.

To accomplish this, a new method (new in process simulation) has been evolved called stochastic simulation. This provides the tool to translate process model uncertainties to uncertainties in simulation results.

This research project has been done in order to graduate on the subject of this thesis. The research took place at the section: Process Integration at the Department of Chemical Engineering at Delft University of Technology.
2 Reactions of NO$\textsubscript{X}$

The reaction system of the NO$\textsubscript{X}$ reactions and absorption in water is very complex. Joshi (1985) reports more than forty equilibrium reactions that occur both in liquid and vapor phase. In this chapter the reactions that play an important role in NO$\textsubscript{X}$ absorption, are outlined. Three models are given who can be used to simulate this absorption.

2.1 Reactions of NO$\textsubscript{X}$ in the gas phase

The nitrogen monoxide gas enters the absorption column at the bottom. Oxygen and nitrogen and other nitrogen oxides enter the column with the monoxide. Several reactions occur in the gas phase. It is believed that the rate limiting reaction is the oxidation of nitrogen monoxide (Thieman, 1991):

$$2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2 .$$  \hfill (4)

Several equilibrium reactions occur in the gas phase. The most important are the dimerisation of nitrogen dioxide:

$$2 \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4 ,$$  \hfill (5)

the formation of nitrogen trioxide:

$$\text{NO} + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_3 ,$$  \hfill (6)

the formation of nitrous acid:

$$\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \leftrightarrow 2 \text{HNO}_2 ,$$  \hfill (7)
Absorption of NO\textsubscript{x} in Water

and the formation of nitric acid:

\[ 3 \text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons 2 \text{HNO}_3 + \text{NO} . \]  \hspace{1cm} (8)

Table 1 gives a detailed description of all equilibrium reactions in the gas phase.

To describe the kinetics of (4) a third order rate equation is used (Thieman, 1991):

\[ r = \frac{k_p}{RT} P^{2}_{\text{NO}} P_{\text{O}_2} \]  \hspace{1cm} (9)

where 
- \( r \) = reaction rate [kmol m\textsuperscript{-3} s\textsuperscript{-1}],
- \( k_p \) = reaction rate constant [atm\textsuperscript{-2} s\textsuperscript{-1}],
- \( R \) = universal gas constant [m\textsuperscript{3} atm kmol\textsuperscript{-1} K\textsuperscript{-1}],
- \( T \) = temperature [K] and
- \( P \) = partial pressure [atm].

The rate constant for reaction (4) is given by:

\[ \log k_p = \frac{652.1}{T} - 1.0366 . \]  \hspace{1cm} (10)

This reaction goes faster at low temperature than at high temperature. Bodenstein (1922) assumed that the oxidation occurred in two steps:

\[ 2 \text{NO} \rightleftharpoons (\text{NO})_2 \]  \hspace{1cm} (11)

\[ (\text{NO})_2 + \text{O}_2 \rightarrow \text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2 . \]

Because the dimerisation of nitrogen oxide is exothermic, the equilibrium of the first reaction of (11) will be to the left at higher temperatures. The equilibrium for reaction (5) is reached very quickly and the dimerisation rate is virtually independent of temperature. Hoftyzer (1972) gave the following equation for the equilibrium constant:

\[ K_p = \frac{P_{(\text{N}_2\text{O}_4)}}{P^2_{\text{NO}} P_{\text{O}_2}} = 0.698 \times 10^{-9} \exp \left( \frac{6866}{T} \right) . \]  \hspace{1cm} (12)

where \( K_p \) = equilibrium constant [atm\textsuperscript{-1}].

The same equilibrium constant can be written for dinitrogen trioxide formation:

\[ K_p = \frac{P_{(\text{N}_2\text{O}_3)}}{P_{\text{NO}} P_{\text{NO}_2}} = 66.3 \times 10^{-9} \exp \left( \frac{4740}{T} \right) . \]  \hspace{1cm} (13)

Jethani (1992) reported the equilibrium constant for the formation of nitrous acid in the gas phase.
Absorption of \( NO_x \) in Water

Table 1
Gas-phase equilibria involving nitrogen oxides and oxyacids (Adapted from Joshi (1985)).

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Equilibrium constant</th>
<th>Value at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( NO + NO_2 + H_2O \rightarrow 2HNO_2 )</td>
<td>( p_{HNO_2}^2 / p_{NO} p_{NO_2} p_{H_2O} )</td>
<td>1.67 ( 10^2 ) [kN/m(^2)](^{-1})</td>
</tr>
<tr>
<td>( 3NO_2 + N_2O_2 + NO )</td>
<td>( p_{N_2O_5} p_{NO} / p_{NO_2}^3 )</td>
<td>4.2 ( 10^{-11} ) [kN/m(^2)](^{-1})</td>
</tr>
<tr>
<td>( 3HNO_2 + HNO_3 + 2NO + H_2O )</td>
<td>( p_{HNO_3} p_{NO}^2 p_{H_2O} / p_{HNO_2}^3 )</td>
<td>3.33 [kN/m(^2)]</td>
</tr>
<tr>
<td>( NO_2 + HNO_3 + HNO_2 + NO )</td>
<td>( p_{HNO_3} p_{NO} / p_{NO_2} p_{HNO_2} )</td>
<td>5.59 ( 10^{-2} ) [-]</td>
</tr>
<tr>
<td>( 2NO_2 + H_2O + HNO_2 + HNO_3 )</td>
<td>( p_{HNO_3} p_{HNO_3} / p_{NO_2}^2 p_{H_2O} )</td>
<td>9.36 ( 10^{-2} ) [kN/m(^2)](^{-1})</td>
</tr>
<tr>
<td>( 3NO_2 + H_2O + 2HNO_2 + NO )</td>
<td>( p_{HNO_3}^2 p_{NO} / p_{NO_2}^3 p_{H_2O} )</td>
<td>5.23 ( 10^{-5} ) [kN/m(^2)](^{-1})</td>
</tr>
<tr>
<td>( N_2O_2 + H_2O + HNO_2 + HNO_3 )</td>
<td>( p_{HNO_3} p_{HNO_3} / p_{NO_2} p_{H_2O} )</td>
<td>1.38 ( 10^{-2} ) [-]</td>
</tr>
<tr>
<td>( N_2O_2 + H_2O + 2HNO_2 )</td>
<td>( p_{HNO_2}^2 / p_{NO_2} p_{H_2O} )</td>
<td>3.18 [-]</td>
</tr>
<tr>
<td>( N_2O_2 + H_2O + 2HNO_3 )</td>
<td>( p_{HNO_3}^2 / p_{NO_2} p_{H_2O} )</td>
<td>1.23 ( 10^9 ) [-]</td>
</tr>
</tbody>
</table>

\[
K_p = \frac{p_{HNO_2}^2}{p_{NO} p_{NO_2} p_{H_2O}} = 1.8501 \times 10^{-7} \exp \left( \frac{4723}{T} \right),
\]  
(14)

and for the formation of nitric acid in the gas phase:

\[
K_p = \frac{p_{HNO_3}^2 p_{NO}}{p_{NO_2}^3 p_{H_2O}} = 1.7498 \times 10^{-9} \exp \left( \frac{4614}{T} \right).
\]  
(15)

2.2 Acid-dissociation Equilibria

Nitric acid and nitrous acid dissolves in water where it is ionized. The following equilibria can be written:

\[
HNO_3(g) \rightleftharpoons HNO_3(l)
\]  
(16)

\[
HNO_3(l) \rightleftharpoons H^+(aq) + NO_3^-(aq).
\]  
(17)
Absorption of NO\textsubscript{x} in Water

The equilibrium constant for the nitric acid dissociation is defined by:

\[ K_{eq} = \frac{a_{H^+} a_{\text{NO}_3^-}}{a_{\text{HNO}_3}} \quad (18) \]

where \( a_i \) = activity for component \( i \).

The value for \( K_{eq} \) for the acid dissociation is 15.4±2.1 kmole/m\(^3\) (Joshi, 1985). The same can be written for the dissociation of nitrous acid:

\[ \text{HNO}_2(g) \rightleftharpoons \text{HNO}_2(l) \quad (19) \]

\[ \text{HNO}_2(l) \rightleftharpoons \text{H}^+(aq) + \text{NO}_2^-(aq) \quad (20) \]

with a value for the \( K_{eq} \) of about 6x10\(^{-4}\) kmole/m\(^3\). It has been found that the value for the equilibrium constant for the dissociation of nitrous acid strongly depends upon the pH of the aqueous solution. Because \( \text{HNO}_2 \) is a weak acid it doesn't dissolve in water as well as nitric acid does. So the formation of nitrous acid in the gas phase plays a more important role then its formation in the liquid phase.

2.3 Heterogeneous equilibria

If you consider equilibrium (7), (19) and (20) then you can write down the following overall reaction:

\[ \text{NO}(g) + \text{NO}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons 2\text{H}^+ + 2\text{NO}_2^- \quad (21) \]

The equilibrium constant can be computed by multiplying the equilibrium constants of the corresponding three reactions.

Several equilibria are listed in table 2 and values are given for dilute aqueous solutions.

An important parameter in describing heterogeneous reactions is the Henry’s-law constant defined as:

\[ H_i = \lim_{x_i \to 0} \frac{P_i}{x_i} \quad (22) \]

where \( H \) = Henry’s-law constant [m\(^3\) atm/kmol],
\( P_i \) = partial pressure of component \( i \) [atm] and
\( x_i \) = concentration of component \( i \) [kmol/m\(^3\)].
Absorption of NO\textsubscript{x} in Water

Table 2

Heterogeneous equilibria (Adapted from Joshi (1985)). Superscript W means that water is involved in the reaction.

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Equilibrium constant</th>
<th>Value at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2NO\textsubscript{2}(g) ⇌ 2H\textsuperscript{+} + NO\textsubscript{3}⁻ + NO\textsubscript{2}⁻</td>
<td>(a_{H^+}^{2}a_{NO_{2}}^{-}a_{NO_{3}}^{-} / p_{NO_{2}}^{2})</td>
<td>2.44 (10^2)</td>
</tr>
<tr>
<td>NO\textsubscript{(g)} + NO\textsubscript{2}(g) ⇌ 2H\textsuperscript{+} + 2NO\textsubscript{2}⁻</td>
<td>(a_{H^+}^{2}a_{NO_{2}}^{-2} / p_{NO_{2}P_{NO}})</td>
<td>3.28 (10^3)</td>
</tr>
<tr>
<td>3NO\textsubscript{2}(g) ⇌ 2H\textsuperscript{+} + 2NO\textsubscript{3}⁻ + NO\textsubscript{(g)}</td>
<td>(a_{H^+}^{2}a_{NO_{3}}^{-2}p_{NO} / p_{NO_{2}}^{3})</td>
<td>1.81 (10^9)</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{4}(g) ⇌ 2H\textsuperscript{+} + NO\textsubscript{3}⁻ + NO\textsubscript{2}⁻</td>
<td>(a_{H^+}^{2}a_{NO_{2}}^{-}a_{NO_{3}}^{-} / p_{NO_{2}4})</td>
<td>3.56 (10^1)</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{3}(g) ⇌ 2H\textsuperscript{+} + 2NO\textsubscript{2}⁻</td>
<td>(a_{H^+}^{2}a_{NO_{2}}^{-2} / p_{NO_{3}})</td>
<td>6.14 (10^3)</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{3}(g) ⇌ 2H\textsuperscript{+} + 2NO\textsubscript{3}⁻</td>
<td>(a_{H^+}^{2}a_{NO_{3}}^{-2} / p_{NO_{3}})</td>
<td>4.25 (10^{17})</td>
</tr>
<tr>
<td>2H\textsuperscript{+} + 3NO\textsubscript{2}⁻ ⇌ NO\textsubscript{3}⁻ + 2NO\textsubscript{(g)}</td>
<td>(a_{NO_{3}P_{NO}}^{2} / a_{H^+}^{2}a_{NO_{2}}^{-3})</td>
<td>2.27 (10^{11})</td>
</tr>
<tr>
<td>NO\textsubscript{2}(g) + NO\textsubscript{2}⁻ ⇌ NO\textsubscript{3}⁻ + NO\textsubscript{(g)}</td>
<td>(a_{NO_{3}P_{NO}} / p_{NO_{2}a_{NO_{2}}})</td>
<td>7.43 (10^6)</td>
</tr>
<tr>
<td>2NO\textsubscript{2}(g) ⇌ HNO\textsubscript{2}(l) + H\textsuperscript{+} + NO\textsubscript{3}⁻</td>
<td>(a_{H^+}a_{NO_{3}}a_{HNO_{2}} / p_{NO_{3}}^{2})</td>
<td>4.78 (10^5)</td>
</tr>
<tr>
<td>NO\textsuperscript{(g)} + NO\textsubscript{2}(g) ⇌ 2HNO\textsubscript{2}(l)</td>
<td>(a_{HNO_{2}}^{2} / p_{NO_{2}P_{NO}})</td>
<td>1.26 (10^2)</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{4}(g) ⇌ HNO\textsubscript{2}(l) + H\textsuperscript{+} + NO\textsubscript{3}⁻</td>
<td>(a_{H^+}a_{NO_{3}}a_{HNO_{2}} / p_{NO_{3}}^{2})</td>
<td>6.98 (10^4)</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{3}(g) ⇌ 2HNO\textsubscript{2}(l)</td>
<td>(a_{HNO_{2}}^{2} / p_{NO_{3}})</td>
<td>2.38 (10^2)</td>
</tr>
<tr>
<td>3HNO\textsubscript{2}(l) ⇌ H\textsuperscript{+} + NO\textsubscript{3}⁻ + 2NO\textsuperscript{(g)}</td>
<td>(a_{H^+}a_{NO_{3}}p_{NO}^{2} / a_{HNO_{2}}^{3})</td>
<td>3.01 (10^1)</td>
</tr>
<tr>
<td>NO\textsubscript{2}(g) + HNO\textsubscript{2}(l) ⇌ H\textsuperscript{+} + NO\textsubscript{3}⁻ + NO\textsuperscript{(g)}</td>
<td>(a_{H^+}a_{NO_{3}}p_{NO} / p_{NO_{2}a_{HNO_{2}}}^{2})</td>
<td>3.79 (10^3)</td>
</tr>
</tbody>
</table>

\(a\) in \([\text{kmole/m}^3]\), \(p\) in \([\text{atm}])

The Henry's-law constant is often taken constant for low concentrations and a small temperature region. When the following reaction is considered (Thieman, 1991):

\[3\ \text{HNO}_2(l) \rightarrow \text{HNO}_3(l) + \text{H}_2\text{O}(l) + 2\ \text{NO}(g).\] (23)

Its kinetics can be described by:

\[r = k \frac{c_{\text{HNO}_2}^4}{p_{\text{NO}}^2} = \frac{k}{H_{\text{NO}}^2} \frac{c_{\text{HNO}_2}^4}{c_{\text{NO}}^2},\] (24)

Reactions of NO\textsubscript{x}
Absorption of NO\textsubscript{x} in Water

where the rate constant \( k \) is defined by:

\[
\log k = -\frac{6200}{T} + 20.1979 .
\]  \hfill (25)

A value for the Henry’s law constant for NO is given by Emig (1979) and is 518 m\textsuperscript{3} atm/kmol.

2.4 Aqueous-phase equilibria

The large number of components and reactions in the gas phase suggests that there is also a complicated reaction scheme in the liquid phase. In principle all the reactions in the gas phase also happen in the liquid phase and vice versa (except the ionic reactions). The main route for the formation of nitric acid is according to the following reaction:

\[
N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2 .
\]  \hfill (26)

The dinitrogen tetroxide dissolves in the water and reacts with the water to produce nitric acid and nitrous acid. The nitric acid is a strong electrolyte and dissolves into H\textsuperscript{3}O\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{−}. Nitrous acid then dissociates to nitric acid, water and nitrogen monoxide. Because the nitrogen monoxide partly dissolves, it will be transported to the vapor phase. Its kinetics is described in (24) and (25). In Thieman a relation for the first order kinetics of (26) is given:

\[
r = 10^{\left(\frac{-41.99}{T} + 16.3415\right)} c_{N_2O_4} .
\]  \hfill (27)

A complete reaction scheme is given by Joshi (1985) and is summarized in table 3.

2.5 Mass transfer

Many studies have been done on the subject of mass transfer of NO\textsubscript{x} in aqueous systems. A variety of mechanisms have been proposed depending on the gas composition and acid concentration. It is believed that the physical absorption of dinitrogen tetroxide to the aqueous phase is the rate limiting step in nitric acid formation. The rate of transport depends primarily on the NO\textsubscript{2}-N\textsubscript{2}O\textsubscript{4} equilibrium (Thieman, 1991):

\[
J_{N_2O_4} = \frac{k_{gNO_2}^p}{2RT} (p_{NO_2}^b - p_{NO_2}^i) + \frac{k_{gN_2O_4}^p}{2RT} (p_{N_2O_4}^b - p_{N_2O_4}^i) .
\]  \hfill (28)

where \( J_{N_2O_4} \) = absorption rate [kmol/m\textsuperscript{2}/s],

\( k_{g_i}^p \) = gas-side mass-transfer coefficient of component \( i \) [m/s],

\( p_{i}^b \) = partial pressure of component \( i \) in the bulk gas [atm] and

\( p_{i}^i \) = partial pressure of component \( i \) in the interface [atm].
Absorption of NO\textsubscript{x} in Water

Table 3
Aqueous phase equilibria. Adapted from Joshi (1985).

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>Equilibrium constant</th>
<th>Value at 25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3HNO\textsubscript{2}(l) \rightleftharpoons H\textsuperscript{+} + NO\textsubscript{3}\textsuperscript{-} + 2NO(l)</td>
<td>$a\text{H}<em>2\text{a}</em>{\text{NO}<em>3}/a</em>{\text{NO}_2}^3$</td>
<td>1.12 \times 10^{-4} [kmole/m\textsuperscript{3}]</td>
</tr>
<tr>
<td>2H\textsuperscript{+} + 2NO\textsubscript{2}(l) \rightleftharpoons 2NO\textsubscript{3}(l)</td>
<td>$a_{\text{NO}<em>3}/a</em>{\text{NO}_2}^3$</td>
<td>8.46 \times 10^5 [kmole/m\textsuperscript{3}]^{-2}</td>
</tr>
<tr>
<td>2NO\textsubscript{2}(l) \rightarrow N\textsubscript{2}O\textsubscript{4}(l)</td>
<td>$a_{\text{N}_2\text{O}<em>4}/a</em>{\text{NO}_2}$</td>
<td>6.54 \times 10^4 [kmole/m\textsuperscript{3}]^{-1}</td>
</tr>
<tr>
<td>NO(l) + NO\textsubscript{2}(l) \rightarrow N\textsubscript{2}O\textsubscript{3}(l)</td>
<td>$a_{\text{N}_2\text{O}<em>3}/a</em>{\text{NO}_2}$</td>
<td>1.37 \times 10^4 [kmole/m\textsuperscript{3}]^{-1}</td>
</tr>
<tr>
<td>2NO\textsubscript{2}(l) \rightleftharpoons HNO\textsubscript{2}(l) + H\textsuperscript{+} + NO\textsubscript{3}\textsuperscript{-}</td>
<td>$a\text{H}\text{a}_{\text{NO}<em>3}/a</em>{\text{NO}_2}^2$</td>
<td>3.8 \times 10^9 [kmole/m\textsuperscript{3}]</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{4}(l) \rightleftharpoons 2HNO\textsubscript{2}(l)</td>
<td>$a_{\text{N}_2\text{O}<em>4}/a</em>{\text{NO}_2}$</td>
<td>3.3 \times 10^2 [kmole/m\textsuperscript{3}]</td>
</tr>
<tr>
<td>NO(l) + NO\textsubscript{2}(l) \rightarrow 2HNO\textsubscript{2}(l)</td>
<td>$a_{\text{H}<em>2\text{a}</em>{\text{NO}<em>3}/a</em>{\text{NO}_2}^2}$</td>
<td>4.52 \times 10^6 [-]</td>
</tr>
</tbody>
</table>

The following equation can be written for the absorption rate of dinitrogen tetroxide (Thiemann, 1991):

$$J_{N_2O_4} = \frac{H_{N_2O_4} p_{N_2O_4}}{k D_{N_2O_4}} \sqrt{k D_{N_2O_4}},$$ \hspace{1cm} (29)

where $k$ = rate constant [s] and $D$ = diffusion constant [m/s\textsuperscript{2}].

Several correlations have been developed for the mass transfer coefficient. Miller (1987) found for sieve trays:

for $W_{HNO_3} > 0.05$

$$H_{N_2O_4} \sqrt{k D_{N_2O_4}} = \exp \left(\frac{-1500}{T} - \frac{2.7648 - 39.614 W_{HNO_3} + 181.98 W_{HNO_3}^2}{T} \right) \left(\frac{-429.65 W_{HNO_3}^3 + 496.99 W_{HNO_3}^4 - 223.24 W_{HNO_3}^5}{T} \right),$$ \hspace{1cm} (30)

and for $W_{HNO_3} < 0.05$

$$H_{N_2O_4} \sqrt{k D_{N_2O_4}} = \exp \left(\frac{-1500}{T} - \frac{0.2548 - 315.73 W_{HNO_3}}{T} \right) \left(\frac{+9256.2 W_{HNO_3}^2 - 223.24 W_{HNO_3}^3}{T} \right),$$

where $W$ = mass fraction and $H$ = Henry's-law constant [m\textsuperscript{3}kPa/kmol].

Reactions of NO\textsubscript{x}
Absorption of NO\(_X\) in Water

and for bubble-cap trays:

\[
H_{\text{NO}_x} \sqrt{k D_{\text{NO}_x}} = \exp \left( \frac{-1500}{T} - 4.3790 - 23.279 W_{\text{NO}_3} + 130.42 W_{\text{HNO}_3}^2 \right) \left( -370.87 W_{\text{HNO}_3}^3 + 486.94 W_{\text{HNO}_3}^4 - 236.54 W_{\text{HNO}_3}^5 \right). \tag{31}
\]

2.6 Simulation models

Hoftyzer (1972) formulated an absorption model for the NO\(_X\) absorption with the main components and reactions. Figure 4 summarizes Hoftyzer's model.

This model describes the absorption problem with the most important reactions. It takes into account for the mass transfer limitation by defining a gas-bulk, interface, liquid-film and liquid bulk phase. Heterogeneous reactions take place at the interface, the fast liquid phase reactions take place in the liquid film and the slow liquid phase reactions occur in the liquid-bulk phase. The gas phase is homogeneous. This model further will be denoted as the Hoftyzer model.
Absorption of \( NO_x \) in Water

Because the ASPEN RADFRAC unit operation module does not have the possibility to use a mass transport rate based approach, the model used for simulation with ASPEN PLUS only has a gas and liquid bulk phase. The original ASPEN PLUS model (further denoted as the ASPEN model) for the simulation of \( NO_x \) absorption incorporates some simplifications (Venkataraman, 1990). Most notable in this model is that the nitric acid is formed in the vapor phase. Also, the nitric acid dissociation has been taken into account. Figure 5 shows the ASPEN model.

The ASPEN model has been extended and most of the reactions from the Hoftyzer model have been used to define the Enhanced model. Figure 6 shows the Enhanced model. It does not describe liquid-film and interface reactions, but it does define nitrous acid and dinitrogen trioxide as reacting compounds.

![Figure 5](image)

*Figure 5*

*Basic model for the simulation of \( NO_x \) absorption (ASPEN model).*
Absorption of NO\textsubscript{x} in Water

\textbf{Figure 6}

Enhanced model for the simulation of NO\textsubscript{x} absorption (Enhanced model).
3 Reactive absorption with ASPEN PLUS

ASPEN PLUS is an advanced steady state flowsheeting program. It got its power from the flexible way of defining your process, a comprehensive set of thermodynamic models and a complete set of unit operations. It also has possibilities of optimizing your flowsheet and performs sensitivity studies. You can add your own thermodynamic or unit-operation models by writing user subroutines in FORTRAN. ASPEN PLUS runs on several platforms, from PC's to supercomputers and under different operating systems like MS-DOS, VMS or unix. There are some disadvantages, such as its difficult user interface and the 'feeling' that you easily can get 'lost' in the program, lacking information on all the possibilities in it. For the different available flowsheet simulators (like ChemCad II, PRO/II, Hysim, ASPEN PLUS), ASPEN PLUS is the most adequate for simulating the NO\textsubscript{x} absorption because of its capability to handle reactions in absorption and distillation columns.

For this problem the flowsheet simulator must contain:
- a complete set of physical properties for all the components (O\textsubscript{2}, N\textsubscript{2}, NO, NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{3}, N\textsubscript{2}O\textsubscript{4}, H\textsubscript{2}O, HNO\textsubscript{2}, HNO\textsubscript{3}, H\textsuperscript{+}, NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-}).
- Thermodynamic models to describe the correct vapour-liquid behavior. These models are: an equation of state for the vapour-phase, Henry's-law for the solubility of the non-condensable gases, an electrolyte model for the dissociation of HNO\textsubscript{2} and HNO\textsubscript{3} and a model for the activity constants of the liquid components.
- A unit operation model for the simulation of simultaneous absorption and reactions on every stage and the possibility to enter duties on every tray.
- A correct way to define a complete set of reactions. There are equilibrium and kinetic reactions, in the liquid and vapor phase.
- Mass-transport models for the simulation of mass-transfer limitation between the liquid and vapor phase.
- Heat-transport models for the simulation of heat-transfer limitation in both phases. The temperature does not have to be uniform on one tray.

In this chapter the different requirements are discussed and is shown how these are implemented with respect to the NO\textsubscript{x} absorption.
3.1 The physical properties of NO$_X$

In Chemical Engineering flowsheeting it is important to provide a rigorous way to calculate the properties of various streams. These include compositions, liquid/vapor equilibria, enthalpies, entropies, densities etc. Most flowsheeting programs provide a variety of models to calculate these. These models require parameters for every component in a stream.

For example, for liquid/vapor equilibria one needs an equation of state. A commonly used equation of state is the Redlich-Kwong equation:

$$ P = \frac{RT}{v-b_m} - \frac{a_m}{v(v+b_m)} $$

$$ a_m = \sum x_i \sqrt{a_i} $$

$$ b_m = \sum x_i b_i $$

(32)

where $T$ is the temperature, $v$ is the volume, $P$ is the pressure, $R$ is the gas-law constant, $x_i$ is the mole-fraction of component $i$, $T_{ci}$ is the critical temperature of component $i$ and $P_{ci}$ is the critical pressure of component $i$.

In order to use this equation, the critical properties of all the components involved have to be provided.

ASPEN PLUS provides a databank for the properties of the often used chemical components. An additional package, the DIPPR-databank provides the properties of more than a thousand components. Unfortunately, none of the databanks has information about the components HNO$_2$ and N$_2$O$_3$. These where just the components that were used in the additional series of reactions for the NO$_X$-model. Literature was searched for the necessary properties, but only limited information could be found. Table 4 summarizes the various constants for HNO$_2$ and N$_2$O$_3$ that were used for simulating the NO$_X$ absorption.
Absorption of NO$_x$ in Water

Table 4
Values for the pure component data for HNO$_2$ and N$_2$O$_3$ used in the ASPEN PLUS simulation of the NO$_x$ absorption.

<table>
<thead>
<tr>
<th>ASPEN name</th>
<th>Description</th>
<th>value for</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HNO$_2$</td>
<td>N$_2$O$_3$</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
<td>47</td>
<td>76</td>
</tr>
<tr>
<td>DHFORM</td>
<td>Standard heat of formation $^*$ [J/kmol]</td>
<td>$-79.53 \times 10^6$</td>
<td>$83.72 \times 10^6$</td>
</tr>
<tr>
<td>DGFORM</td>
<td>Standard energy of formation $^*$ [J/kmol]</td>
<td>$-46.05 \times 10^6$</td>
<td>$139.41 \times 10^6$</td>
</tr>
<tr>
<td>TB</td>
<td>Normal boiling point [K]</td>
<td>295.7</td>
<td>263</td>
</tr>
<tr>
<td>TC</td>
<td>Critical temperature [K]</td>
<td>444.3</td>
<td>400</td>
</tr>
<tr>
<td>PC</td>
<td>Critical pressure [Pa]</td>
<td>$58 \times 10^5$</td>
<td>$80 \times 10^5$</td>
</tr>
<tr>
<td>VC</td>
<td>Critical volume [m$^3$/kmol]</td>
<td>0.160</td>
<td>0.102</td>
</tr>
<tr>
<td>ZC</td>
<td>Critical compressibility factor</td>
<td>0.2516</td>
<td>0.2456</td>
</tr>
<tr>
<td>OMEGA</td>
<td>Pitzer acentric factor</td>
<td>0.493</td>
<td>0.567</td>
</tr>
<tr>
<td>PLXANT</td>
<td>Antoine vapor-pressure constants $\ln(p)=A+B/T+C \ln(T)+D T^E$ $F &lt; T &lt; G$ $T$ in [K], $p$ in [Pa]</td>
<td>$A=21.008$</td>
<td>$22.3847$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B=-3000$</td>
<td>$-2996.36$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C=-3 \times 10^{-6}$</td>
<td>$9.672 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D=8 \times 10^{-6}$</td>
<td>$7 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E=2$</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$F=275$</td>
<td>275</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G=340$</td>
<td>340</td>
</tr>
<tr>
<td>DHVLWT</td>
<td>Heat of vaporization [J/kmol]</td>
<td>$39 \times 10^6$</td>
<td>$39.3 \times 10^6$</td>
</tr>
<tr>
<td>HENRY</td>
<td>Henry’s constant $\ln(h)=A+B/T+C \ln(T)$ $T$ in [K], $h$ in [Pa]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A=27.56$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$B=-2873$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$C=-0.303$</td>
<td></td>
</tr>
<tr>
<td>GMELCC/</td>
<td>Electrolyte-Molecule binary parameters (NRTL) $H_2O^{(1)}, H_3O^+NO_2^{-(2)}, HNO_2^{(3)}$</td>
<td>$1-2$ 7.078 - 154.4</td>
<td>-</td>
</tr>
<tr>
<td>GMELCD</td>
<td></td>
<td>$2-1$ 3.296 - 215.3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3-2$ 7.543 - 447.7</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2-3$ 2.984 - 225.3</td>
<td>-</td>
</tr>
</tbody>
</table>

Ideal gas at 298.2 K
Absorption of NO\(_x\) in Water

Where possible values from literature were used. If not available, a recommended correlation equation was used that could predict the constant on the basis of molecular groups. If all else failed the values of corresponding components (HNO\(_2\)/HNO\(_3\) and N\(_2\)O\(_3\)/N\(_2\)O\(_4\)) were substituted.

To estimate the critical constants, Joback’s group contribution method was used (Reid, 1987). The relations Joback used to estimate the critical constants are:

\[
T_c = \frac{T_b}{0.584 + 0.965 \Sigma \Delta_T - (\Sigma \Delta_p)^2}
\]

\[
P_c = \frac{1}{(0.113 + 0.0032 n_A - (\Sigma \Delta_p)^2)}
\]

\[
V_c = 17.5 + \Sigma \Delta_v
\]

where \(T_B\) is the normal boiling temperature,
\(\Delta_T, \Delta_p, \Delta_v\) are group contributions for the critical properties and
\(n_A\) is the number of atoms in the molecule.

For the boiling and freezing points a very rough estimation can be made by:

\[
T_b = 198 + \Sigma \Delta_b
\]

\[
T_f = 122 + \Sigma \Delta_f
\]

where \(T_b, T_f\) are the boiling and freezing point in Kelvins.

The same functional groups can be used to estimate the enthalpy of formation and the Gibbs free energy of formation:

\[
\Delta H_f^o(298\, \text{K}) = 68.29 + \Sigma \Delta_H
\]

\[
\Delta G_f^o(298\, \text{K}) = 53.88 + \Sigma \Delta_G
\]

\[
C_p^o = (\Sigma \Delta_a - 37.93) + (\Sigma \Delta_b + 0.210) T + (\Sigma \Delta_c - 3.91 \times 10^{-4}) T^2 + (\Sigma \Delta_d + 2.06 \times 10^{-7}) T
\]

where \(H_f^o\) is the enthalpy of formation at 298 Kelvin [kJ/mol],
\(G_f^o\) is the Gibbs free energy of formation at 289 Kelvin [kJ/mol] and
\(C_p^o\) is the ideal gas heat capacity [J/mol.K].

The group contributions used to estimate the pure component data for HNO\(_2\) and N\(_2\)O\(_3\) are summarized in table 5. It must be stated that although the Joback group contribution method is not explicitly designed for organic components the results will be less accurate for inorganic components.
Table 5
Group contributions for the Joback method for estimating pure component constants.

<table>
<thead>
<tr>
<th>Group</th>
<th>Tc</th>
<th>Pc</th>
<th>Vc</th>
<th>Tb</th>
<th>Tt</th>
</tr>
</thead>
<tbody>
<tr>
<td>-N=</td>
<td>0.0255</td>
<td>-0.0099</td>
<td>0</td>
<td>74.6</td>
<td>0</td>
</tr>
<tr>
<td>-NO2</td>
<td>0.0437</td>
<td>0.0064</td>
<td>91</td>
<td>152.54</td>
<td>127.24</td>
</tr>
<tr>
<td>=O</td>
<td>0.0143</td>
<td>0.0101</td>
<td>36</td>
<td>-10.5</td>
<td>2.08</td>
</tr>
<tr>
<td>&gt;NH</td>
<td>0.0295</td>
<td>0.0077</td>
<td>35</td>
<td>50.17</td>
<td>52.66</td>
</tr>
</tbody>
</table>

Table 6 summarizes the results for the estimations of the pure component data for HNO₂ and N₂O₃. Estimations are also made for HNO₃ and N₂O₄. From table 6 it can be concluded that the Joback method is not very accurate here and only the values for the critical temperature are comparable. The differences for the critical temperature vary between the 2% and 5%, but values for the critical volume and pressure vary for more than 20%. Unfortunately Joback’s method is the only method one can use in this case, if critical data are needed.

It is another problem to find a relation for the vapor pressure of HNO₂ and N₂O₃. ASPEN PLUS uses the DIPPR equation or an extended Antoine equation. The DIPPR equation to calculate the vapor pressure is:

\[
\ln(P) = C_1 + \frac{C_2}{T} + C_3 \ln(T) + C_4 T C_5 .
\]

The coefficients for the DIPPR equation (C₁ to C₅) were derived by estimating the vapor pressure at several temperatures. Then the DIPPR-constants could be fitted to match these vapor pressures.
Absorption of NO\textsubscript{x} in Water

Table 6

Estimations of pure component data for HNO\textsubscript{2} and N\textsubscript{2}O\textsubscript{3}, compared to the values for HNO\textsubscript{3} and N\textsubscript{2}O\textsubscript{4}.

<table>
<thead>
<tr>
<th></th>
<th>HNO\textsubscript{3}</th>
<th>HNO\textsubscript{2}</th>
<th>N\textsubscript{2}O\textsubscript{4}</th>
<th>N\textsubscript{2}O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_C) [K]</td>
<td>estimated</td>
<td>539</td>
<td>455</td>
<td>457</td>
</tr>
<tr>
<td></td>
<td>literature</td>
<td>520</td>
<td>444.3</td>
<td>431</td>
</tr>
<tr>
<td>(V_C) [cc/mol]</td>
<td>estimated</td>
<td>180</td>
<td>144</td>
<td>199.5</td>
</tr>
<tr>
<td></td>
<td>literature</td>
<td>145</td>
<td>-</td>
<td>82.5 ((=V_C) NO\textsubscript{2})</td>
</tr>
<tr>
<td>(P_C) [bar]</td>
<td>estimated</td>
<td>91</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>literature</td>
<td>68.9</td>
<td>-</td>
<td>101.3 ((P_C) NO\textsubscript{2})</td>
</tr>
<tr>
<td>(T_b) [K]</td>
<td>estimated</td>
<td>390</td>
<td>401</td>
<td>503</td>
</tr>
<tr>
<td></td>
<td>literature</td>
<td>356.15</td>
<td>295.7</td>
<td>302</td>
</tr>
<tr>
<td>(C_p) (298 K)</td>
<td></td>
<td>60.0</td>
<td>46.7</td>
<td>63.2</td>
</tr>
</tbody>
</table>

Values from literature include DIPPR-databank, Joshi 1985 and Thieman 1891

The methods used for estimating the vapor pressure are the Clapeyron and the Gomez-Thodos equation. For the Clapeyron equation one can derive (Reid, 1987):

\[
\ln(P) = \frac{T_b \ln\left(\frac{P_C}{101325}\right) \left(1 - \frac{T_C}{T}\right)}{T_C \left(1 - \frac{T_b}{T_C}\right)}. \tag{37}
\]
The Gomez-Thodos equation is somewhat more complicated and for polar components it can be written as:

\[
\ln(P) = \beta \left[ \frac{1}{T_r^*} - 1 \right] + \gamma \left[ T_r^* - 1 \right]
\]

with:

\[
T_r = \frac{T}{T_c}
\]

\[
\gamma = a h + b \beta
\]

\[
a = \frac{1 - \frac{1}{T_b^*}}{T_b^* - 1}
\]

\[
b = \frac{1 - \frac{1}{T_b^*}}{T_b^* - 1}
\]

\[
m = 0.466 T_C^{0.166}
\]

\[
\gamma = 0.08594 \exp(7.46210^{-4} T_C)
\]

Vapor pressures calculated with this equation are reasonably good (if supplied with the right critical and boiling temperature) and the DIPPR equation constants used in the ASPEN PLUS simulation, are derived from calculated data with the Gomez-Thodos equation. The DIPPR equation constants are mentioned in table 4.

### 3.2 The electrolyte NRTL model

As stated in chapter 2 the nitrous acid formed in the gas-phase and the nitric acid formed in the liquid phase, dissolve both in the water. Nitric acid is a strong acid and it dissociates almost completely in H$_3$O$^+$ and NO$_3^-$ . Nitrous acid is a weak acid, so it dissociates only partly in H$_3$O$^+$ and NO$_2^-$ . The acid dissociation constant for HNO$_2$ (K$_a$=[H$_3$O$^+$][NO$_2^-$]/[HNO$_2$]) at 298 Kelvin is 4.7 $10^{-4}$ mol/l (Jansen, 1977).

This solution chemistry (dissociation of the nitric/nitrous acid) has major effects on the process simulation of the NO$_x$ absorption. It affects physical properties, phase equilibria and other characteristics of the electrolyte system.

ASPEN PLUS can treat electrolytes in two ways, the true component and the apparent component approach (ASPEN PLUS, 1988). If the following reactions are considered:

\[
\begin{align*}
2 \text{H}_2\text{O} & = \text{H}_3\text{O}^+ + \text{OH}^- \\
\text{HNO}_3 + \text{H}_2\text{O} & = \text{H}_3\text{O}^+ + \text{NO}_3^- \\
\text{HNO}_2 + \text{H}_2\text{O} & = \text{H}_3\text{O}^+ + \text{NO}_2^- ,
\end{align*}
\]

(39)

than all the components shown in the above reactions exist at chemical equilibrium conditions and are the true species of the electrolyte system. The components before considering solution chemistry effects (H$_2$O, HNO$_3$ and HNO$_2$) are the apparent
components of the electrolyte system. The selection of apparent components or true species depends on the type of electrolyte system to be simulated. In this case the true species approach is chosen for the NO$_X$ absorption.

An important characteristic of an electrolyte system is the highly non-ideal liquid phase thermodynamic behavior caused by the presence of ionic species. Special thermodynamic electrolyte models are needed for accurate representation of the deviations from ideal solution behavior.

The chemical equilibrium relationship for reaction $j$ is expressed as:

$$\ln(K_j) = \sum_i v_{ij} \ln(a_i),$$

(40)

where $K_j$ is the chemical equilibrium constant for reaction $j$, $v_{ij}$ is the stoichiometric coefficient for reaction $j$ and component $i$ and $a_i$ is the activity of component $i$.

These equilibrium relationships must be solved simultaneously with the component balances to calculate the liquid phase true species compositions. Both equation-solving and free energy minimization approaches may be applied to solve the solution chemistry.

The most critical properties in flowsheet simulation are the activity coefficients, which determine the flowrates, compositions and phases involved. Many models have been developed on the basis of semi-empirical extensions of the Debye-Hückel expression for the excess Gibbs energy. The excess Gibbs energy defined as:

$$G^e = RT \sum_i n_i \ln(\gamma_i),$$

(41)

is related to the activity coefficient $\gamma_i$ of a component by applying the Gibbs-Duhem equation on (41) (Reid, 1987):

$$RT \ln(\gamma_i) = \left( \frac{\partial G^e}{\partial n_i} \right)_{T,P,n_{<i>}}.$$

(42)

The ion interaction model of Pitzer has proved specially useful. It yields accurate results for aqueous solutions properties up to six-molal concentration (Ball, 1985). The Pitzer model - incorporated in ASPEN PLUS - is a virial expansion equation. The model requires second-order parameters at low concentrations and both second- and third-order parameters at high concentrations. It provides a thermodynamically consistent model capable of representing electrolyte nonideality accurately for many aqueous electrolyte systems.

The electrolyte NRTL (Non-Random Two Liquid) model provides another thermodynamically consistent model for aqueous electrolyte systems. This equation was developed with the local composition concept similar to the Renon NRTL model (Ball, 1985). With only binary parameters, the equation satisfactorily represents physical interactions of true species in aqueous electrolyte systems and multicomponent,
Absorption of NO\textsubscript{x} in Water

multisolvent electrolyte systems. For infinite diluted systems the equation reduces to the Debye-Hückel model, for non-electrolyte systems it reduces to the Renon NRTL model, and it predicts pure fused salts. It provides a connection between all these limiting systems.

The electrolyte NRTL model is based on two basic assumptions:
- The like-ion repulsion. It states that the local composition of cations around cations is zero (and also for the composition of anions around anions). This implies that the repulsive forces between ions of like charge are extremely large.
- The local electroneutrality. That states that the distribution of cations and anions around a central molecular species is such that the net local ionic charge is zero.

The equation for the excess Gibbs energy has three terms, two for the long-rang ion-ion interactions (Pitzer-Debye-Hückel and Born model) and one to represent the local interactions (NRTL). The following expression for the excess Gibbs energy is used:

\[
\frac{G^E}{RT} = \frac{G^E_{\text{Pitzer-Debye-Hückel}}}{RT} + \frac{G^E_{\text{Born}}}{RT} + \frac{G^E_{\text{NRTL}}}{RT}.
\]  

For a detailed description of the electrolyte NRTL model see the ASPEN PLUS electrolyte manual (1988).

3.3 Modeling a reactive absorption with ASPEN PLUS

For this research project ASPEN PLUS was used to model the NO\textsubscript{x} absorption. Although ASPEN PLUS does not incorporate all the demands, it is a flexible simulator with many options and rigorous thermodynamic capabilities.

ASPEN PLUS is a steady-state sequential modular flowsheet simulator. It runs on several hardware platforms like PC's, VAX's, unix-workstations and mainframes. Interoperability is assured because the program works with ASCII input files and writes its results to report files, also in ASCII format. An ASPEN PLUS input-file is build from several keywords and specifications. There is also another program 'ModelManager' that simplifies the task of making an input-file. This is an expert-based program that uses forms to define the flowsheet and then generates an input-file for the simulation program.

The input-file for the NO\textsubscript{x} absorption can be divided in several parts. First there is some global information in it like the title, a description, what kind of units to use globally and the maximum time the computer may spend on the calculations. Figure 7 shows these aspects in ASPEN PLUS 'language'. The next step is the specification of the components together with the databanks to be used (figure 8).

In this case the DIPPR databank is used for all components. Only N\textsubscript{2}O\textsubscript{3} has no entry in de DIPPR databank which is marked with a *. The AQUEOUS databank provides the data for NO\textsubscript{2} and NO\textsubscript{3}+. Automatically the BINARY databank is used to provide the necessary Henry's gas-law constants for the light gases.
Absorption of NO\textsubscript{X} in Water

**Figure 7**
Global information about the flowsheet

<table>
<thead>
<tr>
<th>DATABASES DIPPRPCD</th>
<th>AQUEOUS</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMPONENTS</td>
<td></td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>H\textsubscript{2}O /</td>
</tr>
<tr>
<td>H\textsubscript{NO}3</td>
<td>H\textsubscript{NO}3 /</td>
</tr>
<tr>
<td>H\textsubscript{3}O\textsuperscript{+}</td>
<td>H\textsubscript{3}O\textsuperscript{+} /</td>
</tr>
<tr>
<td>N\textsubscript{O}3\textsuperscript{-}</td>
<td>N\textsubscript{O}3\textsuperscript{-} /</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>N\textsubscript{2} /</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>O\textsubscript{2} /</td>
</tr>
<tr>
<td>N\textsubscript{O}</td>
<td>N\textsubscript{O} /</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{2}</td>
<td>N\textsubscript{2}O\textsubscript{2} /</td>
</tr>
<tr>
<td>H\textsubscript{NO}2</td>
<td>H\textsubscript{NO}2 /</td>
</tr>
<tr>
<td>N\textsubscript{O}2\textsuperscript{-}</td>
<td>N\textsubscript{O}2\textsuperscript{-} /</td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{3}</td>
<td>* N\textsubscript{2}O\textsubscript{3}</td>
</tr>
</tbody>
</table>

**Figure 8**
Definition of the components and databanks.

<table>
<thead>
<tr>
<th>PROPERTIES SYSOP15M HENRY-COMPS\textsuperscript{GAS} CHEMISTRY\textsuperscript{HNOX} TRUE-COMPS\textsuperscript{YES}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HENRY-COMPS GAS N\textsubscript{2} O\textsubscript{2} N\textsubscript{O} N\textsubscript{2}O\textsubscript{4} N\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>CHEMISTRY HNOX PARAM KBASIS\textsuperscript{MOLAL}</td>
</tr>
<tr>
<td>STOIC 1 H\textsubscript{NO}3 -1 / H\textsubscript{2}O -1 / H\textsubscript{3}O\textsuperscript{+} 1 / N\textsubscript{O}3\textsuperscript{-} 1</td>
</tr>
<tr>
<td>K-STOIC 1 15.098 -738.88 0 -0.031534</td>
</tr>
<tr>
<td>STOIC 2 H\textsubscript{NO}2 -1 / H\textsubscript{2}O -1 / H\textsubscript{2}O\textsuperscript{+} 1 / N\textsubscript{O}2\textsuperscript{-} 1</td>
</tr>
</tbody>
</table>

**Figure 9**
Thermodynamic section of the NO\textsubscript{X} input-file.

The next step is the formulation of the thermodynamics. In figure 9 the thermodynamics is defined for the NO\textsubscript{X} absorption.

It contains a line with the thermodynamic model (SYSOP15M=electrolyte NRTL) to be used, it refers to a paragraph with the dissociation reactions (CHEMISTRY HNOX), it defines the light gases in the system (HENRY-COMPS GAS) and it activates the true species approach. For the dissociation of H\textsubscript{NO}3 it contains the dissociation constants for this equilibrium.
Absorption of NO\textsubscript{x} in Water

The equilibrium constant is calculated by:

$$\ln(K_{eq}) = C_1 + \frac{C_2}{T} + C_3 \ln(T) + C_4 T.$$  \hspace{1cm} (44)

The dissociation of H\textsubscript{N}O\textsubscript{2} is calculated by means of minimization of free energy. Henry components are specified to calculate the amount of light gases that dissolve in the aqueous phase.

The next step is to supply all the data that is needed by the ASPEN PLUS program for its thermodynamic calculations. Therefore, a PROP-DATA paragraph is needed. Figure 10 shows how all the pure component data and the thermodynamic data is entered in the input-file. The meaning of the different keywords is explained in table 4.

<table>
<thead>
<tr>
<th>PROP-DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN-UNITS SI</td>
</tr>
<tr>
<td>PROP-LIST MW</td>
</tr>
<tr>
<td>PVAL N203 76</td>
</tr>
<tr>
<td>PROP-LIST VLBROC / DHFORM / DGFORM</td>
</tr>
<tr>
<td>PVAL HN03 0.041771 / -135.06E6 / -74.72E6</td>
</tr>
<tr>
<td>PVAL N203 * / 83.72E6 / 139.41E6</td>
</tr>
<tr>
<td>PVAL HNO2 * / -79.53E6 / -46.05E6</td>
</tr>
<tr>
<td>PROP-LIST TB / TC / PC / VC / ZC / OMEGA</td>
</tr>
<tr>
<td>PVAL HN03 356.15 / 520 / 68.901E5 / 0.145 / 0.231 / 0.7144</td>
</tr>
<tr>
<td>PVAL HNO2 295.7 / 444.3 / 58E5 / 0.160 / 0.2516 / 0.493</td>
</tr>
<tr>
<td>PVAL N203 263 / 400 / 80E5 / 0.102 / 0.2456 / 0.567</td>
</tr>
<tr>
<td>PROP-LIST PLXANT</td>
</tr>
<tr>
<td>PVAL H20 72.55 / -7206.7 0 0 -7.1365 4.046E-6 2</td>
</tr>
<tr>
<td>PVAL HN03 -281.8727 0 0 -1.1358019 58.15114 0 0 231.55 376.1</td>
</tr>
<tr>
<td>PVAL HNO2 21.00814 / -3000 0 0 -3E-6 8E-6 2 275 340</td>
</tr>
<tr>
<td>PVAL N203 22.3847 / -2996.63 0 0 9.672E-3 7E-6 2 275 340</td>
</tr>
<tr>
<td>PROP-LIST CPIG / DHVLWT</td>
</tr>
<tr>
<td>PVAL HN03 356.15 / 520 / 68.901E5 / 0.145 / 0.231 / 0.7144</td>
</tr>
<tr>
<td>PVAL HNO2 45606 / 39E6 298.15</td>
</tr>
<tr>
<td>PVAL N203 66605 / 39.3E5 263</td>
</tr>
<tr>
<td>PROP-LIST DGAOFM / CPAQ0</td>
</tr>
<tr>
<td>PVAL N03- -1.0874E8 / -86600.0 591.8</td>
</tr>
<tr>
<td>PROP-LIST HENRY</td>
</tr>
<tr>
<td>BPVAL N02 H20 30.5647 / -2872.96 / -.30288 / .0 283.0 386.0</td>
</tr>
<tr>
<td>BPVAL N204 H20 27.5647 / -2872.96 / -.30288 / .0 283.0 386.0</td>
</tr>
<tr>
<td>BPVAL N203 H20 27.5647 / -2872.96 / -.30288 / .0 283.0 386.0</td>
</tr>
<tr>
<td>PROP-LIST GMELOCC / GMELOC</td>
</tr>
<tr>
<td>PPVAL H20 ( H3O+ NO3- ) 7.0780 / 154.4</td>
</tr>
<tr>
<td>PPVAL ( H3O+ NO3- ) H20 -3.2960 / -215.7</td>
</tr>
<tr>
<td>PPVAL HNO3 ( H3O+ NO3- ) 7.5430 / 447.7</td>
</tr>
<tr>
<td>PPVAL ( H3O+ NO3- ) HNO3 -2.9840 / -225.3</td>
</tr>
<tr>
<td>PPVAL H20 ( H3O+ NO2- ) 7.0780 / 154.4</td>
</tr>
<tr>
<td>PPVAL ( H3O+ NO2- ) H20 -3.2960 / -215.7</td>
</tr>
<tr>
<td>PPVAL N02 ( H3O+ NO2- ) 7.5430 / 447.7</td>
</tr>
<tr>
<td>PPVAL ( H3O+ NO2- ) HNO2 -2.9840 / -225.3</td>
</tr>
</tbody>
</table>

Figure 10
Specification of all pure component and thermodynamic data.

Reactive absorption with ASPEN PLUS page 29
Absorption of NO\textsubscript{x} in Water

<table>
<thead>
<tr>
<th>FLOWSHEET</th>
<th>BLOCK TOWER IN=WATER NOX-GAS OUT=TAIL-GAS RAW-ACID</th>
</tr>
</thead>
<tbody>
<tr>
<td>STREAM NOX-GAS TEMP=40.0 PRES=11.0</td>
<td></td>
</tr>
<tr>
<td>MOLE-FLOW H\textsubscript{2}O 9.0 /</td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{2} 1680.0 /</td>
<td></td>
</tr>
<tr>
<td>O\textsubscript{2} 105.0 /</td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{0} 27.0 /</td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{0}\textsubscript{2} 71.0 /</td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{2}O\textsubscript{4} 28.0</td>
<td></td>
</tr>
</tbody>
</table>

| STREAM WATER TEMP=20.0 PRES=11.0 |
| MOLE-FLOW H\textsubscript{2}O 400.0 |

**Figure 11**

*Specification of the flowsheet connectivity and feed-streams*

Next, the specification of the flowsheet connectivity (in this case only one column) and the specification of the streams is to be entered. The flowsheet contains one unit-operation block named TOWER. Two streams enter this equipment NOX-GAS and WATER and two streams leave this equipment, TAIL-GAS and RAW-ACID. The specifications for the two streams entering the absorption tower are given in figure 11.

Figure 12 shows the final specifications for the ASPEN PLUS input-file. It contains the specifications for the absorption column and the reactions occurring on each stage. The RADFRAC model of ASPEN PLUS is used because this model allows cooling on each stage. The PARAM sentence is used to enter the number of equilibrium trays in the column. It is also possible to specify the convergence method and maximum number of iterations in this sentence. Several combinations of convergence methods and maximum iteration options have been tried and overall the NEWTON option has proved to be most successful although it takes more time to converge. The FEEDS, PRODUCTS sentences specify on which tray the feeds and products enter or leave the column. The P-SPEC sentence specifies the column pressure. The COL-SPECS are used to enter the necessary specification for the column. In this case the column has no specifications because it is an absorber without condenser or reboiler. Because the absorber needs coolant on each tray the COL-SPECS include a negative duty. ASPEN PLUS lacks the feature to specify stage temperature and to vary the stage duty. This problem can be mastered by using the COOLANT option of RADFRAC. A coolant (water) is used with an unreasonable high flowrate, so the temperature of the stage will be almost the same as the coolant temperature. The T-EST sentence gives an estimation of the tray temperatures on top and bottom of the column. The REAC-STAGES sentence specifies on which trays the reactions take place (in this case on every tray). Finally the holdup for the vapor and liquid phase is specified in the HOLD-UP sentence, which is needed by the kinetic reactions.
Absorption of NO\textsubscript{x} in Water

<table>
<thead>
<tr>
<th>BLOCK TOWER RADFRAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARAM</td>
</tr>
<tr>
<td>NSTAGE=10 ALGORITHM=NEWTON MAXOL=50 MAXIL=20 &amp;</td>
</tr>
<tr>
<td>FLASH-MAXIT=200 DSMETH=NESTED</td>
</tr>
<tr>
<td>DIAG</td>
</tr>
<tr>
<td>MAIN=8 OLVAR1=4 OLVAR2=4 CMBAL=4 EMBAL=4</td>
</tr>
<tr>
<td>FEEDS</td>
</tr>
<tr>
<td>WATER 1 / NOX-GAS 11</td>
</tr>
<tr>
<td>PRODUCTS</td>
</tr>
<tr>
<td>TAIL-GAS 1 V / RAW-ACID 10 L</td>
</tr>
<tr>
<td>P-SPEC</td>
</tr>
<tr>
<td>1 11.0</td>
</tr>
<tr>
<td>COL-SPECS</td>
</tr>
<tr>
<td>Q1=-387 QN=-670780 MOLE-RDV=1.0</td>
</tr>
<tr>
<td>COOLANT</td>
</tr>
<tr>
<td>1 H2O TEMP=25.1 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>2 H2O TEMP=27.3 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>3 H2O TEMP=28.3 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>4 H2O TEMP=28.8 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>5 H2O TEMP=29.2 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>6 H2O TEMP=29.6 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>7 H2O TEMP=30.4 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>8 H2O TEMP=33.1 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>9 H2O TEMP=36.4 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>10 H2O TEMP=37.4 MOLE-FLOW=1E12 UA=1E10 PRES=1</td>
</tr>
<tr>
<td>T-EST</td>
</tr>
<tr>
<td>1 25.1 / 10 37.4</td>
</tr>
<tr>
<td>REAC-STAGES</td>
</tr>
<tr>
<td>1 10 NITRIC</td>
</tr>
<tr>
<td>HOLD-UP</td>
</tr>
<tr>
<td>1 10 VOL-VHLDP=6500 VOL-LHLDP=20</td>
</tr>
</tbody>
</table>

REATIONS NITRIC

| REAC-DATA | 1 KINETIC V CBASIS=MOLEFRAC |
| STOIC     | 1 O2 -1 / NO -2 / NO2 2 |
| RATE-CON  | 1 5594.16 -2284.306 -1 |
| POWLAW-EXP| 1 O2 1 / NO 2 |
| REAC-DATA | 2 EQUIL V KBASIS=P |
| STOIC     | 2 NO2 -2 / N2O4 1 |
| K-STOIC   | 2 -33 6891 |
| REAC-DATA | 3 EQUIL V KBASIS=P |
| STOIC     | 3 NO -1 / NO2 -1 / N2O3 1 |
| K-STOIC   | 3 -28.183 4771 |
| REAC-DATA | 4 EQUIL V KBASIS=P |
| STOIC     | 4 NO -1 / NO2 -1 / H2O -1 / HNO2 2 |
| K-STOIC   | 4 -27.029 4723 |
| REAC-DATA | 5 EQUIL L KBASIS=MOLAL |
| STOIC     | 5 HNO3 -1 / H2O -1 / HNO3 1 / NO3 -1 |
| REAC-DATA | 6 EQUIL L |
| STOIC     | 6 HNO2 -1 / H2O -1 / HNO2 1 / NO2 -1 |
| REAC-DATA | 7 KINETIC L CBASIS=MOLAR |
| STOIC     | 7 N2O4 -1 / H2O -1 / HNO3 1 / HNO2 1 |
| RATE-CON  | 7 2.19533E16 18938.8 |
| POWLAW-EXP| 7 N2O4 1 |
| REAC-DATA | 8 KINETIC L CBASIS=MOLAR |
| STOIC     | 8 HNO2 -3 / HNO3 1 / H2O 1 / NO 2 |
| RATE-CON  | 8 1.5E8 28369.3 |
| POWLAW-EXP| 8 HNO2 4 / NO -2 |

Figure 12
Specification of the absorption tower with the reactions.

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Absorption of NO\textsubscript{X} in Water

The most important (interesting) paragraph contains the reaction model. Eight reactions are specified here. The kinetic reactions contain the reaction stoichiometrics in the STOIC sentence. The rate constants are specified in the RATE-CON sentence. ASPEN PLUS uses the following (Power-Law) rate equation:

\[ \text{rate} = \text{holdup } C_1 \exp\left(\frac{-C_2}{RT}\right) T^{C_3} \prod l a_i^{x_i}. \] (45)

Extra attention must be paid to the value of the gas-law constant \( R \) who has the units \([\text{cal/mol.K}]\) in this case and equals to 1.9872. The order of the kinetic reaction is stated in the POWLAW-EXP sentence where the components in the last part of (45) and its exponent are specified. The description of the constants for the equilibrium reaction is given in (44). For all sentences the KBASIS keyword (or CBASIS) specifies in what units the components are used in the equations for the equilibria or reaction rates.

When all previous parts of the ASPEN PLUS input-file are combined then a complete simulation model is build for the simulation of NO\textsubscript{X} absorption with ASPEN PLUS. Results for this simulation will be discussed later.

3.4 Modeling NO\textsubscript{X} absorption with ASPEN RATEFRAC

Recently AspenTech has released an additional package called RATEFRAC that can be used in ASPEN PLUS. This package consists of a unit operation block called RATEFRAC that is comparable with the RADFRAC unit operation model.

It offers a rate based approach to distillation. RATEFRAC describes the simultaneous mass and heat transfer rate phenomena and for reactive systems it includes the influence of reactions on transfer processes. The supplied models to calculate mass transfer, heat transfer, interfacial area and pressure drop, can be replaced by user routines written in FORTRAN.

The advantage of such an approach is that empirical factors like Murphree efficiencies and HETPs (Height Equivalent to a Theoretical Plate) are not needed anymore. For reactive systems supplying efficiencies with the RADFRAC model was not possible. Due to a late arrival of this package no NO\textsubscript{X} simulations could be completed.
4 Stochastic simulation

After the introduction of the digital computer in engineering, simulation - and in this case process simulation - has become a very popular and useful tool in engineering design and optimization. As the computers became faster and more advanced, methods like stochastic simulation became popular. It must be notified that this simulation tool is very popular in physics and molecular chemistry, but is rarely used in process simulation.

The term Stochastic simulation is often used synonymously with Monte-Carlo simulation. The term Monte-Carlo simulation originates from World War II, were it was used for the stochastic simulation of atomic collisions. Although the two terms are often interchanged, Monte-Carlo simulation has a more specialized meaning like "doing something clever and stochastic with simulation" (Ripley, 1987). This may involve simulation of a system different then the one under study or to simulate with a stochastic model for a deterministic system.

So stochastic simulation is the simulation of a system that is stochastic by nature, or the simulation of a system where the model describing the system has stochastic elements. How stochastic simulation fits in process simulation and primary in ASPEN PLUS is described in this chapter.

4.1 Stochastic process simulation

When an element is stochastic, the value of that element has no explicit value. That means that the value of that element can vary in a specific domain and that it follows a frequency distribution.
Many model parameters by nature follow a normal distribution. Figure 13 is the density for a standard normal distribution. It represents the frequency of a normal distributed parameter with the value 0 as its estimate and a variance of 1. So if this parameter is stochastic varied then its frequency histogram could look like figure 15, which is a normal distributed parameter with mean 0 and variance 1.

To generate a value for a parameter which is normal distributed round its mean $m$ and with a variance $\sigma^2$ several methods can be used. The most general way is to generate a random number between 0 and 1 for the distribution in figure 14 and to determine the corresponding 'x-value' ($x$). The generated value can be calculated by:

$$\text{value} = m + \sigma \cdot x$$  \hspace{1cm} (46)

If the estimation has to be done numerically (as will be the case mostly) the method of Box-Muller can be used (Ripley, 1987):

$$\text{value} = m + \sigma \left( \sqrt{-2 \ln(\text{random})} \ \text{cos}(2\pi \cdot \text{random}) \right)$$  \hspace{1cm} (47)

where 'random' are two random numbers between 0 and 1.

Conventional simulation models or simulators implement a program that produces deterministic results for a particular set of model parameters. Such an approach can be done at a simple way, however, it often results in the addition of large safety or "fudge" factors to accommodate the reality of uncertainty in equipment or process design. Chemical plants are usually faced with uncertain conditions during their operation. These uncertainties can originate from variations either in external parameters, for example the quality of feed streams, or from internal process parameters such as physical properties, kinetic constants and transfer coefficients. If a design is new, then there are additional uncertainties due to limited performance data.
To analyze uncertainty, the capability to perform sensitivity analysis through a series of multiple runs is usually available. However, if the number of parameters becomes large the interpretation of the results needs insight in many dimensions. Then it is possible to overlook important interactions. Also the enormous volume of output data in sensitivity runs, makes this method cumbersome and difficult to interpret. In contrast with sensitivity analysis, stochastic simulation allows you to vary as many parameters as needed, all with their own distributions. A relatively small number of simulations are needed to get accurate results and the output-data can be sampled and presented in distribution histograms or cumulative distribution histograms.

For the problem of the absorption of NOX, the main concern was the uncertainty in the parameters used in the NOX absorption model. The parameters can be divided into three categories, first the uncertainty in the pure component data, especially the data that has been estimated for HNO2 and N2O3. Then there is the uncertainty in thermodynamic interaction parameters, the Henry constants for the gas solubility and the binary NRTL parameters. At last there is the uncertainty in the reaction constants. It is essential to get insight on how the different uncertainties affect the results of the simulation.
4.2 Incorporating stochastic simulation in ASPEN PLUS

Because the concept of stochastic simulation is rather new in process simulation, process simulators like ASPEN PLUS do not incorporate this method of simulation. If stochastic simulation had to be appended to the ASPEN PLUS program, Fortran code should be added with the same functionality as for example a sensitivity block. Here one can select the stochastic parameters and the results that have to be monitored for each simulation. Perhaps this functionality will be built in later but for this research project an other solution was developed.

Fortunately the ASPEN PLUS program works with ASCII input-files where the whole simulation model is specified, including the pure component data, interaction parameters and reaction constants. So it is not difficult to generate input-files with stochastic varied parameters.

Figure 16
Sketch of the hardware used for the stochastic simulation with ASPEN PLUS.

Figure 16 is an illustration of the hardware used to perform the stochastic simulation. ASPEN PLUS runs on an HP Apollo 9000/720 unix workstation. For convenience of the author the program that generates the input files runs under MSDOS on a PC. It is written in Turbo Pascal 6.0 and in such way that it is flexible in use and it can easily be adapted to other problems but the NO\textsubscript{X} absorption. The commented listing of the program is included in appendix A.
Absorption of NO\textsubscript{x} in Water

\begin{codebox}
\begin{verbatim}
start of program STOCHASP
read configuration file STOCHASP.CNF
- name of template file with the basic ASPEN PLUS run
- name of file with the parameters and their position in template file
- name of file with the results that have to be monitored
- name of file where the results will be written (in spreadsheet format)
- name of 'batch' file to start to perform an ASPEN PLUS run
- number of simulations to perform

parse the file containing the positions of the parameters that have to 
be varied

parse the file containing the positions of the results in the ASPEN PLUS 
summary file (the file that contains all simulation results)

call the 'batch' file to perform a basic run, use therefore the template 
file with no parameters varied

if converged, get the results from this simulation and write them to the 
results file

loop until all simulations have been done

  generate an input file with the template file as a basis, and the 
  stochastic parameters varied

  call the 'batch' file to perform an ASPEN PLUS run

  if converged, get the results from this simulation and write them 
to the results file
\end{verbatim}
\end{codebox}

\textbf{Figure 17}

\textit{PSD for stochastic simulation with ASPEN PLUS}

Figure 17 is a Program Structure Diagram (PSD) for the stochastic simulation with ASPEN PLUS. As can be seen in figure 16, the PC and the workstation by means of the network share the same disk drive, so input files generated on the PC can (after conversion from MSDOS to unix format) directly be used by the flowsheet simulator. A PC implementation of the unix rsh (remote-shell) command is used to start the ASPEN PLUS simulations from the PC program.

Results of the simulation are sampled in a LOTUS 123 spreadsheet format file. Each row contains the stochastic parameters and the results that have to be monitored. The spreadsheet has as many rows as simulations that have been performed. There is chosen for a spreadsheet format file, because these programs are very easy to use for digesting the data. In appendix B.1 to B.4 examples are added of a configuration file, a stochastic parameter file, a monitor file and a unix-script to run ASPEN PLUS.
4.3 Stochastic simulation of NO\textsubscript{X} absorption

The implementation should not be very difficult for the NO\textsubscript{X} absorption. It is obvious which parameters are uncertain and there is a tool to perform the simulations. There are several problems to cope with first. Table 4 gives an indication on which parameters are uncertain but there are very few indications about the amount of uncertainty, the standard deviation. For most parameters a guess has to be made to estimate the standard deviation. Sometimes the literature gives information on the experimental uncertainty of the parameter. Sometimes a correlation can be used which has a given accuracy of prediction, or finally it can be guessed by verifying the data with properties of well known components (like the critical constants of HNO\textsubscript{2}/HNO\textsubscript{3} and N\textsubscript{2}O\textsubscript{3}/N\textsubscript{2}O\textsubscript{4}). There is not yet a guide that can be inspected, with typical values for standard deviations for a variety of parameters in chemical engineering.

Figure 18 shows the contents of the stochastic parameter file used for the simulation of the NO\textsubscript{X} absorption. Most standard deviations are given in percentage of the default (mean) value. Some parameters (for example the critical constants of N\textsubscript{2}O\textsubscript{3}) are relatively more uncertain (10%) than others (critical constants for HNO\textsubscript{2}, 5%).

The variation of reaction constants (equilibrium and kinetic constants) introduces an extra problem. Until now the parameters, are supposed to be independent of each other. When one equation contains more parameters they are often dependant. For example the constants in kinetic and equilibrium equations are dependant. One way to overcome this problem is to write this equation in such way that the constants become (almost) independent, then vary these independent constants stochastic and then transform them back to the original constants. For the Arrhenius equation this can be done by introducing a reference temperature \( T_0 \) (preferably the temperature near the temperature where the measurements to determine the reaction rate are done) in the following way:

\[
\begin{align*}
  k &= A \ e^{-\frac{E}{RT}} \\
  \ln k &= \ln A - \frac{E}{RT} \\
  \ln k &= \alpha + \ln \left( \frac{E}{RT_0} \right) \\
  \frac{E}{RT_0} &= \beta + \ln \left( \frac{T}{T_0} \right) - 1 \\
  \ln k &= e^{\alpha} e^{-\beta \left( \frac{T}{T_0} - 1 \right)} \\
  e^{\alpha} &= e^{\ln \left( \frac{E}{RT_0} \right)} \\
  e^{\beta} &= e^{\ln \left( \frac{T}{T_0} - 1 \right)} \\
  e^\alpha - e^\beta &= e^{\alpha - \beta x}.
\end{align*}
\]

The \( \alpha \) and \( \beta \) in this formula can be stochasticly varied and the value of the activation energy and the pre-exponential value can be calculated backwards.

The implementation in STOCHASP is slightly different. Here an indication of the number of measurements, the temperature boundaries and the deviation from measurement must be supplied for the reaction constants. With this information, stochastic values for the Arrhenius constant and the pre-exponential factor are generated.

Stochastic simulation
Absorption of NO\textsubscript{x} in Water

Figure 18

Stochastic simulation page 39

contents of the file with stochastic parameters that have been varied for the simulation of NO\textsubscript{x} absorption.

Figure 19 demonstrates the effect when the Arhenius constant and pre-exponential factor are uncoupled, so the reaction rate constant is normal distributed.
Absorption of $NO_X$ in Water

Figure 19
Stochastic simulation of the reaction rate. The reaction constants are fictive and exaggerated to demonstrate the fact that the Arrhenius constant and pre-exponential factor are correctly varied.

4.4 Other uses of stochastic process simulation

In the stochastic simulation of $NO_X$ absorption it was the intention to translate the uncertainty in model parameters to uncertainty in the results. This is of course a sensible use of stochastic simulation and a lot of information can be retrieved with it. More uses for stochastic simulation has been mentioned previously and will be summarized in this paragraph.

Of great importance is the ability to simulate the stochastic variations in operating parameters and stream specifications like temperatures, pressures and compositions. This gives you the opportunity to detect processing limits and can be an aid in process optimization.

A more advanced approach would be the design and optimization of a process when uncertainties in operating parameters, stream, parameters and unit operation models are considered. For examples a design specification for a distillation column could be: 'given all uncertainties, estimate with a certainty of 95%, the number of required trays in a the distillation column.' In this way the possibility for overdesign is minimized.
Stochastic simulation can also be used in process economics (Holland, 1984). When estimating Discounted Cash Flow Rates of Return (DCFRR) and Net Present Values (NPV)\(^1\) of future projects, uncertainties in future sales volumes, interests and other parameters can be translated to uncertainties in the DCFRR and NPV. Probability data for these factors supports decisions whether to continue a project or not.

One last example for stochastic simulation is its use for testing flowsheet convergence. During a calculation the process simulators spend most of their time solving very large systems of equations. The user can enter convergence specifications which are used to determine if a system of equations is solved. Numerically it is possible for a specific system of equations to have multiple solutions or to have solutions which are insensitive for convergence specifications. By varying the estimations made in process simulation models, one can test the capability and precision of the flowsheet simulator.

---

\(^1\)The Discounted-Cash-Flow Rate of Return (DCFRR) and Net Present Value (NPV) of a project are defined at the following manner:

The Present Value (PV) of a future sum of money (F) after \(n\) years is given by:

\[
PV = F \cdot f_d
\]

\[
f_d = \frac{1}{(1+i)^n}
\]

where \(i\) is the interest rate. Thus cash flow in the early years of a project has a greater value than the same amount in the later years of a project. The annual discounted-cashflow (\(A_{DCF}\)) is related by the annual cash flow (\(A_{CF}\)) by:

\[
A_{DCF} = A_{CF} \cdot f_d
\]

The sum of the annual discounted cash flows over \(n\) years is known as the Net Present Value. The interest rate \(i\) which makes the NPV equal to 0 is called the Discounted-Cash-Flow Rate of Return.
5 Results of the simulations

Several simulations have been realised and they can be arranged in two categories. First there are the standard simulations. By this a simulation is meant with one given set of input parameters and then one solution. These include the simulation with the ASPEN model and the simulation with the Enhanced model. Secondly stochastic simulations have been completed with both models. For a stochastic simulation a set of simulations is done with stochastically varied input parameters. With the Enhanced model also stochastic simulations have been done to determine the influence of two classes of model parameters and the influence of stochastic varying operating parameters and feed compositions.

The results of both the standard as the stochastic simulations will be presented in this chapter. Statistical interesting observations will be given in the last part of this chapter.

5.1 The standard simulations

As discussed in chapter 2 there are several models one can formulate to define the reactions of NO\textsubscript{x} that take place on an absorption tray. For two models (ASPEN and Enhanced) simulations have been completed with ASPEN PLUS. The program cumulates its results in a report file which is added to this thesis in appendix C for the ASPEN model and appendix D for the enhanced model.

Several problems concerning the simulation of the Enhanced model have been resolved. Adding reactions to the ASPEN model showed that every additional reaction makes the simulation more difficult to converge. A practical limit of eight reactions could be implemented. The original ASPEN model used an user kinetics routine for the NO oxidation. The disadvantage of this approach is that no other kinetic reactions can be added to the model. The NO oxidation in the Enhanced model is taken to the input file where its kinetics is described with a standard powerlaw equation. One other disadvantage of the kinetic user routine for the NO oxidation is the empirical factor $\chi$ in this model ($\chi=0.5$) that accounted for the pressure and other 'effects' (Venkataraman, 1990). To be
Absorption of $\text{NO}_x$ in Water

able to converge the Enhanced model, the temperature had to be controlled in the column. Best results have been obtained by using the COOLANT option in a figurative way. By defining huge coolant flows on each tray, the temperatures could be fixed at the same temperature of the coolant. Some experiments with the different convergence methods in ASPEN PLUS have been done and the Newton method seemed to converge better than other methods.

In order to compare the results of the two simulations, the temperature profiles of the absorption columns for both simulation models have been fixed (figure 20). With fixed temperatures reaction rates only depend on tray composition.

![Temperature profile for absorption column](image)

**Figure 20**

Temperature profile in $\text{NO}_x$ absorption column for both ASPEN and Enhanced model.

First some dependent variables have to be chosen to compare the different models. One of the goals was to minimize the $\text{NO}_x$ flowrate out of the absorption column. It is interesting to examine the NO flowrate of the vapor phase on every tray. Another goal is to maximize the nitric-acid production, or to obtain nitric-acid in a significant high concentration. Both results are shown in figure 21 and figure 22. Another aspect in $\text{NO}_x$ absorption is amount of heat to be remove in the column. A duty profile for both simulations is provided in figure 23.

It can be concluded that the nitric acid production takes place on lower third of the column, while the nitrogen oxide concentration decreases slowly in the upper two third of the column. The largest differences of the simulations are in the nitric acid production.
Absorption of NO\textsubscript{x} in Water

phase. Probably the factor $\chi$ in the user supplied kinetics of the ASPEN model plays an important role with respect to the differences in nitric acid formation.

Figure 21
Nitrogen monoxide flowrate on every tray in the NO\textsubscript{x} absorption column. The results of two models (ASPEN and Enhanced) are compared.

Figure 22
Flowrate of H\textsubscript{3}O\textsuperscript{+} in NO\textsubscript{x} absorption column. The H\textsubscript{3}O\textsuperscript{+} flowrate represents the nitric acid flowrate. Two models are compared (ASPEN and Enhanced).
Another consideration with NO\(_X\) absorption is its environmental aspect. Some older nitric acid plant produce stack gases with up to 3000 ppm NO\(_X\). A regulation issued in Germany under The Federal Pollution Control Act (TA-Luft) states that the NO\(_X\) content must not exceed 0.45 g/m\(^3\) (1 atm, 298 K) (Thieman, 1991). In the usual concentration units for waste gases (ppm) the norm of 0.45 g/m\(^3\) equals to 240 ppm. A proper definition of the NO\(_X\) concentration is:

\[
[\text{NO}_X] = [\text{NO}] + [\text{NO}_2] + [\text{HNO}_2] + 2 \times ([\text{N}_2\text{O}_4] + [\text{N}_2\text{O}_3]) .
\]

(49)
Figure 24 shows the NO\textsubscript{X} concentration in the absorption column. For both simulation models the NO\textsubscript{X} concentration on top of the column is about 375 ppm.

### 5.2 The stochastic simulations

Several stochastic simulations have been done and these will be described below:

- Firstly a stochastic simulation has been done with the ASPEN model where only kinetic constants have been varied. Pure component data for the participating components (H\textsubscript{2}O, HNO\textsubscript{3}, NO\textsubscript{3}\textsuperscript{-}, H\textsubscript{3}O\textsuperscript{+}, NO, NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{4}, O\textsubscript{2} and N\textsubscript{2}) among them thermodynamic binary data have been held constant for this simulations. It is assumed that uncertainties in pure component and thermodynamic data of these well known components just adds little to the overall uncertainty in the results. The kinetic constants for the reactions have been varied in such way, that correlation between the coefficients, is taken into account.

- Secondly for the enhanced model the additional parameters are stochastic varied, especially pure component data and thermodynamic data for HNO\textsubscript{2} and N\textsubscript{2}O\textsubscript{3} have been varied. For the reactions, taken over from the ASPEN model, the reaction constants are varied with the same variances. Additional reactions have also stochastic variables.

- To investigate the significance of the two categories of parameters (thermodynamic/pure component and kinetic data) two sets of simulations have been done where the parameters of one category have been held constant while the others vary.
Finally a stochastic simulation have been done on the Enhanced model where operating parameters and feed compositions, temperatures and pressures have been varied.

In appendix E an overview is given with the specifications for these stochastic simulations. Results that have been monitored are the NO vapor fraction and the duty on each, the $\text{H}_3\text{O}^+$, $\text{HNO}_2$ and $\text{HNO}_3$ bottom flowrate and the NO and $\text{NO}_2$ top flowrate.

![Figure 25](image)

*Figure 25*

*Frequency histogram for the top column NO flowrate for both simulation models.*
For the simulation of the ASPEN model and the Enhanced model the NO flowrate is shown in figure 25. The Enhanced model predicts a NO flowrate of 0.54 kmol/h ($\sigma=4.7 \times 10^{-3}$) and the ASPEN model predicts a flowrate of 0.65 kmol/h ($\sigma=1.6 \times 10^{-3}$). Distance between the two values of the flowrates is $24\sigma$ ($\sigma=\sqrt{\sigma_1^2+\sigma_2^2}$).

The same histogram can be made for the acid production. Figure 26 shows the H$_3$O$^+$ flowrate. For the Enhanced model the H$_3$O$^+$ flowrate equals to 134.36 kmol/h ($\sigma=0.031$) and for the ASPEN model 135.05 kmol/h ($\sigma=8.2 \times 10^{-3}$). Distance between these values is $21\sigma$. This proves that the results of the two models differ significantly although the results of the standard simulations show close figures.

The results of the stochastic simulation where only the kinetic constants were varied or only the pure component parameters and thermodynamic parameters are presented in figure 27 and figure 28.
Absorption of $NO_X$ in Water

**Figure 27**

$NO$ flowrate for several stochastic simulations. The line represents approximate 95% of the calculated flowrates.

**Figure 28**

$H_{3}O^{+}$ flowrate for different simulations. The length of the line represents approximate 95% of the calculated flowrates.

It shows that for the stochastic variation of the parameters, the pure components or thermodynamic parameters have the greatest influence on the uncertainty in the results. But if the results are compared with a simulation where also the operating parameters and feed compositions are varied then the variations in the parameters are of very little
importance. Figure 29 and figure 30 show the results of the variation of operating parameters and feed compositions with the other stochastic simulations.

**Figure 29**
This figure includes the results of the variation of operating parameters and feed compositions for the NO flowrate.

**Figure 30**
This figure includes the results of the variation of operating parameters and feed compositions for the H$_3$O$^+$ flowrate.
Absorption of NOx in Water

All parameters were taken to have a normal distribution. This is often the case for model parameters. It is interesting to determine what kind of distribution the results have. Therefore a Kolmogorov-Smirnov test can be used. This test compares two distributions and calculates the probability that the two distribution are the same. It uses the maximum vertical difference in two cumulative distributions (D). If the number of stochastic simulations is N then the probability that the two distributions are equal can be calculated by (Press, 1988):

\[ Q_{KS}(\lambda) = 2 \sum_{j=1}^{n} (-1)^{j-1} e^{-2j^2} \]

\[ \text{Probability} (D > \text{observed}) = Q_{KS}(\sqrt{N}) . \]

To test whether a distribution is a normal distribution then the Kolmogorov-Smirnov test can be used to compare the distribution with the normal distribution. This has been done for two results of the Enhanced model simulation (figure 31 and figure 32).

Appendix F.1 to F.5 contains data and graphs on the most important results.

**Figure 31**
Frequency histogram of the H3O+ flowrate from the column bottom. The Kolmogorov-Smirnov test gives a probability of 0.98 that this distribution is a normal distribution.
5.3 Convergence characteristics

Some of the results do not directly relate to the NO\textsubscript{x} problem but are interesting to note. A stochastic simulation has been done where start estimations for the simulation model have been varied. These start estimations include estimates for tray duties and tray temperatures.

Figure 34 shows a frequency diagram for the HNO\textsubscript{2} flowrate in column bottom. This graph contains some outliers. One could define the maximum value minus the minimum value divided by the mean as a measure for the convergence accuracy. For this particulate flowrate this results in 1.7%. This means that there is a chance that results of two calculations of the HNO\textsubscript{2} flowrate differs for 1.7%. In appendix F.6 results of this simulation is appended.

Another aspect that has to be highlighted is the fact that for some sets of stochastic simulations a substantial amount of simulations (up to 30%) did not converge. Maybe related to this are the apperance of some 5% outliers, which are more then 2\sigma from the mean.
Nitrous acid bottom flowrate. In this stochastic simulation only estimates are varied. Relative difference between minimum and maximum rate is 1.7%
6 Conclusions and discussion

In this chapter conclusions will be drawn on the results described in the previous chapter. At the end a few problems will be highlighted and recommendations will be made for continuation of this research project.

6.1 Modeling of NO\textsubscript{X} absorption

In chapter 2 three models are presented that describe the absorption of NO\textsubscript{X} and production of nitric acid. This most simple model kinetically limits the oxidation of NO. It describes the equilibrium of NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} in the vapor phase and forms nitric acid from NO\textsubscript{2} also in the vapor phase. The last assumption is not correct because it is believed that nitric acid production takes place in the liquid phase (Hoptyzer, 1972). Because ASPEN uses an equilibrium model where for every tray nitric acid in the vapor phase is in equilibrium with the liquid phase are the results for this model satisfactorily. But if in a later stadium mass transport limitation has to be considered then this model would fail.

The enhanced model describes the nitric acid formation in the liquid phase. Therefore N\textsubscript{2}O\textsubscript{4} first dissolves in the liquid phase and reacts fast with water to produce nitric acid and nitrous acid. The nitrous acid reacts slower to produce nitric acid and NO. The NO does not stay in the liquid phase and will be transported back to the vapor phase. Also, the production of nitrous acid and N\textsubscript{2}O\textsubscript{3} in the vapor phase is considered in this model. The Enhanced model comes close to the proposed model of Hoftyzer (1972). The results of the calculations for this model are comparable to the results of the ASPEN model. It is shown that on a ppm basis for the NO\textsubscript{X} column top flow, the results for both simulations are comparable. Difference in both models is the higher concentration of NO\textsubscript{2} in the Enhanced model compared to the higher concentration of NO in the ASPEN model.
Absorption of NO\textsubscript{X} in Water

One of the major deficiencies in the Enhanced model is its lack to handle mass-rate transport models for the absorption of N\textsubscript{2}O\textsubscript{4} and N\textsubscript{2}O\textsubscript{3} in the nitric acid and the desorption of NO out of the nitric acid solution. In literature it is believed that this has a major impact on the modeling of NO\textsubscript{X} absorption (Thiemann, 1991). The standard ASPEN PLUS program is not capable of simulating mass-transport limitation, but an additional package called RATEFRAC does. Because of limited time between the arrival of this package at the faculty and date of graduation it was not yet possible to complete a NO\textsubscript{X} absorption simulation with RATEFRAC.

One further deficiency in the NO\textsubscript{X} absorption model is the lack of heat transport limitation. For most models the temperature on a tray is uniform but the large heat effects that occur in the production of nitric acid can make this assumption not valid (Helmer, 1972). According to the ASPEN RATEFRAC manual, this program can also handle heat transport models.

Another problem with the modeling of the reactions with ASPEN PLUS is the practical limit on the number of reactions that can be simulated. It was not possible to add the remaining equation from the Hoofzyer model. ASPEN PLUS just won’t converge with more than eight reactions for this model. This probably has something to do with the number of participating components and independent reaction equations. The searched literature and the ASPEN PLUS manual do not resolve this question.

One of ASPEN PLUS’s advantage is its strong thermodynamic capabilities. The implementation of the electrolyte NRTL model proved to be very useful. Only the missing pure component data for N\textsubscript{2}O\textsubscript{3} and HNO\textsubscript{2} have been a problem while implementing these components in the absorption model.

As the results showed, the concentration of NO\textsubscript{X} in the top of the absorption column was about 375 ppm. Compared to the regulations in Germany (TA-Luft, maximum 240 ppm), which has been taken over by many other countries (Thiemann, 1991), is it a little too high, but optimization of the column performance will lower that figure.

6.2 Stochastic versus standard simulation

Some additional conclusions can be drawn with the stochastic simulations. One of the major concerns was the introduction of the uncertainties in the enhanced model. With the standard simulation one can not draw any conclusions of the significance of the Enhanced model. By verifying only the standard simulation results one could find out that the results differ but not whether the results differ significantly. Stochastic simulation gives the possibility to translate the uncertainty in model parameters to uncertainty in simulation results.
Absorption of NO$_x$ in Water

The results of the stochastic simulation of the ASPEN model and the Enhanced model indicate that there is a significant difference in the results of the two models. Alas, stochastic simulation cannot indicate if the Enhanced model is better then the ASPEN model for that experimental data have to be verified.

If the variations in operating parameters, feed composition, temperature and pressure are considered then the two models cannot be distinguished from each other. The influence of varying operating parameters is much higher than the influence of uncertainty in model parameters.

For the significance of variation of reaction constant in contrast to the variation in pure component data and thermodynamic binary parameters, it is found that the influence of reaction constants is much lower that the influence of uncertainty in pure component data and thermodynamic data. But the addition of extra uncertainties in a simulation model results in a larger uncertainty (variance) in the dependent results.

Overall can be concluded that stochastic simulation can be a useful tool in process simulation. It provides a base for interpreting results from simulations. Particulary it will be interesting for studying environmental aspects, risk analyses and quality and economic studies.

6.3 Recommendations for work to be done

One of the major problems in with stochastic simulation was the lack of information and literature on this subject for process simulation. A lot of work can be done with respect to stochastic process simulation. Several recommendations will be done to further exploit this simulation method.

Stochastic simulation can be used to perform sensitivity analysis. Diwekar (1991) mentions the possibility to fit the results to an approximate regression model. An output parameter $y$ can be related to i input parameters $x_i$ with the following transformations and equation:

\[
\begin{align*}
y^* &= \frac{(y-\mu_y)}{\sigma_y} \\
x_i^* &= \frac{(x_i-\mu_{x_i})}{\sigma_{x_i}} \\
y^* &= \sum_i b_i^* x_i^* \quad (51)
\end{align*}
\]

where $\mu$ is the mean value,
\[\sigma\] is the standard deviation and
\[b\] is the regression coefficient.
Absorption of NO\textsubscript{x} in Water

The regression coefficients relate the input parameters to the output parameter and its value gives an indication of the importance of an input parameter. To calculate a measure of the nonlinearity of a process simulation model, one can use the following equation for the coefficient of determination:

$$R^2 = \frac{\sum_j (y_j - \mu_j)^2}{\sum_j (y_j - \mu)^2},$$

where \( j \) is the number of simulations done.

Another aspect of stochastic simulation is the problem of correlations between parameters. A method has to be developed to enable the user to calculate or estimate and specify correlation coefficients. For the problem of reaction constants in the Arrhenius equation this have already been done.

Also, a method for the digesting of stochastic simulation results has to be developed. For this project, intensive use have been made of the spreadsheet program Quattro Pro from Borland software, but for efficiency and speed one has to program the statistical methods in an appropriate programming language. One of the options would be to incorporate stochastic simulation in ASPEN PLUS itself. The stochastic module should work on the same 'level' of a sensitivity study block. This would be impossible to accomplish without the aid of Aspen Technology.

For the case of NO\textsubscript{x} absorption a lot of work still can be done. The first priority is the incorporation of mass rate limitation in the reaction model. Also, implementing the heat transport limitation could be considered. RATEFRAC can be used to perform the calculations.

When the model is adequate, then verification can be done with experimental data. Literature does not provide much data, so best would be to contact chemical companies which for example produce nitric acid, to obtain the necessary data. If enough data is supplied then data reconciliation can be done, model parameters can be fitted to match the experimental data as close as possible. Also, literature can be searched (online databanks) to find the missing pure component data for HNO\textsubscript{2} and N\textsubscript{2}O\textsubscript{3} (the latest version of the DIPPR databank provided with ASPEN PLUS 8.5-4 has entries for these components, only the databank was not yet available to the author).

Finally optimization can be done on the subject of NO\textsubscript{x} absorption. Operating parameters like temperatures, duties, pressures and feed compositions can be varied. Also, the column design can be optimized to increase the column efficiency. An economic model can be defined where environmental and column design costs are weighted to the nitric acid profits. Stochastic simulation can also play an important role in this optimization.

I would like to thank the people who supported me during my research project. Particularly Aspen Technology providing the important program, and supplying information when this was required.
Absorption of NO\textsubscript{x} in Water

Literature


Absorption of $NO_X$ in Water


Absorption of NO$_x$ in Water


*Literature*
List of symbols

\(a_i\) = activity for component \(i\).
\(b\) = regression coefficient.
\(C_i^0\) = the ideal gas heat capacity [J/mol.K].
\(D\) = diffusion constant \([m/s^2]\).
\(G_i^0\) = the Gibbs free energy of formation at 298 Kelvin \([kJ/mol]\).
\(H\) = Henry’s-law constant \([m^3 \text{ atm/kmol}]\).
\(H_i^0\) = the enthalpy of formation at 298 Kelvin \([kJ/mol]\).
\(J_{NO_4}\) = absorption rate \([\text{kmol/m}^2\text{s}]\).
\(K_p\) = equilibrium constant \([\text{atm}^{-1}]\).
\(K_j\) = the chemical equilibrium constant for reaction \(j\).
\(k_{gi}\) = gas-side mass-transfer coefficient of component \(i\) \([\text{m/s}]\).
\(k_p\) = reaction rate constant \([\text{atm}^{-2} \text{s}^{-1}]\).
\(n_A\) = the number of atoms in a molecule.
\(P\) = the pressure.
\(P_{ci}\) = the critical pressure of component \(i\).
\(P_i^0\) = partial pressure of component \(i\) \([\text{atm}]\).
\(P_i^i\) = partial pressure of component \(i\) in the interface \([\text{atm}]\).
\(R\) = universal gas constant \([m^3 \text{ atm kmol}^{-1} \text{ K}^{-1}]\).
\(r\) = reaction rate \([\text{kmol m}^{-3} \text{s}^{-1}]\).
\(T\) = temperature \([\text{K}]\).
\(T_b\) = is the boiling point in \([\text{K}]\).
\(T_{ci}\) = the critical temperature of component \(i\).
\(T_f\) = is the freezing point in \([\text{K}]\).
\(v\) = the volume.
\(W\) = mass fraction.
\(x_i\) = concentration of component \(i\) \([\text{kmol/m}^3]\).
\(x_i\) = the mole-fraction of component \(i\).
\(\Delta T, \Delta p, \Delta V\) = group contributions for the critical properties for the Joback method.
\(\mu\) = mean value.
\(\nu_{ij}\) = the stoichiometric coefficient for reaction \(j\) and component \(i\).
\(\sigma\) = the standard deviation.
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Appendixes

A. Commented listing of the Turbo Pascal (version 6.0) program STOCHASP that generates ASPEN PLUS input files with stochastic varied model parameters.

B. 1. Example of a configuration file used by STOCHASP for the stochastic simulation of the Enhanced model.
   2. Example of a stochastic parameter file used by STOCHASP for the stochastic simulation of the Enhanced model. This file contains the definitions and locations of all stochastic parameters in the ASPEN PLUS input file.
   3. Example of a monitor file used by STOCHASP for the stochastic simulation of the Enhanced model. This file contains the definition and location in the ASPEN summary file of the resulting parameters that have to be sampled.
   4. Example of a script file used by STOCHASP for the stochastic simulation of the Enhanced model. This script file runs on the unix workstation and is started by the PC program.

C. 1. ASPEN PLUS input file for the simulation of NO\textsubscript{X} absorption with the ASPEN model.
   2. ASPEN PLUS report file with the results of the simulation of NO\textsubscript{X} absorption with the ASPEN model.

D. 1. ASPEN PLUS input file for the simulation of NO\textsubscript{X} absorption with the Enhanced model.
   2. ASPEN PLUS report file with the results of the simulation of NO\textsubscript{X} absorption with the Enhanced model.

E. Overview of the parameters that were varied in the stochastic simulations.

F. 1. Results of the stochastic simulation with the ASPEN model where only reaction constants are varied.
   2. Results of the stochastic simulation with the Enhanced model where all parameters are varied.
   3. Results of the stochastic simulation with the Enhanced model where only reaction constants are varied.
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   6. Results of the stochastic simulation with the Enhanced model where model estimations are varied to test program on convergence accuracy.
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uses dos, crt, pinput, pdos, psystem, pdistribution, lotus123{, ChildlnWindow};

const MaxStoch = 100; (maximum number of params to be varied)
MaxHon = 100; (maximum number of results to be monitored)
ConfN = PathStr = 'stochasp.cnf'; (default configuration file)

type
  chararr = array[1 .. 65535] of char;
  pchararr = parray of chararr;
  ExtStoch = array[1 .. 65535] of char;
  Achararr;
  record
    defb b, sigma, to, TLr, double;
    num: integer;
  end;
  pExtStoch = parray of ExtStoch;
  StochRec = record
    row, col: word;
    defb tol, curval, Data: double;
    pExtStoch;
    String[25];
  end;
  HonRec = record
    setno, setid, curval, s: word;
    Description: String; (record with info for param to be varied)
    position in template file
    value in template-file (for check) and tol
    current value
    additional info for modeling exponential models
    Description of parameter
    record with info for nth DSET in summary
    ID of DSET for check
    nth valid number in Current value
    Description of result
    result to be file
    DSET
    ID of DSET in summary file
    value in template-file (for check) and tol
    current value
    Description of result
  end;
  var
    tf, 1F file; (Text file variable / log file variable)
    ResF file; (Result file (WKS-format))
    RunAsp, RunDir, RunID; (command to run aspen plus)
    TplFile; (home directory for aspen run)
    InFile; (template file (dos format))
    SumFile; (created inputfile (dos format))
    ConvFile; (one-line-file with convergence info)
    ConvSeq, Stofile; (search string in latter if converged)
    MonFile; (file with parameters to be varied)
    ResFile; (file containing results in WKS format)
    Edit, EtplFile; (if 'YES' results will be added to ResFile)
    Reuse; (if 'YES' make use of edit files)
    EtplFile; (PathStr); (if 'Edit=NO' then name of edit tpl file)
    s, 22; (number of simulations)
    i, typ, len; (Number of simulations)
    t, Lastsim; (if Reuse=NO than startpoint for simulation)
    Offset; (offset to calculate column of spreadsheet)
    data; (pbytearr);
    Counter; (Counter for number of simulations)
    NumStoch, word; (Number of parameters to be varied)
    Stoch: array[1 .. MaxStoch] of StochRec; (parameter records)
    NumHon; word; (Number of results to be monitored)
    Hon: array[1 .. MaxHon] of HonRec; (result records)
    hh, mm, ss; (for timing purposes (gettime))
    Dis; (StorkNormalPtr); (normal-distribution object)
    WithR: boolean;

constructor kineticconstants.SetConstants(l,e:double);
begin
  Ink0:=l;Ea:=e;
end;

function kineticconstants.k(T:double):double;
begin
  k,=s_exp(lnkO+Ea/T)
end;

type
  uncertainkinconsts=object(kineticconstants)
    cov : TwoDSymMat;
    constructor SetFromTempRange(l,e, tlow, thgh, relsigma : double; n:word);
    constructor SetZero;
    procedure Realization(var InkOEa:kineticconstants);
  end;

constructor uncertainkinconsts.SetFromTempRange (l, e, tlow, thgh, relsigma: double; n :word);
begin
  SetConstants(l,e);
dum:=1/sqr(relsigma);
s1:=0;S2:=0;
for i:=1 to n do begin
  t:=tlow+(thgh-tlow)/n*(i-1);
  s1:=s1+1/t;
  s2:=s2+sqr(1/t)
end;
cov:=dum*n,dum*s1,dum*s2):
cov:=cov.inverse(cov);
end;

constructor uncertainkinconsts.SetZero;
begin
  SetConstants(O,O);
cov:=O,O,O;
end;

procedure uncertainkinconsts.Realization(var InkOEa:kineticconstants);
begin
  cov:=cov.transpose;
  with cov do begin
    oneoverTO:=le/ll;
    ee:=ee-sqr(le)/ll;
  end;
end;
le,=O ;
inverse(xtx)
end;
dlnkO = Sqrt(xtx . ll)*DisA.Realization;
deal = Sqrt(xtx.ee)·DisA.Realizationj
lnkOe = SetConstants(lnkO+dlnkO-deal*oneovertO,Ea+deal)
end;

procedure WriteLog(var F:Text;s:string);
{ Write message to log and crt }
begin
{ Window(1,1,80,14); }
{ GotoXY(1,crline); }
WriteLn(F,s);
FlushF;
end;

Procedure Error(s:String);
{ Display error-string and abort program }
begin
if s<>" then WriteLog(F, 'Problem with Template file, '+TpIFileName);
Assign(EditF,InFile);
Rewrite(EditF);
if IOresult<>O then Error('Problem with Input file, '+InFile);
Line:=0;
Stochi:=1;
repeat
Inc(Line);
ReadLn (TplF, sw) ;
if IOresult<>O then Error('Error reading Template file');
if (stochi<=NumStoch)and(stochi(row=line) then with stoch(stochi) do begin
  tmp1s:=copy(sw,1,col-1);
delete(sw,1,col-1);
tmpls:=SplitS(tmp1s);
  if RealVal(tmp1s)<>def then Error('number mismatch in Template file, parameter no '+IntStr(stochi));
else if data=nil then begin
  curval :=disA . realization*tol+def;
  sw :=tmpls+RealStr(curval)+'</'+sw;
end else begin
  curval :=expIKC . lnKO);
  DataA.B:=-KC.Ea*DataA . R;
  sw :=tmpls+ReaIStrICurval]+' '+reaIStr(Data ..... B)+' '+SWi;
end;
inc(stochi);
end;
WriteLn(EditF,sw);
if IOresult<>O then Error('Error writing Edit file');
until eof (TplF);
Close(TplF);
Close(EditF);
end;

function Converged:boolean;
{ Checks 'ConvFile' for occurence of string 'ConvS' to detect convergence }
var f:text;
s:string;
begin
Assign(F,ConvFile);
Reset(F);
if IOresult<>O then Error('Problem with Convergence check file');
ReadLn (F, s) ;
if IOresult<>O then Error('Problem reading from Convergence check file');
end;

function CreateAspenFile(TplFileName:PathStr);
{ Create aspenplus file (dos-format) out of template file }
var TplF ,
    EditF : Text;
    sw ,
Close(F);
Converged := Pos(ConvS, S) > 0;
end;

procedure getdataset(var f: text; var id: string; var len: word; var data: pchararr);
begin
  (Gets new DSET from summary file)
  const lasts: string = 
  var bufp: pchararr;
  begin
    if id = 'reset' then begin
      lasts := "
      if data <> nil then FreeMem(data, len);
      data := nil;
      len := 0;
      end else begin
      if len <> 0 then FreeMem(data, len);
      data := nil;
    if lasts = " then readln(f, lasts);
      if pos('HISTORY', lasts) > 0 then readln(f, lasts);
      while (not eof(f) and pos('DSET', lasts) <> 2) do readln(f, lasts);
      id := SplitS(lasts);
      id := SplitS(lasts);
      Delete(lasts, 1, Pos(' ', lasts));
      Len := 0;
      repeat
        Lasts := RemSp(Lasts);
        GetMem(bufp, len + Length(Lasts) + 1);
        if data <> nil then
          move(data^, bufp^, len);
        move(bufp[l], lasts[l], len);
        buffer[len] := " 
        data := bufp;
        readln(f, lasts);
      until (eof(f) or (Pos('SET', lasts) = 3) or (Pos('SET', lasts) = 4) or
    end;
  end;

function GetNumberFromArr(no: word; Data: PcharArr): Double;
begin
  var v: Double;
  err, i, j, il: word;
  s: string;
  i := 1;
  j := 0;
  repeat
    while Data^[i] <> ' ' do inc(i);
    s := Data^[i]
    while Data^[i] < ' ' do inc(i);
    move(Data^[i], il, i - 1);
    bytes[i] := i - 1;
    if pos('D', s) > 0 then
      s := Pos('D', s);
      Vals[j, v, err, j] := 0;
    if err = 0 then inc(j);
    until j = no;
    GetNumberFromArr(v);
end;

procedure ParseResultsFile;
begin
  Assign(IF, 'stochasp.log');
  Rewrite(IF);
  if ior(result <> 0) then Error('cannot create logfile');
  if commandline parameter exist then this will be the configuration file
  else the configuration file is 'stochasp.cnf'
  if ParamCount > 0 then ConfN := ParamStr(1);
  GetTime(hh, mm, ss, hs);
  while not FileExist(ConfN) do begin
    mm := (mm + 1) mod 60;
    WriteLog(IF, 'Configuration file not found in current directory, searching again on 
    ' + intstr(hh) + ':' + intstr(mm) + '...');
    while mm <> mmst do begin
      GetTime(hh, mm, ss, hs);
      if keypressed then Error('Key pressed while waiting for config file');
    end;
  end;
  Read which parameters to be varied, one parameter per line

Assgin(tF,StoFile);
Reset(tF);
if IORresult<>0 then Error('Problem with Stochastic variables file!');
NumStoch:=0;
repeat
  inc(NumStoch);
s:='GetLine(tF);
if s=' then begin
  Stoch[NumStoch].Data:=nil;
  Stoch[NumStoch].row:=IntVal(Split(s));
  Stoch[NumStoch].col:=IntVal(Split(s));
  Stoch[NumStoch].def:=RealVal(Split(s));
  Stoch[NumStoch].col:=IntVal(Split(s));
  Stoch[NumStoch].def:=RealVal(Split(s));
end;
if pos(';',s)>0 then begin
  delete(s,1,pos(';',s));
  Stoch[NumStoch].Data:=nil;
  Stoch[NumStoch].col:=IntVal(Split(s));
  Stoch[NumStoch].def:=RealVal(Split(s));
end;
if pos(',',s)>0 then begin
  delete(s,1,pos(',',s));
  Stoch[NumStoch].Data:=nil;
  Stoch[NumStoch].def:=RealVal(Split(s));
  Stoch[NumStoch].Data:=null;
  Stoch[NumStoch].col:=IntVal(Split(s));
  Stoch[NumStoch].def:=RealVal(Split(s));
end;
if pos('%',s)>0 then begin
  delete(s,1,pos('%',s)),
  Stoch[NumStoch].Data:=null;
  Stoch[NumStoch].def:=RealVal(Split(s));
end;
if pos('=',s)>0 then begin
  delete(s,1,pos('=',s));
  Stoch[NumStoch].Data:=null;
  Stoch[NumStoch].def:=RealVal(Split(s));
end;
writeLog(lF, intstr(NumMon)+' results to be monitored');
Reset(tF),
WriteLog(lF, intstr(NumStoch)+' parameters to be varied');
repeat
  until (typ=lotusEOF)or eof(ResF),
writeLog(IF, 'Simulation begin from '+convFile);
read parameters used for this run
Close(IF);
WriteLog(IF, instrNumStoch)+' parameters to be varied');
( Read which results to be monitored )
Assign(IF,NonFile);
Reset(IF);
if IORresult<>0 then Error('Problem with Monitor file!');
NumMon:=0;
repeat
  inc(NumMon);
s:='GetLine(IF);
if s=' then begin
  Mon[NumMon].setm :=IntVal(Split(s));
  Mon[NumMon].id :=IntVal(Split(s));
  Mon[NumMon].numpos :=IntVal(Split(s));
  Mon[NumMon].curval :=RealVal(Split(s));
  Mon[NumMon].def :=RealVal(Split(s));
  Mon[NumMon].defB :=RealVal(Split(s));
  Mon[NumMon].data :=nil;
  Mon[NumMon].numpos :=IntVal(Split(s));
end;
end;
( Check if reuse option is set, if so detect number of results in ResFile )
LastSim:=0;
if Reuse='YES' then begin
  Assign(ResF,ResFile);
  reset(ResF);
  if IORresult<>0 then begin
    WriteLog(IF, 'Cannot open Results file!');
    Reuse:='NO';
    end;
  end;
  WriteLog(IF, 'Reuse = YES, results will be added to '+ResFile);
  len:=0;
  for i:=1 to NumMon do begin
    lotus123read(ResF,typ,len,data);
    if i=LastSim then LastSim:=i;
    end;
  lotusEOF :seek(ResF,FilePos(ResF)-4-len);
  until (typ=lotusEOF)or eof(ResF),
  if len<>0 then if FreeMem(data,len) then
    WriteLog(IF, 'Simulation begin from loop '+intstr(LastSim));
  end;
  if Reuse='YES' then begin
    Assign(ResF,ResFile);
    rewrite(ResF,1);
    if IORresult<>0 then Error('Cannot create Results file');
    lotus123OF(ResF);
    lotus123LABEL(ResF,1,1,'loop');
    offset:=0,
    for i:=1 to NumMon do begin
      lotus123LABEL(ResF,1,1+offset,Mon(i).s);
      if Stoch[i].data=nil then begin
        inc(offset),
        lotus123LABEL(ResF,1,1+offset,Mon(i).s);
      end;
    end;
    ( Solve base-case first )
    if Reuse='YES' then begin
      for i:=1 to NumMon do lotus123LABEL(ResF,1,1+offset,Mon(i).s);
      end;
    lotus123NUMBER(ResF,2,1,1+offset,Mon(i).s);
    offset:=0,
    for i:=1 to NumMon do begin
      lotus123LABEL(ResF,1,1+offset,Mon(i).s);
      if Stoch[i].data=nil then begin
        inc(offset),
        lotus123NUMBER(ResF,2,1,1+offset,Mon(i).s);
      end;
    end;
    WriteLog(IF, 'Executing '+RunDir+' on '+intstr(hh)+': '+intstr(mm)+'/···
    if (DosError<>O)or(DosExitCode<>O) then Error('Error executing '+RunDir
if (stoch[i].data <> nil then begin
  inc(offset);
  lotus123NUMBER(ResF,Counter+2,i+1+offset,stoch[i].data);  
end;
end;

Run aspen plus
GetTime(hh,mm,ss,6s);
WriteLog(IF,'Executing '+runasp+' for loop '+intstr(counter)+' on '+intstr(hh)+':'intstr(mm));
   Window(1,16.80.25);
   ClrScr;
   W_Exec(GetEnv('COMSPEC'),'/C '+runasp+' '+RunDir+' '+RunID+' '+InFile+' '+Sumfile+' ConvFile');
   if (DosError<>0) or (DosExitCode<>0) then Error('Error executing '+runasp);

if (If converged parse the summary file and write the results)
if converged then begin
  WriteLog(IF,'Loop '+intstr(counter)+' did converge');
  ParseResultsFile;
  for i:=1 to NumMon do lotus123NUMBER(ResF,Counter+2,i+1+NumStoch+offset,mon[i].curva);
end else begin
  WriteLog(IF,'Loop '+intstr(counter)+' did not converge');
  if Edit='YES' then begin
    WriteLog(IF,'Executing '+runasp+' for base case' on '+intstr(hh)+':'intstr(mm))
    Window(1,16.80.25);
    ClrScr;
    W_Exec(GetEnv('COMSPEC'),'/C '+runasp+' '+RunDir+' '+RunID+' '+InFile+' '+Sumfile+' ConvFile');
    if (DosError<>0) or (DosExitCode<>0) then Error('Error executing '+runasp);
  end;
end;

if escape-pressed stop this program
if KeyPressed and (ReadKey=_27) then Error('escape pressed during simulation');
end;

Get rid of distribution object
Dispose(dis,done);

Close the results file
WriteLog(IF,'Ready.');
Close(IF);
lotus123EOF(ResF);
Close(ResF);
end.
$STOCHASP configuration file, created 15th June 1992

Michiel Spoor

c:\\nfs\csh dutsh5 $home/aspen/distri/prob3/stochasp.csh

$home/aspen/distri/prob3

noxabs

noxabs.tpl

noxabs.in

noxabs.out

noxabs.chk

WERE COMPLETED NORMALLY

1000

1000

file with one line containing following

: convergence string

string if converged

: stochastic configuration file

: results to be monitored

: results of stochastic simulation

: number of simulations (0=only base-case)

: YES = reuse last results (.WKS) file.

: NO

: use edit runs

: edit template file

: edit directory

: run-id (no .inp extension)

: dos-format input-file

: dos-format output-file (summary file)

Appendix B.1
Stochastic variable file
Created 17 June 1992, for use with stochasp.exe

One variable per row.

Format:
- row: row of aspen input file variable occurs,
- col: column of aspen input file variable occurs,
- def: default value, present in template file.
- sigma: sigma (adding % means percentage)
- s: meaning of variable

For models like \( \ln(y) = a + b/T \) where \( y \) has a normal distribution
the sigma is defined: \( e, \) value of \( b, \) sigma in measurements, number of
measurements, lower temperature range, higher temp range.
If sigma starts with \( k \) then the model is \( \ln(y) = \ln(a) - b/RT \) with \( R \)
as the last value.

<table>
<thead>
<tr>
<th>row</th>
<th>col</th>
<th>def</th>
<th>sigma</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>26</td>
<td>83.72E6</td>
<td>1%</td>
<td>Hform HN03</td>
</tr>
<tr>
<td>60</td>
<td>26</td>
<td>139.41E6</td>
<td>1%</td>
<td>Gform HN03</td>
</tr>
<tr>
<td>61</td>
<td>25</td>
<td>-79.53E6</td>
<td>1%</td>
<td>Hform N203</td>
</tr>
<tr>
<td>62</td>
<td>25</td>
<td>-46.05E6</td>
<td>1%</td>
<td>Gform N203</td>
</tr>
<tr>
<td>70</td>
<td>15</td>
<td>295.7</td>
<td>1%</td>
<td>TB [K] HN02</td>
</tr>
<tr>
<td>71</td>
<td>15</td>
<td>444.3</td>
<td>1%</td>
<td>TC [K] HN02</td>
</tr>
<tr>
<td>72</td>
<td>15</td>
<td>583E5</td>
<td>1%</td>
<td>PC [Pa] HN02</td>
</tr>
<tr>
<td>73</td>
<td>15</td>
<td>0.160</td>
<td>5%</td>
<td>VC [kJ/Kmol] HN02</td>
</tr>
<tr>
<td>74</td>
<td>15</td>
<td>0.3516</td>
<td>5%</td>
<td>SC HN02</td>
</tr>
<tr>
<td>75</td>
<td>15</td>
<td>0.493</td>
<td>5%</td>
<td>OMEGA HN02</td>
</tr>
<tr>
<td>76</td>
<td>15</td>
<td>263</td>
<td>5%</td>
<td>TB [K] N203</td>
</tr>
<tr>
<td>77</td>
<td>15</td>
<td>400</td>
<td>10%</td>
<td>TC [K] N203</td>
</tr>
<tr>
<td>78</td>
<td>15</td>
<td>805E5</td>
<td>10%</td>
<td>PC [Pa] N203</td>
</tr>
<tr>
<td>79</td>
<td>15</td>
<td>0.102</td>
<td>10%</td>
<td>VC [kJ/Kmol] N203</td>
</tr>
<tr>
<td>80</td>
<td>15</td>
<td>0.2456</td>
<td>10%</td>
<td>SC N203</td>
</tr>
<tr>
<td>81</td>
<td>15</td>
<td>0.567</td>
<td>10%</td>
<td>OMEGA N203</td>
</tr>
<tr>
<td>85</td>
<td>15</td>
<td>21.00814</td>
<td>0 1</td>
<td>ANTOINE A HN02</td>
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<tr>
<td>86</td>
<td>15</td>
<td>22.3847</td>
<td>0 1</td>
<td>ANTOINE A N203</td>
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<tr>
<td>87</td>
<td>15</td>
<td>45666</td>
<td>2%</td>
<td>CPi4 HN02</td>
</tr>
<tr>
<td>88</td>
<td>15</td>
<td>3926</td>
<td>5%</td>
<td>Hvap HN02 298 K</td>
</tr>
<tr>
<td>89</td>
<td>15</td>
<td>65605</td>
<td>2%</td>
<td>CPi4 N203</td>
</tr>
<tr>
<td>93</td>
<td>15</td>
<td>39.366</td>
<td>5%</td>
<td>Hvap N203 263 K</td>
</tr>
<tr>
<td>94</td>
<td>15</td>
<td>27.5647</td>
<td>0 2</td>
<td>Henry, A, N203</td>
</tr>
<tr>
<td>117</td>
<td>10</td>
<td>7.0780</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>118</td>
<td>10</td>
<td>154.4</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>119</td>
<td>10</td>
<td>-3.2960</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>120</td>
<td>10</td>
<td>-215.7</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>121</td>
<td>10</td>
<td>7.5430</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>122</td>
<td>10</td>
<td>447.7</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>123</td>
<td>10</td>
<td>-2.9840</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>124</td>
<td>10</td>
<td>-225.3</td>
<td>1%</td>
<td>GMELCC H202[H3O+ NO2-]</td>
</tr>
<tr>
<td>129</td>
<td>10</td>
<td>2.884.106</td>
<td>0 0</td>
<td>K2NO2 NO2 K2 NO2</td>
</tr>
<tr>
<td>130</td>
<td>10</td>
<td>-334</td>
<td>0.005</td>
<td>20,298,378</td>
</tr>
<tr>
<td>131</td>
<td>10</td>
<td>-28.183</td>
<td>0.005</td>
<td>20,298,378</td>
</tr>
<tr>
<td>132</td>
<td>10</td>
<td>-27.029</td>
<td>0.005</td>
<td>20,298,378</td>
</tr>
<tr>
<td>133</td>
<td>10</td>
<td>2.1953E16</td>
<td>0 0</td>
<td>K,NO2 HNO3 K2 NO2 HNO3</td>
</tr>
<tr>
<td>134</td>
<td>10</td>
<td>1.568</td>
<td>0.005</td>
<td>20,298,378</td>
</tr>
</tbody>
</table>

Appendix B.2
#!/bin/csh

script file to run aspen-plus
arguments:
$1 : run-directory
$2 : run-ID
$3 : dos-format inputfile
$4 : dos-format summaryfile
$5 : file containing one line with convergence check

echo stochasp .csh
cd $1
getridof $2
if (-w $4) then
  rm $4
endif
if (-w $5) then
  rm $5
endif
if (-w core) then
  rm core
endif

echo converting $3 to $2 . inp
dos2ux $3 > $2 . inp
echo starting aspen plus
aspen $2

echo converting $2 . sum to $4
ux2dos $2 . sum > $4
grep -i completed $2 . rep > $5
Monitor file for Stochastic simulation.

Created 17 June 1992, by Michiel Spoor for use with stochasp

Use GETSETS to delete IDSET's and LSET's from summary file
and to number the DSET's

Format:

<table>
<thead>
<tr>
<th>Set no</th>
<th>Set id</th>
<th>Var pos</th>
<th>Descr</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>BLOCK 1</td>
<td>1</td>
<td>DUTY [CAL/S] TRAY 1</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 2</td>
<td>2</td>
<td>DUTY [CAL/S] TRAY 2</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 3</td>
<td>3</td>
<td>DUTY [CAL/S] TRAY 3</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 4</td>
<td>4</td>
<td>DUTY [CAL/S] TRAY 4</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 5</td>
<td>5</td>
<td>DUTY [CAL/S] TRAY 5</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 6</td>
<td>6</td>
<td>DUTY [CAL/S] TRAY 6</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 7</td>
<td>7</td>
<td>DUTY [CAL/S] TRAY 7</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 8</td>
<td>8</td>
<td>DUTY [CAL/S] TRAY 8</td>
</tr>
<tr>
<td>21</td>
<td>BLOCK 9</td>
<td>9</td>
<td>DUTY [CAL/S] TRAY 9</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 7</td>
<td>10</td>
<td>DUTY [CAL/S] TRAY 10</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 7</td>
<td>11</td>
<td>Y NO, TRAY 1</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 31</td>
<td>12</td>
<td>Y NO, TRAY 2</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 43</td>
<td>13</td>
<td>Y NO, TRAY 3</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 55</td>
<td>14</td>
<td>Y NO, TRAY 4</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 67</td>
<td>15</td>
<td>Y NO, TRAY 5</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 79</td>
<td>16</td>
<td>Y NO, TRAY 6</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 91</td>
<td>17</td>
<td>Y NO, TRAY 7</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 103</td>
<td>18</td>
<td>Y NO, TRAY 8</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 115</td>
<td>19</td>
<td>Y NO, TRAY 9</td>
</tr>
<tr>
<td>30</td>
<td>BLOCK 115</td>
<td>20</td>
<td>Y NO, TRAY 9</td>
</tr>
<tr>
<td>39</td>
<td>STREAM 2</td>
<td>21</td>
<td>RATE HNO3 [KMOL/H] BOTTOM</td>
</tr>
<tr>
<td>38</td>
<td>STREAM 3</td>
<td>22</td>
<td>RATE H30+ [KMOL/H] BOTTOM</td>
</tr>
<tr>
<td>38</td>
<td>STREAM 10</td>
<td>23</td>
<td>RATE HNO2 [KMOL/H] BOTTOM</td>
</tr>
<tr>
<td>38</td>
<td>STREAM 7</td>
<td>24</td>
<td>RATE NO [KMOL/H] TOP</td>
</tr>
<tr>
<td>40</td>
<td>STREAM 8</td>
<td>25</td>
<td>RATE NO2 [KMOL/H] TOP</td>
</tr>
</tbody>
</table>
**Title: HNO\(_3\) Oxidation-Absorption**

**Description:**

Simulation of nitric acid absorption tower. The purpose of the tower is to oxidize the NO in the vapor phase and to form HNO\(_3\) in the liquid. HNO\(_3\) is removed in the raw acid stream while the NOx concentration in the tail gas should be as low as possible. The reactions occurring in the absorption tower are:

1. NO oxidation,
2. NO\(_2\) dimerization,
3. HNO\(_3\) formation and
4. HNO\(_3\) dissociation in water.

Since the reactions are highly exothermic, cooling is required on every stage of the column.

**In-units Met Temperature=C**

**Run-Control Max-Time=10000**

**Databases ASPENPCD/DIPPRPCD/AQUEDUS**

**Components:**

<table>
<thead>
<tr>
<th>Component</th>
<th>H2O</th>
<th>H2O</th>
<th>H2O</th>
<th>H3O(^+)</th>
<th>NO(^-)</th>
<th>NO(^-)</th>
<th>NO(^2-)</th>
<th>NO2</th>
<th>NO2</th>
<th>NO2</th>
<th>N204</th>
<th>N204</th>
<th>N204</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx-Gas</td>
<td>9</td>
<td>1690</td>
<td>105</td>
<td>27</td>
<td>71</td>
<td>28</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Chemistry HNO\(_3\)**

<table>
<thead>
<tr>
<th>Stoic</th>
<th>HNO(_3)</th>
<th>-1.0</th>
<th>H2O</th>
<th>-1.0</th>
<th>H3O(^+)</th>
<th>1.0</th>
<th>HNO(_3)</th>
<th>1.0</th>
</tr>
</thead>
</table>

**PROP-DATA**

**Properties**:

- **VALUES**:
  - **PVAL H2O**: 72.55
  - **PVAL H2O**: 298.15
  - **PVAL H2O**: 298.15
  - **PVAL H2O**: 298.15
  - **PVAL H2O**: 298.15
  - **PVAL H2O**: 298.15
  - **PVAL H2O**: 298.15

**Reactions: Oxidation Reactions and Nitric Acid Hydrolysis**

**PARAM**:

- **SUBROUTINE=NOX**

**Real Value-List=0.5**

**React-DATA 1**

- **KINETIC**:
  - **PHASE=V**
  - **STOIC 1**: O2 | NO | NO2 | N204 |
  - **K-STOIC 1**: A=-33.0 B=6991.0 C=0.0 D=0.0

**React-DATA 2**

- **EQUIL**:
  - **PHASE=V**
  - **K-BASIS=P**
  - **STOIC 2**: H2O | N2O4 |
  - **K-STOIC 2**: A=-17.0 B=3625.0 C=-2.0 D=0.0

**React-DATA 3**

- **EQUIL**:
  - **PHASE=V**
  - **K-BASIS=P**
  - **STOIC 3**: H2O | N2O4 |
  - **K-STOIC 3**: A=-17.0 B=3625.0 C=-2.0 D=0.0

**React-DATA 4**

- **EQUIL**:
  - **PHASE=V**
  - **K-BASIS=P**
  - **STOIC 4**: H2O | N2O4 |

**Flowsheet**

- **Block Tower In=NOx-Gas Water Out=TAIL-GAS RAW-ACID**

**Stream Water**

- **SUBSTREAM MIXED TEMP=20 PRES=11.0**

- **Mole-Flow H2O 9 / N2 1690 / O2 105 / NO 27 / NO2 71 / N204 28**

**Reactors**

- **NITRICATION**

- **Max-I=50 Max-II=8**

- **Feed NOx-Gas 11**

- **Product TAIL-GAS 1 VOL=500.0 T-EST 1 25.0 / 10.37.0**

**Reactors**

- **NITRIC**

- **Max-I=50 Max-II=8**

- **Feed NOx-Gas 11**

- **Product RAW-ACID 10 VOL=500.0 T-EST 1 25.0 / 10.37.0**

**Summary**

- **Mole-Flow H2O 9 / N2 1690 / O2 105 / NO 27 / NO2 71 / N204 28**

- **Stream Water**

- **Substream Mixed Temp=20 Pres=11.0**

- **Mole-Flow H2O 400**

**Reactor**

- **NITRICATION**

- **Max-I=50 Max-II=8**

- **Feed NOx-Gas 11**

- **Product TAIL-GAS 1 VOL=500.0 T-EST 1 25.0 / 10.37.0**

**Summary**

- **Mole-Flow H2O 9 / N2 1690 / O2 105 / NO 27 / NO2 71 / N204 28**
Simulation of Nitric Acid Absorption Tower. The purpose of the tower is to oxidize the NO in the vapor phase and to form HNO3 in the liquid. HNO3 is removed in the raw acid stream while the NOx concentration in the tail gas should be as low as possible. The reaction occurring in the absorption tower are: (1) NO oxidation, (2) NO2 dimerization, (3) HNO3 formation and (4) HNO3 dissociation in water. Since the reactions are highly exothermic, cooling is required on every stage of the column.

**Block Status**

* All unit operation blocks were completed normally
**Block Status (Continued)**

**Flowsheet Connectivity by Streams**

<table>
<thead>
<tr>
<th>Stream</th>
<th>Source</th>
<th>Dest</th>
<th>Stream</th>
<th>Source</th>
<th>Dest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tail-Gas</td>
<td>Tower</td>
<td>---</td>
<td>Tower</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Tower</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Flowsheet Connectivity by Blocks**

<table>
<thead>
<tr>
<th>Block</th>
<th>Inlets</th>
<th>Outlets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tower</td>
<td>NOX-GAS WATER</td>
<td>TAIL-GAS RAW-ACID</td>
</tr>
</tbody>
</table>

**Computational Sequence**

Sequence Used Was:

**Overall Flowsheet Balance**

<table>
<thead>
<tr>
<th><strong>Mass and Energy Balance</strong></th>
<th><strong>In</strong></th>
<th><strong>Out</strong></th>
<th><strong>Generation</strong></th>
<th><strong>Relative Diff.</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conventional Components</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H2O</td>
<td>409.000</td>
<td>197.781</td>
<td>-211.219</td>
<td>-359390E-11</td>
</tr>
<tr>
<td>NO3-</td>
<td>.000000E+00</td>
<td>17.2699</td>
<td>17.2699</td>
<td>.617182E-15</td>
</tr>
<tr>
<td>NO3+</td>
<td>.000000E+00</td>
<td>135.056</td>
<td>135.056</td>
<td>.000000E+00</td>
</tr>
<tr>
<td>NO3-</td>
<td>.000000E+00</td>
<td>135.056</td>
<td>135.056</td>
<td>.000000E+00</td>
</tr>
<tr>
<td>N2</td>
<td>1680.00</td>
<td>1680.00</td>
<td>.000000E+00</td>
<td>.125962E-11</td>
</tr>
<tr>
<td>O2</td>
<td>105.000</td>
<td>53.7443</td>
<td>-51.2557</td>
<td>.492969E-09</td>
</tr>
<tr>
<td>N2O</td>
<td>27.0000</td>
<td>.651618</td>
<td>-26.3484</td>
<td>.387512E-08</td>
</tr>
<tr>
<td>NO2</td>
<td>71.0000</td>
<td>.464790E+01</td>
<td>-70.9535</td>
<td>.147472E-08</td>
</tr>
<tr>
<td>N2O4</td>
<td>28.0000</td>
<td>.487908</td>
<td>-27.5121</td>
<td>.126883E-15</td>
</tr>
<tr>
<td><strong>Total Balance</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO3- (MOL/MM)</td>
<td>2320.00</td>
<td>2220.09</td>
<td>-99.9067</td>
<td>.255556E-10</td>
</tr>
<tr>
<td>MASS (Kg/MM)</td>
<td>64442.8</td>
<td>64442.8</td>
<td>.000000E+07</td>
<td>.238648E-06</td>
</tr>
<tr>
<td>ENTHALPY (CAL/SEC)</td>
<td>-.734791E+07</td>
<td>-.820848E+07</td>
<td></td>
<td>.104839</td>
</tr>
</tbody>
</table>
### COMPONENTS

<table>
<thead>
<tr>
<th>ID</th>
<th>TYPE</th>
<th>FORMULA</th>
<th>NAME OR ALIAS</th>
<th>REPORT NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>C</td>
<td>H2O</td>
<td>H2O</td>
<td>H2O</td>
</tr>
<tr>
<td>HNO3</td>
<td>C</td>
<td>HNO3</td>
<td>HNO3</td>
<td>HNO3</td>
</tr>
<tr>
<td>H2O+</td>
<td>C</td>
<td>H2O+</td>
<td>H2O+</td>
<td>H2O+</td>
</tr>
<tr>
<td>NO3-</td>
<td>C</td>
<td>NO3-</td>
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**SUPERCRITICAL COMPONENT LIST**

- N2
- O2
- NO
- NO2
- N2O4

### PHYSICAL PROPERTIES SECTION

**REPORT NAME**

- H2O
- HNO3
- H2O+
- NO3-
- O2
- NO2
- N2O4

### BLOCK: TOWER MODEL: RADFRAC

**INLETS - NOX-GAS STAGE 10**

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<th>WATER STAGE 1</th>
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<tbody>
<tr>
<td>OUTLETS - TAIL-GAS STAGE 1</td>
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**PROPERTY OPTION SET:**

- SYSPHIS
- ELECTROLYTE NRTL
- REDLICH-KWONG-SOAVE

**HENRY-COMPS ID:**

- GAS

**CHEMISTRY ID:**

- HNO3 - TRUE SPECIES

*** MASS AND ENERGY BALANCE ***

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### INPUT PARAMETERS

- **NUMBER OF STAGES:** 10
- **ALGORITHM OPTION:** NONIDEAL
- **INITIALIZATION OPTION:** NONIDEAL
- **HYDRAULIC PARAMETER CALCULATIONS:** NO
- **INSIDE LOOP CONVERGENCE METHOD:** NEWTON
- **MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS:** 50
- **MAXIMUM NUMBER OF FLASH ITERATIONS:** 50
- **FLASH TOLERANCE:** 0.00010000
- **OUTSIDE LOOP CONVERGENCE TOLERANCE:** 0.00010000

### COL-SPECS

- **CONDENSER DUTY (W/O SUBCOOL):** CAL/SEC 10.0000
- **REBOILER DUTY:** CAL/SEC -355,000.0000

**MASS VAPOR DIST / TOTAL DIST**

- 1.00000
## HN03 OXIDATION-ABSORPTION
### U-O-S BLOCK SECTION
#### BLOCK: TOWER MODEL: RADFRAC (CONTINUED)
##### STAGE TO STAGE SPECIFICATIONS
- **REACTIONS/CHEMISTRY ID**: NITRIC
- **STAGE TO STAGE LIQUID HOLDUP**
  - Stage 1: 6500.0000 L
- **HEATERS**
  - Stage 2: -1.770.00 CAL/SEC
  - Stage 3: -2.600.00 CAL/SEC
  - Stage 4: -4.060.00 CAL/SEC
  - Stage 5: -7.150.00 CAL/SEC
  - Stage 6: -15.000.0 CAL/SEC
  - Stage 7: -40.000.0 CAL/SEC
  - Stage 8: -135.000.0 CAL/SEC
  - Stage 9: -300.000.0 CAL/SEC
- **PROFILES**
  - P-SPEC: Stage 1 pressure, atm: 11.0000
  - TEMP-SET: Stage 1 temperature, °C: 25.0000

### RESULTS
- **TOP STAGE TEMPERATURE**: 25.2364°C
- **BOTTOM STAGE TEMPERATURE**: 37.3442°C
- **STAGE LIQUID FLOW**: 400.825 KNOL/HR
- **STAGE VAPOR FLOW**: 1.739.76 KNOL/HR
- **MOLAR REFLUX RATIO**: 0.23039
- **MOLAR BOILUP RATIO**: 3.83468
- **CONDENSER DUTY (W/O SUBCOOL)**: 10.0000 CAL/SEC
- **REBOILER DUTY**: -355.000.0 CAL/SEC
- **MAXIMUM FINAL RELATIVE ERRORS**
  - Stage 6: 25.2364%
  - Stage 7: 37.3442%
  - Stage 8: 400.825%
  - Stage 9: 480.335%
  - Stage 10: 1.842.02%

### PROFILES
- **STAGE TEMPERATURE PRESSURE**:
  - Stage 1: 25.236°C, 11.000 atm
  - Stage 2: 27.359°C, 11.000 atm
  - Stage 3: 28.350°C, 11.000 atm
  - Stage 4: 28.854°C, 11.000 atm
  - Stage 5: 29.182°C, 11.000 atm
  - Stage 6: 29.552°C, 11.000 atm
  - Stage 7: 30.380°C, 11.000 atm
  - Stage 8: 33.137°C, 11.000 atm
  - Stage 9: 36.374°C, 11.000 atm
  - Stage 10: 37.344°C, 11.000 atm

### ENTHALPY
- **CAL/MOL HEAT DUTY**:
  - Stage 1: -68288. -170.65 CAL/MOL
  - Stage 2: -68243. -177.95 CAL/MOL
  - Stage 3: -68214. -180.77 CAL/MOL
  - Stage 4: -68187. -180.32 CAL/MOL
  - Stage 5: -68151. -177.10 CAL/MOL
  - Stage 6: -68104. -170.35 CAL/MOL
  - Stage 7: -67898. -156.49 CAL/MOL
  - Stage 8: -67634. -104.90 CAL/MOL
  - Stage 9: -63349. 90.796 CAL/MOL
  - Stage 10: -60903. 289.73 CAL/MOL

### FEED RATE PRODUCT RATE
- **KMOL/HR**:
  - Stage 1: 400.80
  - Stage 2: 401.3
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## HNÖ3 oxidation-absorption

### Rate of Generation

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## HNO3 Oxidation-Absorption

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**Title**: HNO₃ Oxidation-Absorption

**Description**: Simulation of nitric acid absorption tower. The purpose of the tower is to oxidize the NO in the vapor phase and to form HNO₃ in the liquid. HNO₃ is removed in the raw acid stream. While the NOx concentration in the tail gas should be as low as possible, the reactions occurring in the absorption tower are:

1. NO oxidation,
2. NO₂ dissociation,
3. HNO₂ formation,
4. HNO₃ formation,
5. Block tower formation,
6. HNO₃ and HNO₂ dissociation in water.

Since the reactions are highly exothermic, cooling is required on every stage of the column.

**In-Units Net Pres-Atm Temperature°C**: 20

**Run-Control Max-Time=1000**

**Databanks**: DIPPRPCD / AQUEOUS

**Components**:
- H₂O
- HNO₃
- NO
- NO₂
- HNO₂
- HNO₃
- N₂
- O₂
- NO
- NO₂
- H₂O
- HNO₂
- HNO₃

**Properties**:
- H₂O
- HNO₃
- NO
- NO₂
- HNO₂
- HNO₃

**Henry-Comp's Gas N2**: 0
**Henry-Comp's N2**: 0

**Chemistry**:
- HNO₃
  - **Paraw Xbase=MOLAL**
  - Stoic 1: HNO₃ / H₂O / NO / NO₂
  - Stoic 2: HNO₃ / H₂O / NO / NO₂

**Prop-Data**

**Prop-List**
- **In-Units SI**
- **Prop-List**
  - **Prop-List W**
  - **Prop-List VL/wt**
  - **Prop-List**
  - **Prop-List TB**
  - **Prop-List FLXAT**
  - **Prop-List DCFL**
  - **Prop-List CCFL**
  - **Prop-List**
  - **Prop-List CTPC / DCFL**
  - **Prop-List**
  - **Prop-List**
  - **Prop-List**
  - **Prop-List**
  - **Prop-List**

**BPVAL**
- H₂O 20.56470 / -2872.960 / -302880.0 / 283.0 / 386.0
- HNO₃ 20.5647 / -2872.960 / -302880.0 / 283.0 / 386.0

**Prop-List**
- **GMECC / GMECD**
- **BPVAL**
  - H₂O / HNO₃ / NO / NO₂

**Prop-List**
- **GMECC / GMECD**
- **BPVAL**
  - H₂O / HNO₃ / NO / NO₂

**Prop-List**
- **GMECC / GMECD**
- **BPVAL**
  - H₂O / HNO₃ / NO / NO₂

**Blocks**

**Tower Radfrac**
- **Param**: 
  - **Flash-10 Algorithm=Newton MaxNL=50 MaxIt=20

**Diag**
- **Mol=8 OLVAR=4 OLVAR2=4 CMRA=4 EMBA=4

**Streams**
- **H₂O/GAS 40.0 PRE=11.0**
  - Mole-Flow H₂O: 9.0 / Mole-Flow NO: 1.0 / Mole-Flow NO₂: 1.0 / Mole-Flow HNO₃: 1.0

**Streams**
- **H₂O TEMP=25.1 MOLE-FLOW=1E12**
  - H₂O TEMP=33.1 MOLE-FLOW=1E12
  - H₂O TEMP=30.4 MOLE-FLOW=1E12
  - H₂O TEMP=28.3 MOLE-FLOW=1E12
  - H₂O TEMP=28.8 MOLE-FLOW=1E12

**React-Stages 1**
- **H2**
  - **Hold-Up 10 VOL-VNL0=6500 VOL-LHL0=20**

**Reactions**
- **Nitric**
  - **Description**: Oxidation reactions and nitric acid hydrolysis
  - **Gas-Phase reactions**:
    - **O2 + NO**: 
      - **2 NO**: 
        - **NO**: 
          - **2 NO**: 
            - **HNO₃**: 
              - **HNO₂**: 
  - **Liquid-Phase reactions**:
  - **HNO₂ + H₂O**: 
  - **HNO₃ + H₂O**: 
  - **HNO₂ + H₂O**: 
  - **HNO₃ + H₂O**: 
  - **HNO₂ + H₂O**: 
  - **HNO₃ + H₂O**: 
  - **HNO₂ + H₂O**: 
  - **Reac-Data 1 KINETIC V/CBASE=MOLEFRAC**

**Appendix D**
PRESENT IN ORIGINAL NOX-INPUT FILE BUT ELIMINATED.
THIS REACTION IS AN OVERALL REACTION AND NITRIC ACID IS FORMED HERE IN VAPOR PHASE, WHAT IS NOT THE CASE

REAC-DATA 3 EQUIL V KBASIS=P
STOIC 3 H2O -1 / N02 -3 / NO 1 / HN03 2
K-STOIC 3 -17 3625 -2

REAC-DATA 4 EQUIL V KBASIS=P
STOIC 4 NO -1 / N02 -1 / N203 1
K-STOIC 4 -28.183 4771

REAC-DATA 5 EQUIL V KBASIS=P
STOIC 5 NO -1 / N02 -1 / H2O -1 / HN03 2
K-STOIC 5 -27.029 4723

REAC-DATA 6 EQUIL L KBASIS=MOLAL
STOIC 6 HN03 -1 / H2O -1 / H30+ NO3-

REAC-DATA 7 EQUIL L
STOIC 7 HN02 -1 / H2O -1 / H30+ NO2-

REAC-DATA 8 KINETIC L CBASIS=MOLAR
STOIC 8 N204 -1 / H2O -1 / HN03 1 / NO2- 2
RATE-CON 8 2.19513E16 18938.8
POWLAW-EXP 8 HN02 -3 / N0 -2

REAC-DATA 9 KINETIC L CBASIS=MOLAR
STOIC 9 HN03 -3 / HN03 1 / H2O 1 / NO 2
RATE-CON 9 1.565 29369.3
POWLAM-EXP 9 HN02 4 / NO -2

STREAM-REPORT MOLEFLOW MASSFLOW MOLEFRAC MASSFRAC
## RUN CONTROL SECTION

### RUN CONTROL INFORMATION

This version of Aspen Plus licensed to Delf University of Technology.

The following layered products have been installed:

- RATEFRAC RELEASE 1.5-4 installed on 07/21/92 at 19:51:00

### INPUT FILE NAME: nox.inp

**OUTPUT PROBLEM DATA FILE NAME:** nox

**VERSION NO.:**

**LOCATED IN:** /disc/users/spoor/aspen

**PDF SIZE USED FOR INPUT TRANSLATION:**

- Number of file records (PSIZE) = 9999
- Number of in-core records = 400
- PSIZE needed for simulation = 2000

**CALLING PROGRAM NAME:** apmod

**LOCATED IN:** /disc/users/aspr85/aspenplus

### SIMULATION REQUESTED FOR ENTIRE FLOWSHEET

### DESCRIPTION

Simulation of nitric acid absorption tower. The purpose of the tower is to oxidize the NO in the vapor phase and to form HNO3 in the liquid. HNO3 is removed in the raw acid stream while the NOx concentration in the tail gas should be as low as possible. The reactions occurring in the absorption tower are: (1) NO oxidation, (2) NO2 dimerization, (3) HNO3 formation, (4) HNO2 formation, (5) HNO3 formation, (6) HNO2 and HNO dissociation in water. Since the reactions are highly exothermic, cooling is required on every stage of the column.

### BLOCK STATUS

- All unit operation blocks were completed normally

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<td>PHYSICAL PROPERTIES SECTION</td>
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BLOCK STATUS (CONTINUED)

FLOWSEET CONNECTIVITY BY STREAMS

STREAM SOURCE DEST STREAM SOURCE DEST
NOX-GAS ---- TOWER WATER ---- TOWER
TAIL-GAS TOWER ---- RAW-ACID TOWER ----

FLOWSEET CONNECTIVITY BY BLOCKS

BLOCK INLETS DEST OUTLETS DEST
TOWER WATER NOX-GAS TAIL-GAS RAW-ACID

COMPUTATIONAL SEQUENCE

SEQUENCE USED WAS:
TOWER

OVERALL FLOWSHEET BALANCE

*** MASS AND ENERGY BALANCE ***

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**LISTID**

**SUPERCRITICAL COMPONENT LIST**

- N2
- O2
- NO
- N2O4
- N2O3
**HN03 OXIDATION-ABSORPTION**

**U-O-S BLOCK SECTION**

**BLOCK, TOWER MODEL, RADFRAC (CONTINUED)**

### Stage to Stage Specifications

- **Reactions/Chemistry ID**
  - Nitric

### Stage to Stage Hold-Up Specifications

- **Stage to Stage Liquid Holdup and Vapor Holdup**
  - 1 10
  - 20,000 L
  - 6500,000 L

### Coolant Specifications

- **Stage Comp ID**
  - 1 H2O
  - 2 H2O
  - 3 H2O
  - 4 H2O
  - 5 H2O
  - 6 H2O
  - 7 H2O
  - 8 H2O
  - 9 H2O
  - 10 H2O

#### Stage Comp ID

- **Optn Set**
- **Phase**
- **Pressure**
- **Temperature**
- **Atm**

### Stage Coolant Specifications

#### Stage Comp ID

- **Expected Liquid**
- **Actual Liquid**
- **Expected Temperature**
- **Actual Temperature**
- **Flow Rate**
- **Enthalpy**
- **Heat Duty**
- **Product Rate**

**Profiles**

#### Profiles

- **Stage**
- **Pres. ATM**
- **Temp. C**

### Results

- **Top Stage Temperature C**
- **Bottom Stage Temperature C**
- **Top Stage Liquid Flow KMOL/HR**
- **Bottom Stage Liquid Flow KMOL/HR**
- **Top Stage Vapor Flow KMOL/HR**
- **Bottom Stage Vapor Flow KMOL/HR**
- **Molar Reflux Ratio**
- **Molar boilup Ratio**
- **Reboiler Duty CAL/SEC**
- **Condenser Duty (W/O Subcool) CAL/SEC**

**Maximum Final Relative Errors**

- **Bubble Point**
- **Condensate Mass Balance**
- **Energy Balance**

**Profiles**

#### Profiles

- **Stage**
- **Flow Rate**
- **Enthalpy**
- **Heat Duty**

**Profiles**

- **Stage**
- **Flow Rate KMOL/HR**
- **Feed Rate KMOL/HR**
- **Product Rate KMOL/HR**

**Profiles**

- **Stage**
- **Flow Rate**
- **Feed Rate**
- **Product Rate**
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**K-VALUES**

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**RATES OF GENERATION**

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### HN03 Oxidation-Absorption

#### U-0-S Block Section

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### Stream Section

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#### Phase Components

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### ASPEN Plus Version: HP-PA REL 8.5-4

**Page 11 of 10**
### NOX-GAS RAW-ACID TAIL-GAS WATER (CONTINUED)

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**Total Flow:**
- Kmol/hr: 1920.0000
- Kg/hr: 5.7237E-04
- L/min: 7.4752E-04

**State Variables:**
- Temp C: 40.0000
- Pres atm: 11.0000
- LFRAC: 0.0000
- SFRAC: 0.0000

**Enthalpy:**
- Cal/mol: 472.0657
- Cal/gm: -6.0759E+04
- Cal/sec: 2.5177E+05

**Entropy:**
- Cal/mol-K: -4.9064
- Cal/gm-K: -4.4679

**Density:**
- Mol/cc: 4.2800E-04
- GM/cc: 1.2762E-02

**Avg MW:**
- 29.8108

**AVG MW:**
- 32.1165
Parameters for the different stochastic simulations, entries include default value and standard deviation ($\sigma$).

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<th>Operating parameters</th>
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Appendix E
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<th>GMELEC H$_2$O/NO$_2^-$</th>
<th>GMELEC NO$_3^-$/H$_2$O</th>
<th>GMELEC NO$_2^-$/H$_2$O</th>
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<td>$T_{low}$-$T_{high}$ [K]</td>
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<td>2NO$_2$+N$_2$O$_4$: A, B</td>
<td>-33, 6891</td>
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<td>NO+NO$_2$+H$_2$O→2HNO$_3$: A, B</td>
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Appendix E
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<th>Reaction</th>
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<th>Flow</th>
<th>Temp</th>
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<td>N₂O₅ + H₂O + HNO₃ + HNO₂</td>
<td>k₁</td>
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<td>H₂O + 3NO₂ + NO₂</td>
<td>k₃</td>
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<td>10, 0.05</td>
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<td>TEMP NOX-GAS [°C]</td>
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<td>PRES NOX-GAS [Atm]</td>
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<td>FLOW H₂O NOX-GAS [kmol/h]</td>
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<td>FLOW NO₂ NOX-GAS [kmol/h]</td>
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<td>FLOW N₂O₄ NOX-GAS [kmol/h]</td>
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<td>TEMP WATER [°C]</td>
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<td>PRES WATER [Atm]</td>
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<td>11 ± 5%</td>
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<td>FLOW H₂O WATER [kmol/h]</td>
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<td>TEMP TRAY 1 [°C]</td>
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<td>est. 25.1 ± 10%</td>
<td>25.1 ± 5%</td>
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<td>TEMP TRAY 10 [°C]</td>
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<td>est. 37.4 ± 10%</td>
<td>37.4 ± 5%</td>
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<td>TEMP TRAY 2 [°C]</td>
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<td>est. 27.3 ± 10%</td>
<td>27.3 ± 5%</td>
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<td>est. 28.3 ± 10%</td>
<td>28.3 ± 5%</td>
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<td>TEMP TRAY 4 [°C]</td>
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<td>est. 28.8 ± 10%</td>
<td>28.8 ± 5%</td>
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<td>TEMP TRAY 5 [°C]</td>
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<td>est. 29.2 ± 10%</td>
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<tr>
<td>TEMP TRAY 6 [°C]</td>
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<td>est. 29.6 ± 10%</td>
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<td>TEMP TRAY 7 [°C]</td>
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<td>est. 30.4 ± 10%</td>
<td>30.4 ± 5%</td>
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<tr>
<td>TEMP TRAY 8 [°C]</td>
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<td>est. 33.1 ± 10%</td>
<td>33.1 ± 5%</td>
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<tr>
<td>TEMP TRAY 9 [°C]</td>
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<td>est. 36.4 ± 10%</td>
<td>36.4 ± 5%</td>
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<tr>
<td>EST DUTY TRAY 1 [Cal/s]</td>
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<td>-387 ± 10%</td>
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<td>EST DUTY TRAY 10 [Cal/s]</td>
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<td>-670780 ± 10%</td>
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</table>
count 977  Column bottom liquid flowrate H3O+

sum 131944.9  Rate H3O+ [kmol/h]

avg 135.0511  Epanechnikov estimate

vars 6.78E-05  Probability curve

min 135.0217  Density histogram, 25 classes

max 135.0815

median 135.0508

1e kw 135.0466  Basic run for original ASPEN PLUS run

3e kw 135.0568  Only kinetic params varied

stds 0.008233

b 0.004116

glow 135.0135

ghigh 135.0897

gpoints 50  hpoints 25

gwidth 0.001555  hwidth 0.003176

Kolmochorov-Smirnov test (prob D > stnd)
D 0.049248
Qks(D9N) 0.017492

Column bottom liquid flowrate H3O+

Density histogram, 25 classes

Column bottom liquid flowrate H3O+

Epanechnikov estimate

Column bottom liquid flowrate H3O+

Probability curve
count 977 Column top vapor flowrate NO
sum 635.0096 Rate NO [kmol/h]
sig 0.649959 Epanechnikov estimate
tol 2.7E-06 Probability curve
max 0.644452 Density histogram, 25 classes
min 0.655424
mean 0.64998
le kw 0.648897 Basic run for original ASPEN PLUS run
le kw 0.65101 Only kinetic params varied
h 0.001644
sil 0.642808
glim 0.657068
gpoints 50 hpoints 25
gwidth 0.000291 hwidth 0.000594

Kolmochorov-Smirnov test (prob D > std)
D 0.016391
Qks(DBN) 0.955505

Column top vapor flowrate NO
Epanechnikov estimate

Column top vapor flowrate NO
Density histogram, 25 classes

Column top vapor flowrate NO
Probability curve
count 372 Column top flowrate NO
sum 200.0503 Rate NO [kmol/h]
avg 0.5377 Epanechnikov estimate
vars 2.24E-05 Probability curve
min 0.526758 Density histogram, 25 classes
max 0.563509
median 0.537435
lekw 0.534289 Basic run for changed input file
3ekw 0.540547 All parameters varied
stds 0.004737 Compensation done for kinetics
h 0.003
glow 0.522021
ghigh 0.568247
gpoints 50 hpoints 25
gwidth 0.000943 hwidth 0.001926

Kolmochorov-Smirnov test (prob D > std)
D 0.048192
Qks(DBN) 0.353318

Column top flowrate NO
Epanechnikov estimate

Column top flowrate NO
Density histogram, 25 classes

Column top flowrate NO
Probability curve
count 372 Column bottom flowrate H3O+
sum 49981.74 Rate H3O+ [kmol/h]
avg 134.3595 Epanechnikov estimate
vars 0.000987 Probability curve
min 134.2689 Density histogram, 25 classes
max 134.4757
median 134.3595
le kw 134.3392 Basic run for changed input file
3e kw 134.3803 All parameters varied
stds 0.031413 Compensation done for kinetics
h 0.02
glow 134.2374
ghigh 134.5071
gpoints 50 hpoints 25
gwidth 0.005503 hwidth 0.011234

Kolmochorov-Smirnov test (prob D > stnd)
D 0.024589
Qks(DBN) 0.978079
count 1000  Column bottom liquid flowrate H3O+
sum 134352.2  Rate H3O+ [kmol/h]
avg 134.3522  Epanechnikov estimate
vars 5.92E-05  Probability curve
min 134.3231  Density histogram, 25 classes
max 134.3771
median 134.3523
1e kw 134.3469  Basic run for changed input file
3e kw 134.3571  Only kinetics varied
stds 0.007696
h 0.003848
glow 134.3154
ghigh 134.3848
gpoints 50  hpoints 25
gwidth 0.001417  hwidth 0.002892
Kolmochorov-Smirnov test (prob D > std)
D 0.015406
Qks(DBN) 0.97155

Column bottom liquid flowrate H3O+
Density histogram, 25 classes

Column bottom liquid flowrate H3O+
Epanechnikov estimate

Column bottom liquid flowrate H3O+
Probability curve
count 1000 Column top vapor flowrate NO
sum 536.8462 Rate NO [kmol/h]
avg 0.536846 Epanechnikov estimate
vars 1.25E-06 Probability curve
min 0.533711 Density histogram, 25 classes
max 0.539893
median 0.536822
lekw 0.536077 Basic run for changed input file
3ekw 0.537649 Only kinetics varied
stds 0.001118
h 0.000559
glow 0.532593
ghigh 0.54101
gpoints 50 hpoints 25
gwidth 0.000172 hwidth 0.000351
Kolmochorov-Smirnov test (prob D > std)
D 0.01795
Qks(DBN) 0.904032
count 771  Column top flowrate NO
sum 414.1936  Rate NO [kmol/h]
avg 0.537216  Epanechnikov estimate
vars 2.07E-05  Probability curve
min 0.526259  Density histogram, 25 classes
max 0.56259
median 0.537141
1e kw 0.533796  Basic run for changed input file
3e kw 0.540634  Pure component parameters varied
stds 0.004554  component interaction parameters varied
h 0.002277
glow 0.521705
ghigh 0.567143
gpoints 50  hpoints 25
gwidth 0.000927  hwidth 0.001893

Kolmochorov-Smirnov test (prob D > std)
D 0.044088
Qks(DBN) 0.099832
count 771  Column bottom liquid flowrate H3O+
sum 103587.1  Rate H3O+ [kmol/h]
avg 134.3543  Epanechnikov estimate
vars 0.001027  Probability curve
min 134.2545  Density histogram, 25 classes
max 134.4989
median 134.3529
le kw 134.3323  Basic run for changed input file
3e kw 134.3761  Operating parameters varied
stds 0.032043  Feed composition varied
h 0.016022
glow 134.2224
ghigh 134.5309
gpoints 50  hpoints 25
gwidth 0.006296  hwidth 0.012854

Kolmochorov-Smirnov test (prob D > std)
D 0.025283
Qks(DBN) 0.707867
count 937 Rate NO in column top
sum 511.8905 Rate NO [kmol/h]
avg 0.546308 Epanechnikov estimate
vars 0.008104 Probability curve
min 0.298336 Density histogram, 25 classes
max 0.851518
median 0.537242
lekw 0.486166 Basic run for changed input file
3ekw 0.600072 Operating parameters varied
stds 0.090022 Feed composition varied
h 0.036009
glow 0.208313
ghigh 0.941541
gpoints 50 hpoints 25
gwidth 0.014964 hwidth 0.030551

Kolmochorov-Smirnov test (prob D > std)
D 0.045742
Qks(DBN) 0.039638
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<td>Rate H3O+ [kmol/h]</td>
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<td>Density histogram, 25 classes</td>
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<td>Operating parameters varied</td>
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<tr>
<td>Feed composition varied</td>
<td>0.12</td>
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</table>

Kolmochorov-Smirnov test (prob D > std)

| D   | 0.0188 |
| Qks(DN) | 0.894991 |

Density histogram, 25 classes
count 424  Column top flowrate NO
sum 227.6138  Rate NO [kmol/s]
avg 0.536825  Epanechnikov estimate
vars 4.61E-08  Probability curve
min 0.535217  Density histogram, 25 classes
max 0.538108
median 0.5368
le kw 0.536822  Basic run for changed input file
3e kw 0.53686  Start estimations varied
stds 0.000215  Check for convergence accuracy
h 6.44E-05
glow 0.535002
ghigh 0.538323
gpoints 50  hpoints 25
gwidth 6.78E-05  hwidth 0.000138

Kolmochorov-Smirnov test (prob D > std)
D 0.313966
Qks(DBN) 9.95E-37
count 424
sum 56965.12
avg 134.3517
vars 5.6E-05
min 134.2791
max 134.3945
median 134.3519
1e kw 134.3511
3e kw 134.3524
stds 0.007484
h 0.001
glow 134.2716
ghigh 134.402
gpoints 50
hpoints 25
gwidth 0.002662
hwidth 0.005434

Kolmochorov-Smirnov test (prob D > stnd)
D 0.300425
Qks(DBN) 1.15E-33

Column bottom flowrate H3O+
Density histogram, 25 classes

Column bottom flowrate H3O+
Epanechnikov estimate

Column bottom flowrate H3O+
Probability curve
count 424  Column bottom flowrate HN02
sum 823.5806  Rate HNO2 [kmol/s]
avg 1.942407  Epanechnikov estimate
vars 4.26E-06  Probability curve
min 1.921226  Density histogram, 25 classes
max 1.954481
median 1.942472
1e kw 1.942259  Basic run for changed input file
3e kw 1.942607  Start estimations varied
stds 0.002064  Check for convergence accuracy
h 0.00031
glow 1.919162
ghigh 1.956545
gpoints 50  hpoints 25
gwidth 0.000763  hwidth 0.001558

Kolmochorov-Smirnov test (prob D > std)
D 0.289303
Qks(DBN) 3E-31

Column bottom flowrate HNO2
Density histogram, 25 classes

Column bottom flowrate HNO2
Epanechnikov estimate

Column bottom flowrate HNO2
Probability curve