ADIABATIC CALORIMETRIC STUDIES OF HYDROXYLAMINE COMPOUNDS

A Dissertation

by

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ABSTRACT

Adiabatic Calorimetric Studies of Hydroxylamine Compounds. (August 2002)

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Chair of Advisory Committee: Dr. M. Sam Mannan

In the present work, the thermal decomposition reaction of HA and some of its derivatives (aqueous solutions of hydroxylamine, hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine o-sulfonic acid) were studied using adiabatic calorimetry. The effect of some metal contaminants such as Ti, stainless steel, carbon steel, ferric ion, and ferrous ion was also analyzed. Useful information was generated such as safe storage temperatures (onset temperature), maximum temperature, maximum pressure, pressure of noncondensables, heat and pressure generation rates as functions of temperature, temperature vs. pressure and time to maximum rate. To get an insight about the possible decomposition mechanisms, HA decomposition reactions were carried out with and without air above the sample. The thermokinetics of the respective systems was modeled using the heat generation rates. From such kinetic models, reaction order, activation energies, and frequency factors for the overall decomposition reactions were obtained. The kinetic parameters were used in computer simulations to obtain models for the temperature vs. time curves. Since several members of the hydroxylamine family were studied, a comparison of their thermal behavior is presented.
To my husband Javier, my brothers Rodolfo, Francisco Javier and José Juan, and my parents Rodolfo and Olivia…
ACKNOWLEDGMENTS

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CHAPTER I
INTRODUCTION

Technological development has necessitated the design of chemical processes that require higher pressures, higher temperatures, and new substances as raw materials. Generally, the main or desired reaction is well studied by the specific company before its implementation in the plant. Unfortunately, the unwanted pathways such as side or decomposition reactions, which may lead to industrial incidents, are often overlooked.

A typical example of the situation described above is what happened with hydroxylamine. The expansion of the electronics industry generated a larger demand for hydroxylamine/water 50 wt.% (HA) and resulted in the construction of a new plant, Concept Sciences, Inc. (1999), and the increase in capacity of an existing plant, Nissin Chemical Co., Ltd (1998). On February 19, 1999, an explosion at Concept Sciences, Inc., near Allentown, Pennsylvania, killed five people, injured 13 more, and destroyed a 45,000 square-foot area. The explosion occurred during the distillation of the first commercial batch of HA produced by this company. Nissin Chemical Co., Ltd. in Japan also had a fatal incident on June 10, 2000. In this incident four workers were killed, another four were seriously hurt, and 54 people outside the plant were injured. Presently, the only manufacturer of hydroxylamine free base is the German firm BASF.

This dissertation follows the style and format of Journal of Hazardous Materials.
Although the root cause of these incidents have not yet been established, these tragic incidents stress the importance of obtaining information about the reactive behavior of hydroxylamine and its derivatives.

Calorimetry is used to study thermal behavior and therefore to evaluate the potential hazards of chemical reactions. The two main types of thermal hazard evaluation calorimeters in current industrial use are screening and adiabatic. Screening calorimeters such as the Reactive System Screening Tool (RSST) are used for rapid tests of systems for thermal hazards. In general, only materials that have shown potential hazards with a screening method are evaluated using adiabatic calorimetry, because the time and costs of tests associated with adiabatic calorimetry are usually much higher.

Adiabatic calorimetric experiments are important when testing for thermal hazards because they simulate the worst-case scenario, or in other words, these experiments generate pressure and temperature profiles when all the heat produced by the reaction is utilized in accelerating the reaction rate itself. This self-accelerating cycle is called a runaway reaction; where the heat released by the reaction is used to increase the reaction rate, which increases the heat production rate even further. Frequently, a runaway reaction stops only when the reactants are depleted or the sample vessel fails.

Unfortunately, thermal hazard and thermal stability data for HA were not available at the time of the incidents. Some derivatives of hydroxylamine such as hydroxylammonium
chloride, hydroxylammonium sulfate, and hydroxylamine o-sulfonic acid are used widely in industry without knowledge of the thermal hazard risks posed by them. This work presents information about the thermal decomposition reactions of HA and some of its derivatives (hydroxylammonium chloride or sulfate, hydroxylamine o-sulfonic acid) which is urgently needed to provide a basis for safer handling, use, and storage of hydroxylamine compounds.

The thermal decomposition reactions of HA and some of its derivatives (aqueous solutions of hydroxylamine, hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine o-sulfonic acid) were studied using mainly adiabatic calorimetry. The effects of some metal contaminants such as Ti, stainless steel, carbon steel, ferric ion, and ferrous ion also were analyzed.

Useful information such as safe storage temperatures (onset temperature), maximum temperature, maximum pressure, pressure of noncondensables, heat and pressure generation rates as functions of temperature, temperature vs. pressure, and time to maximum rate are presented in this work.

Due to its industrial importance, stability tests for aqueous solutions of hydroxylamine free base (pure) at 100 °C are reported. To obtain an understanding of the possible decomposition mechanisms, HA decomposition reactions were carried out with and without air above the sample. The thermokinetics of the respective systems were
modeled using the heat generation rates. From such kinetic models, reaction order, activation energies, and frequency factors for the overall decomposition reactions were obtained. The kinetic parameters were used in computer simulations to obtain models for the temperature vs. time curves. Since several members of the hydroxylamine family were studied, a behavior analysis was performed.

Chapter II presents a review of calorimetry including the fundamental equations that are used to evaluate and model the experimental data. Chapter III provides detailed information about experimental equipment and methods used in this dissertation. The body of knowledge gathered in this work is presented in Chapters IV through IX. Chapter IV is dedicated to hydroxylamine. Chapter V presents the effect of metal contaminants in the hydroxylamine decomposition. Chapter VI is dedicated to hydroxylamine hydrochloride, Chapter VII to hydroxylamine sulfate, and Chapter VIII to hydroxylamine-o-sulfonic acid. A comparison of the studied hydroxylamine-related compounds is presented in Chapter IX. Chapter X summarizes this dissertation by stating the conclusions of this work.

The data generated in this work are extremely useful for industry and can help in the design of relief devices, process control strategies (temperatures to set alarms, temperatures of no return, etc.), selection of process equipment materials, design of process emergency procedures, and can also prevent catastrophes. Scientific knowledge
is a milestone for safety because there are no hazardous substances, only hazardous ways of handling substances.
CHAPTER II
ABOUT CALORIMETRY

1. Introduction

Calorimetry has been used extensively in the area of process safety since it provides critical information about thermal behavior of chemical substances; therefore it is a fundamental method in the study of potential hazards of chemical reactions. The thermodynamic and kinetic data provided by calorimetry can be used to prevent runaway reactions, to design pressure relief systems for process equipments, to test for storage compatibility, to design chemical process, and to aid in the scale up process, among other applications.

The two main types of calorimeters in current industrial use are screening and adiabatic. Screening calorimeters, such as the Reactive System Screening Tool (RSST), are used for rapid tests of systems for thermal hazards. In industrial practice, only materials that have shown potential hazards with a screening method are evaluated using adiabatic calorimetry, because the time and costs of tests associated with adiabatic calorimetry are usually much higher. A discussion of these two types calorimeters together with a comparison of results produced by them is provided by Leung and Fisher.
The industrial applications of adiabatic calorimetry include, but are not limited to: determination of onset temperatures, $T_{on}$ (temperature at which the rate of reaction is high enough to produce a detectable adiabatic temperature rise), information concerning heat release as a function of temperature, thermokinetics (how fast energy is released), and determination of gas evolution.

There are several adiabatic calorimeters available, including ARC, APTAC, Phi-Tec, and VSP. Probably the most used adiabatic calorimeter is the accelerating rate calorimeter ARC, which was developed by Dow in the late seventies [34][35][36][37]. Nevertheless, there are some drawbacks to the ARC such as the necessary use of thick walled 10 cc cells, since there is no mechanism to back up the cell pressure. This kind of sample cells absorbs a greater portion (compared with thin walled cells) of the generated heat lowering the measured self-heat values. Another disadvantage is that the “sample” thermocouple is positioned in the outside wall of the ARC sample cell, which may lead to inaccuracies in the reading. A further drawback of the ARC is that only metallic sample cells can be used, which diminishes the number of materials that can be tested.

The automatic pressure tracking adiabatic calorimeter (APTAC) is a recently developed adiabatic calorimeter, which can use thin, low thermal inertia, 130 cc sample cells [38]. Due to its pressure compensation mechanism, samples can be run even in glass cells.
(which is necessary if the sample reacts with metals). One drawback of the APTAC is its expensive and time-consuming maintenance in contrast to the simpler design of the ARC.

Part of the goals of the Mary Kay O’Connor Process Safety Center at Texas A&M Chemical Engineering Department is to provide industry with process-safety-related scientific knowledge needed for safe industrial design and operations so costly incidents can be prevented. As mentioned in Chapter I, hydroxylamine has recently been involved in two major fatal industrial incidents. We know also (due to personal communications) that hydroxylamine has caused incidents during laboratory and pilot plant operations. As shown in their respective chapters, hydroxylamine-compound thermal decomposition data are practically nonexistent, which may be explained by the impossibility of performing accurately certain measurements in other than an APTAC calorimeter. There are no more than ten APTACs in the world and most of them are used to generate proprietary or internal data.

2. Data gathering using adiabatic calorimetry

The main purpose of performing adiabatic calorimetric studies is to obtain information about the temperature and pressure changes as functions of time during a runaway event. The runaway represents an uncontrolled reaction where sufficient cooling capabilities of the system are lost and the energy generated by the reaction is utilized to accelerate the
reaction rate itself. The data measured using adiabatic calorimetry consist mainly of the following: temperature vs. time, pressure vs. time, temperature vs. pressure, heat rate vs. temperature, and pressure rate vs. temperature profiles.

As expected, most of these data are useful for industrial applications. The shape of the curves stated above gives an idea of the potential hazard that the reaction poses (the steeper the slope the greater the hazard). In addition to the shapes of the curves, there are some data values that are of paramount industrial importance. Among those values are:

- Onset temperature ($T_{on}$). Onset temperature provides an idea of safe storage and process temperatures. In industrial practice, a safety gap of at least 30 °C is recommended to avoid the $T_{on}$ of an undesired reaction.
- Maximum adiabatic temperature ($T_{max}$). This measurement is necessary to ensure that in the worst-case scenario, the mechanical integrity (due to thermal effects) of the container and/or reactors would not be compromised.
- Maximum pressure ($P_{max}$). This is the main risk factor to consider, since normally the mechanical failure of containers and/or reactors is compromised by over pressurization during a runaway. This is an important parameter in the design of safety-relief valves.
- Maximum heat rate is used in the design of safety-relief equipment.
- Maximum pressure rate is used in the design of safety-relief equipment.
• Time to maximum rate ($t_{MR}$) provides an estimate of the time available to respond to and prevent a runaway reaction.

The sections that follow explain how fundamental principles of kinetics, reaction engineering, and thermodynamics are used to interpret the experimental calorimetric data.

3. Kinetic analysis

To rationalize adiabatic data, the material and energy balances must be coupled and a rate law (an empirical algebraic expression that gives the amount of a specific product produced per unit time per unit volume as a function of temperature and concentration of the reacting species) is used so these three equations can be solved numerically.

The general material balance Equation (independent of reactor type) for component A is:

$$F_{Ao} - F_{A} + \int_{V} r_{A} dV = \frac{dN_{A}}{dt}$$  \hfill (2.1)

where $F_{Ao}$ is the rate of flow of A into the system (moles/time), $F_{A}$ is the rate of flow of A out of the system (moles/time), $r_{A}$ is the rate law, $V$ is the reacting volume, $N_{A}$ is the number of moles of A inside the reactor, and $t$ is time. The general energy balance is the
first law of thermodynamics, which for an open system without nuclear reactions and ignoring the flow potential and kinetic energies is:

\[
\frac{d(U + Ek + Ep)}{dt}_{sys} = \dot{Q}^s + \dot{W}^s - P \frac{dV_{sys}}{dt} + \sum_{i} F_{io} H_{io} - \sum_{i} F_{i} H_{i},
\]

(2.2)

where U, Ek, Ep are the internal, kinetic, and potential energies respectively, H is the enthalpy (energy per mol), and n is the number of species. The subscript “o” denotes the inlet conditions, and the unsubscripted symbols denote the outlet conditions. The subscript “sys” refers to a system property. \(\dot{Q}^s\) is the heat flow given to the system (energy/time), and \(\dot{W}^s\) is the shaft work (energy/time), which is positive when input to the system. If the system changes volume over time that needs to be accounted for in the energy balance, but for the APTAC experiments the system volume is fixed and the \(- P \frac{dV_{sys}}{dt}\) term of the energy balance will be ignored.

The data produced by adiabatic calorimetry can be utilized to create a kinetic model for the reaction. The form of the model depends on the assumptions, such as type of reactor (completely adiabatic or with correction for the degree of adiabaticity), reaction pathway type (single, parallel, or auto catalytic reactions, etc.), mass transfer effects (whether or not concentration and/or temperature gradients within the reactor are simulated), volume behavior (whether or not volume is assumed constant during the reaction), among other
factors. As an example of the methodology, the discussion below illustrates the development of a kinetic model using adiabatic data.

The energy balance in Equation 2.2 can be put into a more workable expression. If we neglect changes in potential and kinetic energy and considering an ideal solution, the system energy can be written in terms of the enthalpy as:

$$U_{sys} = \sum_{i=1}^{n} N_i U_i = \sum_{i=1}^{n} N_i (H_i - PV_i) \quad (2.3)$$

where $N$ is number of moles and $P$ is pressure. The subscript “$i$” refers to the $i$ species.

Equation 2.2 requires the derivative with respect to time of Equation 2.3 to give:

$$\left[ \sum_{i=1}^{n} N_i \frac{\partial H_i}{\partial t} + \sum_{i=1}^{n} H_i \frac{\partial N_i}{\partial t} - \frac{\partial}{\partial t} \left( P \sum_{i=1}^{n} N_i V_i \right) \right]_{sys} = \dot{Q}_{sys} + W_{sys} + \sum_{i}^{n} F_{io} H_{io} - \sum_{i}^{n} F_{i} H_{i} \quad (2.4)$$

If we consider the total reaction volume constant, the effect of pressure negligible, and:
\[ H_i = H^0(T_R) + \int_{T_s}^{T} Cp_i dT \]  

(2.5)

\[ \frac{dH_i}{dt} = Cp_i \frac{dT}{dt} \]  

(2.6)

\[ \frac{dN_i}{dt} = -\nu_i r_A V + F_{io} - F_i \]  

(2.7)

\[ \Delta H_{rxn}(T) = \sum_{i=1}^{n} \nu_i H_i(T) \]  

(2.8)

where \( T \) is temperature, \( T_R \) is the reference temperature, \( H^0 \) is the reference enthalpy, \( Cp \) is the heat capacity at constant pressure, \( \nu_i \) is the stoichiometric coefficient of the \( i \) species, and \( \Delta H_{rxn} \) is the overall heat of reaction. Equation 2.4 then becomes:

\[ \frac{dT}{dt} = \frac{Q + W - \sum_{i=1}^{n} F_{io} (H_i - H_{io}) + (\Delta H_{rxn})(-r_A V)}{\sum_{i=1}^{n} N_i Cp_i} \]  

(2.9)

If we assume that the sample cell is our system, with experiments carried out in a closed cell environment, the flow terms in Equation 2.1 are not necessary. If we assume that there are no spatial gradients of temperature and concentration in the reacting volume, the rate law is a constant and can be pulled out of the integral. Then Equation 2.1 reduces to:
\[
\frac{dN_A}{dt} = r_A V \tag{2.10}
\]

If we also assume that the reaction volume is constant during the reaction, the volume can be brought inside the differential, and Equation 2.10 becomes:

\[
\frac{d[A]}{dt} = r_A \tag{2.11}
\]

The energy balance in Equation 2.9 can be simplified assuming that the system is completely adiabatic and that the stirrer work is negligible. If we also assume that the reaction takes place in the liquid phase, then

\[
\sum N_i C_{p,i} = N_{Ao} C_{ps}
\]

where the $C_p$ of the reacting mass ($C_{ps}$) is constant during the reaction:

\[
\frac{dT}{dt} = \frac{(-\Delta H_{rxn})(-r_A V)}{N_{Ao} C_{ps}} \tag{2.12}
\]

The material balance, Equation 2.10, and the energy balance, Equation 2.12, can be coupled and then integrated to give an expression for $N_A$ as a function of temperature. If we assume that $\Delta H_{rxn}$ is independent of temperature, this relationship becomes:
where \( N_{Ao} \) is the initial number of moles at the onset temperature of the reaction, \( T_{on} \).

\( \Delta H_{rxn} \) can be deduced from Equation 2.13 by applying a boundary condition, assuming that the reaction goes to completion (\( N_A = 0 \)) at the maximum temperature \( T_{max} \):

\[
- \Delta H_{rxn} = (T_{max} - T_{on}) C_{ps}
\]  

(2.14)

The expression of \( N_A \) as a function of temperature can be written as:

\[
N_A = \frac{N_{Ao}}{T_{max} - T_{on}} \frac{(T_{max} - T)}{C_{ps}}
\]  

(2.15)

or since reaction volume has been assumed constant:

\[
[A] = [A]_{on} \frac{(T_{max} - T)}{(T_{max} - T_{on})}
\]  

(2.16)

where \([A]\) is the concentration of species A at any given temperature between \( T_{on} \) and \( T_{max} \). \([A]_{on}\) is the concentration of A at the onset temperature and is normally assumed to be approximately equal to the initial concentration. All the above equations are
independent of the rate law; to give an insight of the kinetics a rate law should be assumed. Since in this work several decomposition reactions were studied, a power law kinetic model can be assumed:

\[ A \rightarrow \text{Products} \quad (2.17) \]
\[ r_A = -k[A]^p \quad (2.18) \]

where \( p \) is the reaction order and \( k \) is the kinetic constant, which is known to increase exponentially with temperature. If \( k \) is assumed to follow a classical Arrhenius Equation then:

\[ k = \alpha e^{-\frac{E_a}{RT}} \quad (2.19) \]

where \( \alpha \) is the frequency factor (assumed here to be independent of temperature), \( E_a \) is the activation energy, and \( R \) is the gas constant.

Differentiating Equation 2.16 with respect to time and combining Equations 2.11 and 2.18, an expression for the derivative of temperature with respect to time is obtained:

\[ \frac{dT}{dt} = k \left( \frac{[A]_{in}}{T_{max} - T_{on}} \right)^{p-1} (T_{max} - T)^p \quad (2.20) \]
Rearranging Equation 2.20:

\[
k^* = k[A]^{p-1}_{on} = \frac{dT}{dt} \frac{(T_{max} - T_{on})^{p-1}}{(T_{max} - T)^p}
\]  

(2.21)

Assuming a value for the reaction order, the pseudo kinetic constant \( k^* \) can be calculated, since the adiabatic data provides the heat rate as a function of \( T, T, T_{max}, T_{on}, \) and \( [A]_{on} \approx [A]_o, \) which is known.

Combining Equations 2.19 and 2.21:

\[
\ln(k^*) = \ln([A]^{p-1}_{on} \alpha e^{\frac{Ea}{RT}}) = \ln([A]^{p-1}_{on} \alpha) - \frac{Ea}{R} \frac{1}{T}
\]

(2.22)

If the assumed reaction order is correct, an Arrhenius plot of \( \ln(k^*) \) vs. \( 1/T \) will give a straight line. Statistical methods such as simple linear regression can be used to extract the unknown parameters (\( \alpha, Ea \)) from Equation 2.22.

Using a linear regression model:

\[
Y = \beta_0 + \beta_1 X
\]

(2.23)
And for each observation:

\[ y_i = \beta_o + \beta_1 x_i + \varepsilon_i \]  

(2.24)

where \( Y \) is the expected value of \( \ln(k^*) \), \( X \) is \( 1/T \), \( y_i \) is the calculated value of \( \ln(k^*) \) at a specific inverse temperature \( x_i \) (1/Ti), \( \varepsilon_i \) is the random error, and \( \beta_o, \beta_1 \) are the regression coefficients. The expected value of the regression coefficients is

\[ \ln([A]_{on}^{\rho-1} \alpha) \text{ and } -\frac{E_a}{R}, \text{ respectively.} \]

If the least squared method is used to estimate the regression coefficients, then:

\[ \hat{\beta}_o = \bar{y} - \hat{\beta}_1 \bar{x} \]  

(2.25)

\[ \hat{\beta}_1 = \frac{\sum_j x_j y_j - \left[ \sum_j y_j \right] \left[ \sum_j x_j \right]}{n_{obs}} \]  

(2.26)

\[ \sum_j x_j^2 = \frac{\sum_j x_j^2 - \left[ \sum_j x_j \right]^2}{n_{obs}} \]

\[ \bar{y} = \left( \frac{1}{n_{obs}} \right) \sum_j y_j \]  

(2.27)
\[
\bar{x} = \left( \frac{1}{n_{\text{obs}}} \right) \sum_{j} x_j
\]

(2.28)

where \( n_{\text{obs}} \) is the number of data points collected. The circumflex above the regression values indicates that those are estimators of the real regression values. Once the estimates of the regressors have been calculated, the values of the activation energy and frequency factor can be obtained.

Once the kinetic parameters and the heat of reaction are known, Equations 2.11, 2.13, 2.18 and 2.19 can be combined to obtain a differential equation of the form

\[
\frac{d[A]}{dt} = f([A]) \quad \text{with initial condition} \quad [A] (t = 0) = [A]_{\text{ion}} = [A]_o.
\]

This equation can be integrated numerically (Euler’s, Runge-Kutta or Gear’s method) to obtain the temperature vs. time profile.

4. Correcting for heat lost

Due to the nature of the heat control system of an adiabatic calorimeter, part of the heat produced by the sample is consumed in heating the sample cell. An energy balance can be written as follows:

\[
m_s C_s [\Delta T_{\text{ad}}]_{\text{corrected}} = (m_s C_s + m_c C_c) [\Delta T_{\text{ad}}]_{\text{measured}}
\]

(2.29)
where $m_s$ is the sample mass, $C_s$ is the sample heat capacity, $m_c$ and $C_c$ are the sample cell mass and heat capacity, respectively, and $\Delta T_{adb}$ is the adiabatic temperature rise

$$\Delta T_{adb} = T_{\text{max}} - T_{on} \quad (2.30)$$

From Equation 2.29 it can be seen that the adiabatic temperature rise when there are no heat losses to the sample cell, $[\Delta T_{adb}]_{\text{corrected}}$, is given by:

$$[\Delta T_{adb}]_{\text{corrected}} = \frac{m_s C_s + m_c C_c}{m_s C_s} [\Delta T_{adb}]_{\text{measured}} \quad (2.31)$$

One commonly used methodology to assess the deviation from adiabaticity is the use of the thermal inertia factor, $\phi$, defined as the ratio of the heat consumed by the sample and sample cell to the heat consumed by the sample:

$$\phi = \frac{m_s C_s + m_c C_c}{m_s C_s} \quad (2.32)$$

The inverse of the thermal inertia factor is known as the degree of adiabaticity of a particular experiment.
From Equation 2.31 and 2.32 it can be seen that the relationship between the adiabatic temperature rise measured and corrected is a linear function of $\phi$.

$$[\Delta T_{\text{adib}}]_{\text{corrected}} = \phi [\Delta T_{\text{adib}}]_{\text{measured}}$$

(2.33)

Higher thermal inertia factors slow the reaction in a nonlinear fashion and lower the maximum heat rate temperature. Commonly, $\phi$ factors are close to unity in industrial processes making important the development of mathematical models that account for the heat losses. Such models will include the kinetic parameters of the reactions. Described below is one such model developed using a power law kinetic model to describe the overall, single, well-characterized reaction.

Experiments with different $\phi$ factors will have different temperatures for the same heat rate including the initial heat rate at which the onset temperature is detected; therefore an adjusted initial onset temperature must be calculated. Equation 2.20 represents the heat rate, which is the same for the onset temperature $T_{on_1}$ at a particular $\phi$ factor, $\phi_1$, and for $T_{on_2}$ at a particular $\phi_2$.

$$\alpha e^{-\frac{E_a}{RT_{on_1}}} \left( \frac{T_{max_1} - T_{on_1}}{\Delta T_{adib_1}} \right)^p \Delta T_{adib_1} [A]^{p-1} = \alpha e^{-\frac{E_a}{RT_{on_2}}} \left( \frac{T_{max_2} - T_{on_2}}{\Delta T_{adib_2}} \right)^p \Delta T_{adib_2} [A]^{p-1}$$

(2.34)
Combining Equations 2.30, 2.33, and 2.34 yields a relationship between the onset temperatures of two experiments ran at different thermal inertia factors:

\[
\frac{1}{T_{on_2}} = \frac{1}{T_{on_1}} + \frac{R}{Ea} \ln \left( \frac{\phi_1}{\phi_2} \right) \tag{2.35}
\]

Combining Equations 2.30 and 2.33 results in an expression to adjust the temperature measurements:

\[
T_2 = T_{on_2} + \frac{\phi_1}{\phi_2} \left( T_1 - T_{on_1} \right) \tag{2.36}
\]

Equation 2.36 can be used to predict temperature values at \( \phi_2 \) using measured temperatures at \( \phi_1 \) (\( T_1 \)) once an adjusted \( T_{on_2} \) has been calculated from Equation 2.35.

A relationship for the heat rate at two different thermal inertia factors can be derived by using Equations 2.19, 2.20, 2.33, and 2.36.

\[
\left. \frac{dT}{dt} \right|_{\phi_2} = \frac{\phi_1}{\phi_2} e^{\frac{Ea}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]} \left. \frac{dT}{dt} \right|_{\phi_1} \tag{2.37}
\]
Equation 2.37 should be used once the adjusted temperatures at the new thermal inertia factor \( \phi_1 \) have been calculated using Equation 2.36. It is important to measure reactions at different \( \phi \), since the evolution of heat of the first reaction can be so abrupt that it can mask other reactions.

5. Analysis of pressure data

We can deduce the kind of system (gassy, hybrid, or vapor pressure controlled) that the decomposition reaction represents. This information will aid in the process design stages of industrial work. From thermodynamics we know that a plot of \( \ln P_{\text{sat}} \) vs. \( 1/T \) is approximately a straight line. If the data fit that model, the system is tempered and, in the event of a runaway, the energy necessary to evaporate the solvent when the reactive mass reaches for equilibrium (\( P_{\text{sat}} \)) will create a heat sink decelerating the runaway. In this kind of system the pressure increase is due to the increase in temperature of the reactive mass (but not due to the production of gas in the reaction).

Using the Clausius/Clapeyron equation, an approximation for the heat of vaporization, \( \Delta H^v \), of the reaction mixture can be extracted from the pressure vs. temperature data prior to the runaway assuming that during the wait and search period the pressure measured is the saturation pressure of the mixture, \( P^a \).
\[
\Delta H^\text{iv} = -R \frac{d \ln P^\sigma}{d \left( \frac{1}{T} \right)}
\]  

(2.38)

The degree of reaction for the isothermal and ramped experiments can be interpreted using the gas evolution. Gas evolution also can be employed to discriminate against possible decomposition products.

6. Catalytic effects

When dealing with heterogeneous catalysis, it is important to measure the surface area of the catalyst, so the ratio of metal surface contact area to sample volume (SVR) is calculated as a measure of catalyst surface area.

\[
SVR = \frac{2\pi \cdot rh}{V}
\]  

(2.39)

where \(V\) is the sample volume, \(r\) is the cell internal radius, and \(h\) is the sample height, which is calculated from the following Equation:

\[
\left(\frac{1}{3} \pi\right) h^3 - (r\pi)h^2 + V = 0
\]  

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CHAPTER III
EXPERIMENTAL DETAILS

1. Introduction

Some of the heat effects in the physical and chemical properties of substances have been known since 600 BC [39]. Phase transition (a process in which energy is consumed with no increment in temperature) has been studied experimentally since 1760, and the adiabatic method was first used by Person in 1849 [40]. Nevertheless, the term thermal analysis (the measurement of material properties as a function of temperature) was not used until 1903. At present, the term calorimetry is commonly used in a broader sense than its etymological meaning (measurement of heat [41]), and instruments are called calorimeters even when they do not measure energy in or out of the sample.

The term adiabatic calorimetry has been historically related to the measurement of heat capacities [42][43][44][45][46][47][48][49], and some books even define adiabatic calorimeter as an instrument to measure heat capacities [50]. Table 3.1 presents several kinds of calorimeters and/or thermal analysis instruments each one producing somewhat different data. It can be seen that the APTAC is an adiabatic calorimeter that is not used to determine heat capacities since it does not directly measure the energy in or out of the sample.
Table 3.1
Types of calorimeters and thermal analysis instruments

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Name</th>
<th>Output</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCC</td>
<td>Mixing Cell Calorimeter</td>
<td>Energy as function of time</td>
<td>Mostly proprietary designs</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimeter</td>
<td>Measurement of thermal energy input to sample compared to reference</td>
<td>[51][52][53]</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetric Calorimeter</td>
<td>Mass as a function of temperature</td>
<td>[54][55][56]</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis Calorimeter</td>
<td>Temperature difference between sample and reference as function of temperature</td>
<td>[57][58]</td>
</tr>
<tr>
<td>RSST</td>
<td>Reactive System Screening Tool</td>
<td>Temperature vs. time and pressure vs. time profiles</td>
<td>[59]</td>
</tr>
<tr>
<td>ARC</td>
<td>Accelerating Rate Calorimeter</td>
<td>Temperature vs. time and pressure vs. time profiles</td>
<td>[60][61]</td>
</tr>
<tr>
<td>APTAC</td>
<td>Automatic Pressure Tracking Adiabatic Calorimeter</td>
<td>Temperature vs. time and pressure vs. time profiles</td>
<td>[38]</td>
</tr>
<tr>
<td>VSP</td>
<td>Vent Sizing Package</td>
<td>Temperature vs. time and pressure vs. time profiles</td>
<td>[62]</td>
</tr>
</tbody>
</table>

Beginning in the 1950’s, the necessity to evaluate the possibility of runaway reactions as a chemical process hazard became evident. It is believed that around 20% of process incidents are caused by lack of thermochemical knowledge [63], runaway reactions being one of the most common and dangerous results of this lack of information.
Although there have been some efforts to predict the hazard potential of chemical substances \[64\] \[65\], at the present, there is no substitute for experimentation to obtain the thermokinetic and vapor pressure information during runway conditions.

From the calorimeters presented in Table 3.1, only the ARC, VSP, and APTAC had been specifically developed to obtain thermokinetic and vapor pressure data during runaway reactions to aid in the design of chemical processes. The RSST is basically a screening tool, so when a strong exothermic behavior is detected, the same reaction is tested in one of the other three apparatus. Safe handling temperatures, compatibility, catalysis effect of contaminants, and information to design safety relief devices are some of the uses for data provided by these calorimeters.

Accelerating rate calorimetry (ARC) was first developed by Dow Chemical in the 1970’s. This technique consists of heating the sample to a reaction initiation temperature and then minimizing heat losses by keeping the temperature of the sample surroundings as close as possible to the temperature of the sample. When an exothermic reaction is initiated, the heat produced will increase the sample temperature, since the heat losses to the surroundings are minimized. This increased temperature will increase the reaction rate in an exponential fashion releasing even more heat, which will increase the reaction rate even further and lead to a runaway reaction. The ARC was the first calorimeter designed to study the temperature and pressure profiles generated during a
runaway reaction. It is important to understand that the heat of reaction has to be estimated since the ARC does not directly measure energy in or out of the sample.

In 1976 the Design Institute for Emergency Relief Systems (DIERS) was created as part of an AIChE effort to understand the runaway hazards and to protect chemical plants against those hazards. By the time DIERS was dissolved (1986), they had created a manual for emergency relief design, a computational program (SAFIRE), and the VSP apparatus. The VSP uses the same accelerating rate principle as the ARC but it has the advantage of producing low thermal inertia data since the sample size can be bigger and, due to a pressure compensating procedure, the sample cell walls can be thin since they are not required to withstand large pressure differentials. In mid 1980’s Union Carbide designed an improved accelerating rate calorimeter that later became the APTAC.

The APTAC is a low thermal inertia reaction calorimeter that uses the accelerating rate principle of the ARC, the pressure compensating principle of the VSP, and has an improved heater and software design that minimizes heat losses. The improved design makes the APTAC very flexible in terms of sample cell materials, experiment environment (open and/or closed cell test) and heating modes (adiabatic or isothermal modes). Table 3.2 compares some of the characteristics of the ARC, VSP, and APTAC calorimeters.
### Table 3.2
Comparison of calorimeters used to obtain process safety data

<table>
<thead>
<tr>
<th></th>
<th>ARC</th>
<th>VSP</th>
<th>APTAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum adiabatic follow up, °C/min</td>
<td>10</td>
<td>100</td>
<td>400</td>
</tr>
<tr>
<td>Pressure follow up psi/min</td>
<td>-</td>
<td>3,000</td>
<td>10,000*</td>
</tr>
<tr>
<td>Minimum thermal inertia attainable</td>
<td>2</td>
<td>1.05</td>
<td>1.1</td>
</tr>
</tbody>
</table>

*Depending on test cell material

When first developed, these process safety calorimeters were used only by large chemical companies that had the resources for the costly and time consuming operation of those calorimeters. The great potential to prevent runaway reaction catastrophes remained minimal since the companies kept the experimental information proprietary.

Although the open literature has little information regarding thermal stability behavior, the use of these process safety calorimeters to obtain vapor pressure and thermokinetic data for runaway reactions has become more popular in recent years [70][71][72][73][74][75][76][77][78] which benefits society by providing information that can help to prevent incidents in medium and small sized companies.

The work presented in this dissertation was performed mainly in an APTAC, which will be described in detail in the following section. A flux calorimeter Setaram C 80 I I also was used in this study. This chapter describes also the analytical equipment that was used in this work.
2. APTAC apparatus

2.1. Description

A schematic of the APTAC calorimeter is shown in Figure 3.1. A more detailed schematic is presented in [38]. The spherical sample cell is screwed at the top of the high-pressure vessel, which is protected from overpressure by a rupture disk set at 2,200 psia. The APTAC can operate in range of 30-500 °C and a maximum pressure of 2,000 psia. There are 7 type N thermocouples: one of them is directly touching the sample, one is located in the external surface of the sample cell wall, one measures the temperature of the nitrogen gas surrounding the sample cell, the other thermocouples each measure the temperature of one specific heater. There are four heaters: top, bottom, wall, and tube. These heaters completely surround the sample cell. The tube heater is wrapped around a special fitting that connects the tubing and thermocouple through the pressure vessel head. The pressure vessel contains ceramic insulation to aid in the adiabatic operation of the heaters.
The pressure generated inside the sample cell during a reaction is dynamically compensated by the injection of nitrogen to the pressure vessel, which keeps the pressure differential across the cell wall typically within 5 psia of the specified value. This feature allows the use of thin walled test cell materials. A typical APTAC test cell is 2.5 in. diameter and has 0.02 in. wall thickness. The free volume of a sample cell is ~ 130 cm³. Sample cells are available in titanium, hastelloy, tantalum, stainless steel, and glass. The spherical bombs have a 0.5” diameter neck so they can be attached to the top part of the pressure vessel using a nut and a graphite ferrule.
The sample adiabaticity is obtained by controlling the heaters output, since each heater element has a PID controller assigned to it. The temperature of the nitrogen surrounding the sample is maintained by the control system as close as possible to the sample temperature to achieve adiabaticity. A PC with a Windows operating system controls the heaters, pressure control mechanism, data logging, and some of the safety devices of the calorimeter (shutdown criteria). A reaction can be followed adiabatically up to 400 °C/min. Pressure rates of ~10,000 psi/min in metal cells and ~1,000 psi/min in glass cell can be followed.

The thermocouple and pressure transducer signals are digitized and processed by a signal conditioning unit available from National Instruments SCXI series and a 16 bit A/D board. The analog output signals are controlled by a National Instruments 12-bit D/A board.

The on/off valves are air operated ball valves. A pneumatic flow control valve regulates the flow of nitrogen in and out of the pressure chamber. Pressure is measured by strain-gauge pressure transducers with a 0-2,500 psia range and 0.1% of full scale error.

2.2. Heating modes

Open and closed cell experiment can be performed in the APTAC, and its heating modes include Heat-Wait-Search (HWS), Ramp, and Isothermal.
In the Heat-Wait-Search mode, the sample is heated to an initial search temperature and the temperature is allowed to stabilize (20 minutes). Then if exothermic activity is detected, as exhibited by a threshold sample temperature rise of 0.05-0.1°C/min, the apparatus follows the reaction adiabatically until the reaction ends or until one of the pre-selected safety shutdown criteria is met. If no exothermic activity is detected within 20 minutes, the sample is heated to the next search temperature and the procedure is repeated until a preset maximum search temperature is reached.

In the Ramp experiment a fixed heating rate is selected and the temperature and pressure of the sample are monitored. The calorimeter will or will not switch to adiabatic operation during an exotherm depending on user specification. If the temperature of the sample goes above the programmed temperature increase and the adiabatic mode on exotherm was not specified, there will be heat losses, so this mode of operation is equivalent to the RSST.

In the Isothermal mode the temperature of the sample is kept at a preset value for a fixed amount of time. If the sample heats itself the heaters will maintain the system adiabatic. Every 30 min the self-heat rate is measured and if it is lower than the apparatus detection limit for an exotherm (0.05-0.1 °C/min), the sample is returned to the isothermal value.

In any heating mode the type of collected data are the same. The frequency of data collection depends on sample activity and can vary from every 10 minutes to less than
one second. The recorded data includes: time (min), sample temperature (°C), N₂ temperature (°C), wall temperature (°C), sample pressure (psia), vessel pressure (psia), heat rate (°C/min), pressure rate (psia/min), and the temperature in °C of each heater (tube, top, side, and bottom).

2.3. Equipment safety

The heater elements can be easily overheated since the power available to them is 5 KW. To protect the heaters, the required output is compared to a programmed output, and when the output is higher than programmed the power to the heaters is interrupted. There are manually set temperature breakers, which will shutdown the main power supply if the temperature in the heaters exceeds the manually preset value. A thermocouple malfunction (infinite reading) can be detected by the program, which immediately shuts down power to the heaters.

To protect against an over pressurization of the container vessel, the operating program is designed to shut down the experiment if the pressure in the container vessel exceeds 2,000 psia. The container vessel is protected also by a rupture disk set at 2,200 psia.

To minimize personnel exposure, there are safety interlocks in the calorimeter doors, which prevent power to the heaters when the doors are opened. Also, the container vessel cannot be opened when it contains pressure due to the safety collars design. Also,
a “watch-dog” timer ensures that the power to the heaters will shut down in the event of
a computer malfunction.

2.4. Equipment modifications

The APTAC’s original setup was modified to run experiments according to the research
needs. This section describes the main modifications performed to: create a metal free
testing environment, obtain a vacuum in the sample cell while the pressure vessel is
open, run extremely corrosive samples, and inject small amount of reactants when the
experiment is running.

To create a metal free environment a Teflon-coated thermocouple of 1/16” diameter was
used. The standard all 1/16” OD tubing tube heater assembly shown in Figure 3.2 and
3.3 was changed for a new tube heater assembly in which one of the tubes was 1/8” OD
so the Teflon coated thermocouple could fit inside.
Figure 3.2. Lateral view of the APTAC tube heater assembly.

Figure 3.3. Tube heater assembly top view. The inner circle represents the copper rod on which the tube heater is wrapped. The copper rod has five 1/16" channels and a 1" deep well for the tube heater thermocouple.

To create a vacuum inside the sample cell while maintaining the pressure vessel open, a manual valve was added to the tubing below the pressure vessel before it connects to the vacuum line. This modification is represented in Figure 3.1.
To run extremely corrosive samples such as hydroxylamine hydrochloride, the copper core of the tube heater assembly was modified not only to use a Teflon-coated thermocouple, but also the tubing was made out of hastelloy C-296 instead of stainless steel, which dramatically increased corrosion resistance.

During the research, the apparatus was modified so a small amount of liquid (approximately one gram) could be added to the sample cell during an experiment. For this purpose, a two 1/8” and two 1/16” orifice tube heater assembly was designed and fabricated. The extra 1/8” hole was used to introduce a 25 cm long metal needle to inject the reactants.

2.5. Assurance of APTAC data integrity

Care was taken to assure the quality of the data collected. Approximately every 20 runs, and when a new thermocouple was installed, the following operations were performed: test for leaks, verification of similar thermocouple readings, ice point check, and thermocouple calibration.

To test for leaks, a soap and water solution was used. The absolute pressure and the rate of pressure change inside the container were recorded over time. When a rate of pressure change of 0.01 psi/min or less was obtained, the search for leaks was suspended and the apparatus was judged leak free.
When the calorimeter was in equilibrium (left without sample cell overnight), similar thermocouple readings were expected (± 0.5 °C) for all the thermocouples. This was true most of the time, however when it was not, the proper thermocouple offset was adjusted.

The ice point check is an easy way to check the integrity of the sample, nitrogen and wall thermocouples. A water/ice mixture was prepared and put in contact with each of these thermocouples and a reading of 0 °C was adjusted when necessary. The water used to perform the ice point check was Aldrich reagent grade catalog number 32,007-2 and the ice was taken from the chemical engineering unit operations laboratory.

When a calibration run is programmed, the thermocouple offsets at different temperatures were automatically stored. Figure 3.4 presents the temperature vs. time and pressure vs. time data for a typical calibration. Figure 3.5 presents the vapor pressure data for the same calibration.
Figure 3.4. Typical temperature and pressure profiles for an APTAC calibration run.

Figure 3.5. Vapor pressure plot for an APTAC calibration run.
The calibration results are important to assess the calorimeter performance, and as shown in Figure 3.4 the steps of temperature and pressure should be well defined. Since the sample cell is filled with air during a calibration, a straight line is expected when plotting pressure vs. temperature data. In a calibration vapor pressure plot such as Figure 3.5, the data collected during the heating period should overlap the data collected during the cooling period to assure that there are no leaks in the sample cell and connecting tubing.

To compare the values generated by the APTAC to open literature values two kinds of experiments were performed periodically: water vapor pressure and tert-butyl-peroxide (TBP) standard runs.

Figure 3.6 presents a typical water vapor pressure run and compares it to the steam table values. Since water was the solvent for the hydroxylamine family samples, these experiments served also to test for possible control drifts such as false exotherm detection. When the heat of vaporization for a temperature range of 25-266 °C was calculated using the methodology described in Chapter II, a value of $\Delta H_{lv} = 8.14$ Kcal/mol was obtained from the APTAC and $\Delta H_{lv} = 9.77$ Kcal/mol from the steam tables, which yields an error of 16.7%. This error is small considering the large temperature range.
A 20 wt.% TBP in toluene standard was run periodically to compare the data obtained with the accepted values provided by the APTAC designers. Table 3.3 presents a summary of the measured parameters and Figure 3.7 presents the heat rate data for the exotherm. It can be seen that the values are in excellent agreement.

### Table 3.3
Measured experimental parameters for the TBP standard

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{on}$ °C</th>
<th>$T_{max}$ °C</th>
<th>$P_{max}$ psia</th>
<th>Non condensable pressure psi</th>
<th>$dT_{max}$/°C/min</th>
<th>$dP_{max}$/psi/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBP 20%, Sep 00</td>
<td>132.9</td>
<td>234.6</td>
<td>681</td>
<td>260.3</td>
<td>149</td>
<td>1,386</td>
</tr>
<tr>
<td>TBP 20%, Sep 01</td>
<td>132.6</td>
<td>236.7</td>
<td>750</td>
<td>260.5</td>
<td>150</td>
<td>1,618</td>
</tr>
<tr>
<td>TBP 20%, Standard</td>
<td>130.7</td>
<td>232.9</td>
<td>652</td>
<td>247.2</td>
<td>140</td>
<td>1,249</td>
</tr>
</tbody>
</table>
Figure 3.7. APTAC standard sample heat rate with 20 wt.% TBP in toluene.

### 3. Flux calorimeter

A few of the experiments presented in this work were performed in the National Research Institute for Fire and Disaster (NRIFD) located in Tokyo, Japan. The calorimeter used for these experiments was a flux calorimeter, Setaram C80 II, which measures the energy in or out of the sample cell and provides experimental values for reaction heat.
The Setaram calorimeter uses the Calvet principle to measure the heat flux when two experimental vessels (one for the sample and one for reference) are placed in a calorimetric block, which imposes a temperature ramp or maintains the temperature constant.

This calorimeter has two identical fluxmeters made from several thermocouples connected in series. The fluxmeters are the connection between the sample vessels and the calorimetric block and their electrical output is proportional to the energy exchanges between the samples and the calorimetric block. The output of this calorimeter is power as a function of time and the integration of the area under an exothermic peak yields the energy released.

For the experiments reported in this work, 0.2 gr of HA from Nissin Chemical were placed in the sample vessel and 0.2 g. of α-alumina in the reference vessel. The scanning rate was 0.1 °C/min from 25-300 °C.

4. Analytical equipment

For the analytical measurements of the gas phase, a three Tesla Fourier Transform Mass Spectrometer (FTMS), also known as Ion Cyclotron Resonance Mass Spectrometry, (ICR-MS) located in the chemistry department of TAMU was used. The source was an electron impact (EI) at 70 eV for 5 ms with scanning ranging from 11-10,000 m/z (mass
to charge). The sample was introduced into the FTMS chamber until a pressure of 3.0E-8 Torr was achieved. The species detected all have ionization energy well below 70 eV, so the relative counts obtained can be translated into relative percentages. A standard containing N₂, NO, and N₂O was analyzed in the instrument to validate the aforementioned assumption.

The gaseous products were analyzed also using a gas chromatograph (GC), since the possible H₂ contained in the decomposition products is not detected in the EI-FTMS. The equipment was a GC Varian 3400 connected to a thermal conductivity detector (TCD) and to a flame ionization detector (FID). The sample size was 0.5 ml for the TCD and 0.25 ml for the FID. A Chromsorb 107 12’ x 1/8” 80/100 13X molecular Sieve 6’x1/8’ 40/60 column was used for the TCD detector and an alumina plot capillary column 40 m x 0.53 mm x15 microliters was used for the FID detector. The temperature program was as follows: 4 min at 35 °C, then a 10 °C/min ramp until 200 °C, and finally 20 min at 200 °C. Actually, only the TCD detector was useful for our particular gas mixture, since the FID detector enables mainly hydrocarbon analysis.

Liquid products were analyzed for ammonia, water, and Cu in the TAMU Agricultural Analytical Service Laboratory. The ammonia quantification method consisted of adding MgO to the ammonia-containing sample and titrating the resulting mixture with NaOH using methyl red as an indicator. The water content of the liquid residue was analyzed
using a Karl Fischer moisture method. Atomic Absorption (AA) proved the presence of a bluish ammonia-copper complex.

Semi-quantitative energy disperse spectrums were run for some solid residues using a Cameka electron microscope located in the TAMU Geology Department.


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CHAPTER IV

HYDROXYLAMINE STUDIES

1. Background

With a world capacity of around 800,000 tons per year [79], hydroxylamine is widely used in industry. Hydroxylamine salts, either chloride or sulfate, (hydroxylammonium chloride or sulfate) are used in commercial plants, because free base (pure) hydroxylamine aqueous solutions are less stable. For some chemical processes, especially in the electronics and pharmaceutical industries, hydroxylamine free base is required. New syntheses in which hydroxylamine or its derivatives play an important role are constantly being developed [80][81][82][83][84].

Pure hydroxylamine is a white crystal that can decompose violently at ambient temperatures. Hydroxylamine free base is commercialized as 50 wt.% solution in water (HA), and proprietary stabilizers are added to these solutions [85]. Some of the presently available properties of hydroxylamine crystal are presented in Appendix A. Due to its simple structure, hydroxylamine has been the subject of theoretical studies [86][87][88][89][90][91][92][93][94]. Relatively little experimental information is

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available [95][96][97][98][99][100][101][102][103][104], and data concerning its thermal decomposition behavior are practically nonexistent [105].

Information about hydroxylamine-derivatives thermal behavior is also scarce with the exception of some references about hydroxylammonium nitrate [106][107][108][109]. The ability of hydroxylamine to react with metals and the catalytic effect of those in the hydroxylamine reaction are known [110][111][112][113][114][115][116][117][118], nevertheless, to the best of our knowledge, metal effects on the heat generation rates in the overall thermal decomposition reaction of hydroxylamine or its derivatives have not been studied.

The thermal decomposition products of HA are not completely known. Some well recognized process safety handbooks such as Sax’s Dangerous Properties of Industrial Materials report the decomposition products to include NOx gases [119]. A possible overall reaction for the formation of these products is the following:

\[
3\text{NH}_2\text{OH}_{(\text{liq})} \rightarrow \text{NO}_{(\text{gas})} + \text{NO}_2(\text{gas}) + \text{NH}_3(\text{gas}) + 3\text{H}_2(\text{gas}) \quad (4.1)
\]

Due to the scarcity of heat of formation data for hydroxylamine, calculation of the energetics of this reaction is uncertain. Reported values for the standard heat of formation of hydroxylamine liquid vary from -21.7 Kcal/mol [120] to -25.5 Kcal/mol [121] for \(\Delta H_{\text{rxn}}\) for Equation 4.1 of 27.9 and 31.7 Kcal/mol\text{NH}_2\text{OH}, respectively. These
values are endothermic contrary to our experimental observations for HA decomposition, which will be presented in this chapter. Therefore, Equation 4.1 is not dominant in the overall decomposition reaction. Reference [120] suggests the following reaction:

\[
2\text{NH}_2\text{OH}_{\text{gas}} + 0.5\text{O}_2 \rightarrow 3\text{H}_2\text{O}_{\text{gas}} + \text{N}_2 \tag{4.2}
\]

This reference also mentions that Equation 4.2 yields an estimated heat release of -59.2 Kcal/mol (This value differs from the -76.5 Kcal/mol\(_{\Delta f \text{H}^0 \text{NH}_2\text{OH}}\) obtained when a \(\Delta f \text{H}^0 \text{NH}_2\text{OH}_{\text{gas}}\) of -10.2 Kcal/mol reported in [122] is used). If Equation 4.2 is important in the overall decomposition reaction of HA then, at least some of the experimental measurements (onset temperatures, non condensable pressure, time to maximum rate, heat and pressure rates vs. temperature, and vapor pressure of the mixture) for samples run with air should differ from those of the samples run in vacuum.

Additional references describe the complex nature of the HA decomposition reaction system by addressing the possibility of distinct pathways depending on the pH [123]:

\[
3\text{NH}_2\text{OH} \rightarrow \text{NH}_3 + \text{N}_2 + 3\text{H}_2\text{O} \quad \text{in alkaline solutions} \tag{4.3}
\]

\[
4\text{NH}_2\text{OH} \rightarrow 2\text{N}_2\text{O} + 2\text{NH}_3 + 3\text{H}_2\text{O} \quad \text{in acid solutions} \tag{4.4}
\]
Both of these reactions are exothermic. Because HA samples are alkaline (pH >10), Equation 4.3 can be thought as the predominant reaction during the thermal runaway of HA. This hypothesis is proven wrong when compared to the experimental values presented in this chapter.

There are qualitative reports of HA decomposition products under a variety of conditions. The species NO, N₂O, N₂, and NH₃ have been detected when hydroxylamine decomposes over Nuchar© in refluxing isopropanol [114]. N₂O and NH⁺₄ were detected when HA disproportionates in acid media [83]. Lunak [113] stated that the decomposition products of HA in alkaline media are NH₃, N₂, N₂O, and hyponitrite (N₂O₂²⁻) and assumed that the reaction proceeds through the nitroxyl (HNO) intermediate. Lunak confirmed the presence of intermediates N₂ and N₂O when the decomposition reactions were carried out under certain conditions and with various metal catalysts. It was assumed by Lunak that HA decomposition does not occur without a metal catalyst.

For process safety, it is important to determine the decomposition products under runaway conditions, which are similar to the conditions in the event of a process upset. HA decomposition products under runaway conditions have not been measured and could be different than those mentioned above, mainly because:

1) The liberated self-heat significantly increases the temperature, which can activate a wider spectrum of reactions.
2) Because the experiments are carried out in a closed cell environment, all of the decomposition products and reactants can react further.

This chapter advances the understanding of the HA thermal decomposition reaction by providing useful parametric information such as $T_{on}$, $T_{max}$, $P_{max}$, and non-condensable pressure for experiments run with air above the sample and in vacuum. Decomposition products under runaway conditions and heat of decomposition are also presented. A kinetic model that fits the experimental data is presented. To the best of our knowledge none of this process safety-related and critically needed information has been previously reported.

2. Experimental details

2.1. Samples

Two sources of 50 wt.% hydroxylamine/water were used in the present study: Aldrich hydroxylamine 99.999% 50 wt.% solution in water, catalog No. 46,780-4, and hydroxylamine 50 wt. % solution in water with added stabilizers, supplied by an industrial source (HA ind). The Aldrich hydroxylamine samples featured a nominal high purity and contained no added stabilizers. All HA samples were used in the received condition without further analysis or purification.
2.2. Apparatus

Most of the data presented in this chapter were generated utilizing an APTAC calorimeter (adiabatic, isothermal or ramped mode), some data about the heat of reaction of HA were generated utilizing a flux calorimeter (Setaram C 80 II), as described in Chapter III.

2.3. Analytical methods

For the analytical measurements of the gas phase, a three Tesla Fourier Transform Mass Spectrometer (FTMS) also known as Ion Cyclotron Resonance Mass Spectrometry (ICR-MS) was used. The source was electron impact (EI) at 70 eV for 5 ms with scanning ranging from 11-10,000 m/z (mass to charge). The sample was introduced into the FTMS chamber until a pressure of 3.0E-8 Torr was achieved. Also, a gas chromatograph (GC) was used as described in Chapter III.

Liquid products were analyzed for ammonia using titration with NaOH. Semi-quantitative energy disperse spectrums were run for some solid residues using a Cameka electron microscope. Atomic Absorption (AA) proved the presence of a bluish ammonia-copper complex.
2.4. *Experimental method*

For the present work, all APTAC experiments were performed in a closed cell environment. Some experiments were run with ambient air above the sample and for the others the air was evacuated. The air evacuation procedure consisted of two parts:

1) HA samples were transferred to glass sample cells using disposable plastic pipettes. Sample masses were obtained by weight differences. Because of the relative small amounts of sample, no stirring was used during the APTAC runs.

2) The sample cell was mounted into the APTAC calorimeter. Liquid nitrogen was used to freeze the sample to -102 °C before removing air by vacuum once (< 0.5 psia). For some samples this procedure was repeated up to three times with no difference in the results. After the air above the sample was removed, the sample cell was sealed for the run but it remained connected to a pressure transducer and a thermocouple.

A sample thermocouple with a black Teflon-coated sheath (0.06” ID) was used to prevent the metal sheath from contacting the sample and catalyzing the HA decomposition. Experimental runs were performed in borosilicate glass sample cells of 130 cm³ nominal volume. It was presumed that glass cells provided a neutral environment without significant catalysis for the HA decomposition.
2.5. **Uncertainties**

A type N thermocouple was used to measure sample temperatures with an overall absolute uncertainty of ~ ± 1 °C, and was periodically checked at 0 °C using an ice bath. Sample pressures were measured with Sensotec absolute pressure transducers within an overall uncertainty of ~ ± 2 psi and were frequently checked for agreement with ambient pressures. Sample weights were measured with accuracy to within ± 0.01 gr. Sample cell volumes were within ± 5 cm³ of 130 cm³.

3. **Results and discussion**

3.1. **Effect of industrial stabilizers in the thermal decomposition of HA**

Heat-wait-search experiments were performed to obtain onset temperatures, lumped kinetics of the overall decomposition reaction system, heat generation rates, pressure generation rates, and pressures of noncondensable products. Figure 4.1 shows a typical plot of temperature as a function of time for a HA decomposition test with the search mode of the APTAC above and below the HA exotherm region. Because the sample cell absorbs some of the generated thermal energy, the use of relatively high nominal φ factors ~3.4 with sample sizes of ~2.2 g was needed for the APTAC to follow the exothermic decompositions of HA to completion. The value of onset temperature reported here is about 0.1 °C/min, which approaches the detection limit of the APTAC.
Figure 4.1. Typical temperature vs. time plot for the decomposition of 50 wt.% hydroxylamine/water in glass cell.

It can be seen from Figure 4.1 that there is only one overall exotherm for the 50 to 400 °C temperature spectrum studied. A summary of the decomposition tests in borosilicate glass cells is presented in Table 4.1. In all the Tables, uncertainties reported correspond to one standard deviation of the experimental replicas. As shown in Table 4.1, there is no significant difference in the onset temperature of the HA thermal decomposition reaction with and without stabilizers. The heat generation rate is higher in samples without stabilizers than in samples with stabilizers, but this difference did not significantly affect the calculated activation energy within the experimental uncertainty.
Table 4.1
HA decomposition parameters for samples with and without stabilizers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rep*</th>
<th>T_{on} °C</th>
<th>T_{max} °C</th>
<th>P_{max} psia</th>
<th>dT/dt_{max} °C/min</th>
<th>dP/dt_{max} psia/min</th>
<th>Ea kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>2</td>
<td>136 ± 1</td>
<td>207 ± 6</td>
<td>338 ± 41</td>
<td>4.5 ± 1.0</td>
<td>20 ± 3</td>
<td>34 ± 5</td>
</tr>
<tr>
<td>HA ind</td>
<td>3</td>
<td>133 ± 2</td>
<td>216 ± 8</td>
<td>402 ± 45</td>
<td>1.9 ± 0.7</td>
<td>27 ± 34</td>
<td>29 ± 4</td>
</tr>
</tbody>
</table>

* Replicas. $\phi = 3.4$

Figure 4.2 shows the decomposition kinetics plot of HA with and without stabilizers for the first half of the overall reaction, which can be represented approximately as first order.

Figure 4.2. HA with stabilizers (HA ind) and without stabilizers (HA) decomposition kinetics (50% of reaction).
The noncondensable pressure generated was approximately 47 psia at 50 °C for both kinds of samples (with and without stabilizers) with a remaining liquid weight of 74-60 % of the initial sample weight. The final color was bluish for the HA with stabilizers and green-bluish or teal for the HA without stabilizers.

3.2. Effect of air in the thermal decomposition of HA

Table 4.2 presents a summary of the experimental conditions along with the physical appearance of the sample residues after the experiments were completed and the samples returned to room temperature and exposed to air. No differences were observed in the physical aspects of the residue between samples run with air or in an evacuated environment. In all the experiments the liquid residues were crystal clear when attached to the calorimeter, but some of the liquid samples turned blue when removed from the calorimeter. Seven samples were run with air above the sample and six samples were run in a vacuum environment. The liquid remains range from 40-80mass% of the original sample weight.
Table 4.2  
Summary of HA decomposition data for samples run with and without air

<table>
<thead>
<tr>
<th>Run conditions</th>
<th>Sample identification</th>
<th>Initial g ± 0.01</th>
<th>Final g ± 0.01</th>
<th>Liquid residue</th>
<th>Solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>HA, air 1</td>
<td>8.09</td>
<td>3.13</td>
<td>Bluish*</td>
<td>White</td>
</tr>
<tr>
<td>Air</td>
<td>HA, air 2</td>
<td>8.04</td>
<td>3.54</td>
<td>Bluish*</td>
<td>White</td>
</tr>
<tr>
<td>Air</td>
<td>HA, air 3</td>
<td>8.03</td>
<td>5.15</td>
<td>Clear</td>
<td>White</td>
</tr>
<tr>
<td>Air</td>
<td>HA, air 4</td>
<td>8.01</td>
<td>4.98</td>
<td>Clear</td>
<td>White</td>
</tr>
<tr>
<td>Air</td>
<td>HA, air 5</td>
<td>8.02</td>
<td>3.90</td>
<td>Clear</td>
<td>White</td>
</tr>
<tr>
<td>Air</td>
<td>HA, air 6</td>
<td>8.01</td>
<td>1.39</td>
<td>Bluish*</td>
<td>White</td>
</tr>
<tr>
<td>Air</td>
<td>HA, air 7</td>
<td>8.00</td>
<td>2.66</td>
<td>Clear</td>
<td>White</td>
</tr>
<tr>
<td>Vacuum</td>
<td>HA, vacuum 1</td>
<td>8.01</td>
<td>3.62</td>
<td>Bluish*</td>
<td>White</td>
</tr>
<tr>
<td>Vacuum</td>
<td>HA, vacuum 2</td>
<td>8.03</td>
<td>3.08</td>
<td>Bluish*</td>
<td>White</td>
</tr>
<tr>
<td>Vacuum</td>
<td>HA, vacuum 3</td>
<td>8.01</td>
<td>2.88</td>
<td>Clear</td>
<td>White</td>
</tr>
<tr>
<td>Vacuum</td>
<td>HA, vacuum 4</td>
<td>8.01</td>
<td>4.12</td>
<td>Clear</td>
<td>White</td>
</tr>
<tr>
<td>Vacuum</td>
<td>HA, vacuum 5</td>
<td>8.01</td>
<td>3.86</td>
<td>Bluish*</td>
<td>White</td>
</tr>
<tr>
<td>Vacuum</td>
<td>HA, vacuum 6</td>
<td>8.02</td>
<td>3.20</td>
<td>Clear</td>
<td>White</td>
</tr>
</tbody>
</table>

*When exposed to air

Some of the liquid residue was put into an amber container to see if light affected the change in color but this residue also turned blue. When the pH was changed from basic to acid the blue color disappeared, but when the pH was set basic, the color appeared again. That behavior was an indication of a possible complex formation. It is known that the copper II ion ammonia complex Cu(NH₃)₄²⁺ has a deep blue color, and 165 ppm of copper was measured in the liquid residue samples using Atomic Absorption. The probable source of the copper is the tube heater assembly of the APTAC.
Apart from the liquid residue, there was a thin layer of a white solid attached to the glass sample cell. This layer was not soluble in water, acid, or basic solutions and could not be removed. No solid residue was expected given the species involved in the reaction. The solid residue, tested using a Cameka electron microprobe, consisted mostly of Si. It is a well-documented fact that silica (SiO₂), the main component of the glass sample cells, has increased solubility as pH increases. A consistent explanation for the formation of this solid is that part of the glass sample cell dissolved at the high temperature generated during the runaway reaction and the high pH of the solution (the liquid remains had a pH of 11.5) and then recrystalized to form the white solid residue. As mentioned above, the presence of NOₓ components in the gas products gas suggested by some references, it is well known that NO₂ has a characteristic brown color so, for some experiments, the APTAC header assembly was opened to see the color of the gas phase. The gas phase had no color, which quickly eliminated NO₂ as a significant decomposition product. This observation was corroborated by the analytical results presented below.

A summary of the data measured is presented in Table 4.3. The reported uncertainties are one standard deviation measured within the experimental replicas. The onset temperatures and the maximum adiabatic temperatures agree within experimental uncertainty for the experiments performed with and without air (T_{on} = 117.5 and 118.5 °C; T_{max} = 273 and 274 °C, respectively), which correspond to similar adiabatic temperature rises (ΔT_{adb}) of 155 °C and 156 °C, respectively.
Table 4.3
Measured HA decomposition parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Runs</th>
<th>T_{on} °C</th>
<th>T_{max} °C</th>
<th>ΔT_{adb} °C</th>
<th>ΔP_{max} psia</th>
<th>Non condensable pressure psia</th>
<th>t_{MR} min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA, air</td>
<td>7</td>
<td>117.5 ± 6</td>
<td>273 ± 5</td>
<td>155 ± 7</td>
<td>901 ± 64</td>
<td>51 ± 12</td>
<td>161 ± 27</td>
</tr>
<tr>
<td>HA, vacuum</td>
<td>6</td>
<td>118.5 ± 5</td>
<td>274 ± 4</td>
<td>156 ± 7</td>
<td>916 ± 56</td>
<td>57 ± 12</td>
<td>156 ± 33</td>
</tr>
</tbody>
</table>

ϕ ≈ 2

Because the samples run in vacuum start at a lower pressure, the maximum increase in pressure, ΔP_{max}, (pressure at T_{max} - pressure at T_{on}) is reported instead of the maximum pressure. The non-condensable pressure is the difference between the pressure after the experiment was completed and cooled to 50 °C and the pressure when the sample was first heated to 50 °C. The non-condensable pressure provides an estimate of the produced gas, which is the primary danger during a runaway, since this increase in pressure results from the gaseous products formed and cannot be tempered by the consumption of latent heat.

The time to maximum heat rate, t_{MR}, estimates the time available to prevent a possible catastrophe from the moment that a process deviation is first detected (0.1 °C/min of heat
of reaction). \( \Delta P_{\text{max}} \), non-condensable pressure, and \( t_{\text{MR}} \) reported in Table 4.3 in the two oxygen environments are equal within experimental error.

Some clues about the decomposition pathway are provided by the pressure data. Note that although the \( \Delta P_{\text{max}} \) is high (901 psia in air and 916 psia in vacuum), the non-condensable pressure is relatively low (51 psia in air and 57 psia in vacuum), which indicates that much of the pressure is due to the vapor pressure of the solvent and products that are liquid at ambient temperature but mainly vapor at \( T_{\text{max}} \). The vapor pressure of water at \( T_{\text{max}} \) is approximately 873 psia, which suggests that much of \( \Delta P_{\text{max}} \) is due to water and is consistent with the low non-condensable pressure observed. It is important to note that the heat produced in the reaction vaporized water with a large heat of vaporization. If the reaction were carried out in another solvent with a lower heat of vaporization the increase in temperature during the reaction should be higher.

Figure 4.3 presents the measured vapor pressure curves for the experiments run in the two different environments. The initial pressure pad above the sample at the beginning of the experiment has been subtracted to make a fair comparison of the experiments run with air and in vacuum. This plot is consistent with the fact that there is relatively little gas generation, which puts the HA thermal decomposition reaction in the limit between the hybrid and tempered system classification \([124]\). The pressure generated during the reaction is produced by both vapor pressure and gas generation (hybrid system), but that
the vast majority of the pressure is generated by solvent vapor pressure (tempered system).

Figure 4.3. HA decomposition vapor pressure.

The non-condensable pressure is a clue to the moles of generated vapor, which can be compared to the theoretical moles of vapor generated by a proposed pathway. Table 4.4 presents the moles generated during the reaction calculated as an ideal gas. Assuming the decomposition of HA in alkaline solutions in Equation 4.3, the nitrogen gas produced is 0.04 moles, which is approximately twice the observed value. This observation
suggests that, even though our samples are alkaline, Equation 4.3 is not the only reaction involved in the thermal decomposition of HA during runaway conditions.

Table 4.4
Moles generated and calculated heat release (HR) by HA decomposition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moles of non condensables generated</th>
<th>φ factor</th>
<th>HR (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA, air</td>
<td>0.017 ± 0.004</td>
<td>2.06</td>
<td>14.1 ± 0.6</td>
</tr>
<tr>
<td>HA, vacuum</td>
<td>0.019 ± 0.004</td>
<td>2.08</td>
<td>14.3 ± 0.6</td>
</tr>
</tbody>
</table>

Because the APTAC does not measure directly the heat released, the heat of reaction must be estimated. The energy released by the reaction under adiabatic conditions is utilized in three ways: in heating the reaction mass, in heating the reaction cell, and in vaporizing some of the liquid reaction mixture. Table 4.4 presents estimated heat releases using an average Cp for the sample of 0.669 cal/(g °C), for which it was assumed that the Cp of the reacting mixture was constant over the entire temperature range. This method is common for heat of reaction estimation in adiabatic calorimetry. Nevertheless, this heat release does not include the heat necessary for evaporating some of the reaction mass, which in this case is significant.
To correct for the evaporation effect, a novel approach was taken using the steam Tables [125], since approximately 90 mol% of the vapor at $T_{\text{max}}$ and a significant portion of the liquid mass is water. This approach, yielding an approximate $\Delta H_{\text{rxn}}$ of -28 Kcal/mol, accounts also for some of the non-idealities of the liquid and the gas at high temperatures and pressures. This value is an approximation and includes the following uncertainties: the compositions of the liquid and vapor phases are not known at the initial and final states, some of the heat may be dissipated during the runaway, and some of the sample reacts before the onset temperature. Even though some sample reacts during the heat-wait-search steps below the exotherm, no significant differences in $T_{\text{on}}$ or $T_{\text{max}}$ were measured when the starting search temperature was 80 °C instead of the standard 50 °C.

When evaluating reaction hazards, we must know not only the amount of heat produced but also how fast this heat is liberated. Figure 4.4 shows the measured heat rate with respect to temperature, and Figure 4.5 presents the measured pressure rate with respect to temperature. The reproducibility of the experiments can be clearly observed in these graphics. There are no significant differences in these rates between the samples run with air and the samples run in vacuum.
Figure 4.4. HA decomposition heat generation, $\phi = 2$.

Figure 4.5. HA decomposition pressure generation, $\phi = 2$. 
Table 4.5 presents a summary of the measured maximum heat and pressure rates and the calculated activation energies, frequency factors (A), and reaction orders for samples run with air and in vacuum. It is shown that both overall reactions can be represented with the same reaction order and similar activation energies.

Table 4.5
Summary of HA decomposition kinetic parameters for samples run in air and in vacuum

<table>
<thead>
<tr>
<th>Sample</th>
<th>$dT/dt_{\text{max}}$</th>
<th>$dP/dt_{\text{max}}$</th>
<th>Order</th>
<th>$E_a$</th>
<th>$\ln(A/\text{min}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA, air</td>
<td>152 ± 61</td>
<td>2072 ± 750</td>
<td>1</td>
<td>28.9 ± 1</td>
<td>29.5 ± 1.0</td>
</tr>
<tr>
<td>HA, vacuum</td>
<td>148 ± 79</td>
<td>1913 ± 999</td>
<td>1</td>
<td>28.5 ± 2</td>
<td>28.9 ± 2.6</td>
</tr>
</tbody>
</table>

Figure 4.6 presents an Arrhenius plot for all experiments assuming an overall reaction order of one. As shown, all experiments have essentially the same Arrhenius plot.
Figures 4.7 and 4.8 present the Arrhenius plots for different assumed reaction orders for experiments run with air and in vacuum, respectively. It can be observed from these plots that a good estimate for the overall reaction order is one, because it yields a straight line to validate the model.
Figure 4.7. HA decomposition reaction order in air (99% reaction).

Figure 4.8. HA decomposition reaction order in vacuum (99% reaction).
For comparison, the thermal safety investigation software from ChemInform [126] was used to obtain the model parameters by performing a non-linear parameter estimation. The results of both methodologies yielding similar results are shown in Table 4.6. It can be seen that the overall activation energy is lower than the 61.3 Kcal/mol required to break the H₂N–OH bond [122], which is the weakest bond of the hydroxylamine molecule.

Table 4.6
HA decomposition kinetic parameters using different methodologies, φ ≈ 2

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Linear parameter estimation</th>
<th>Non linear parameter estimation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ea, Kcal/mol</td>
<td>28.9</td>
<td>29.3</td>
</tr>
<tr>
<td>p</td>
<td>1.0</td>
<td>1.08</td>
</tr>
<tr>
<td>Ln (A/min⁻¹)</td>
<td>29.5</td>
<td>29.7</td>
</tr>
</tbody>
</table>

The simulated temperature vs. time plot can be observed in Figure 4.9. As shown in the Figure, there is very good agreement between simulated and experimental values, which indicates that, despite the model assumptions discussed in Chapter II, the principal physical and chemical traits of the system are represented by the model.
Figure 4.9. Simulation of temperature vs. time plot for HA thermal decomposition, $\phi \approx 2$.

It is very important to consider the thermal inertia factor when scaling up the experimental results. Table 4.7 presents $T_{on}$, $T_{max}$ and $dT/dt_{max}$ for experiments run in air with different $\phi$ factors. Figure 4.10 presents the heat rate vs. temperature values for the experiments shown in Table 4.7, which includes a prediction of heat rate assuming no heat loss to the sample cell ($\phi = 1$) using the methodology described in Chapter II. As shown in Figure 4.10, the predicted $T_{on}$ and $dT/dt_{max}$ for $\phi = 1$ are 115 °C and 53,246 °C/min respectively. Thermal inertia is an important issue for scaling up of laboratory results to industrial processes, where $\phi$ factors typically are low.
Figure 4.10. Effect of thermal inertia on the self heat rate of HA decomposition.

Table 4.7
HA decomposition parameters at different $\phi$ factors

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>$T_{on}$ °C</th>
<th>$T_{max}$ °C</th>
<th>$dT/dt_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>115*</td>
<td>431*</td>
<td>53246*</td>
</tr>
<tr>
<td>1.37</td>
<td>120</td>
<td>282</td>
<td>469</td>
</tr>
<tr>
<td>2.00</td>
<td>125</td>
<td>277</td>
<td>83</td>
</tr>
<tr>
<td>3.40</td>
<td>136</td>
<td>211</td>
<td>4</td>
</tr>
</tbody>
</table>

*Simulated datum
3.3. *HA ramped experiment*

For comparison, one HA ramped experiment was performed using a heat rate of 2 °C/min and air above the sample. A summary of the results is presented in Table 4.8 and the temperature and pressure profiles for the experiments are presented in Figure 4.11. The only experimental parameter reported in Table 4.8 that can be considered different from the experimental results from the HWS experiments is the onset temperature (178.6 °C for ramp experiment vs. 118 °C for HWS experiment). The ramp value is well above the uncertainty range for the HWS experiments. This can be explained by the fact that the onset temperature in the ramp experiment is determined by a deviation from a baseline that is not apparent until the heat rate is above 2 °C/min.

The HWS experiments are considered more sensitive which explains why adiabatic calorimetry (ARC, APTAC) is preferred over screening ramp methods (RSST) to assess thermal hazard.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial g.</th>
<th>Final g.</th>
<th>T_on °C</th>
<th>T_max °C</th>
<th>P_max psia</th>
<th>Non condensables psia</th>
<th>dT/dt_max °C/min</th>
<th>dP/dt_max psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA, ramp</td>
<td>8.015</td>
<td>3.172</td>
<td>178.6</td>
<td>268</td>
<td>919.6</td>
<td>50.1</td>
<td>80.5</td>
<td>1097</td>
</tr>
</tbody>
</table>
3.4. HA isothermal stability

The thermal stability of HA with stabilizers at 100 °C was tested over a period of three days, as shown in Figure 4.12. A summary of the tests is presented in Table 4.9, which shows that the HA with stabilizers reacted slowly at this temperature, as determined by the average pressure generation rate and by the total noncondensable pressure produced during the experiments (26-29 psia at 100 °C). The appearance of the remaining sample was clear as in the beginning of the experiment. Although, HA with stabilizers is very stable at temperatures below 100 °C, HA without stabilizers decomposes over time even at sub-ambient temperatures. Stored at ~15 °C for a period of five months, an industrial sample without stabilizers generated gaseous decomposition products that expanded the plastic container. An Aldrich HA sample, 99.999% 50wt. % solution in water, that had
been stored at ~15 °C for five months was tested in a glass cell. This older sample exhibited a much more energetic decomposition with an onset temperature of 67 °C and a maximum self-heat rate of 132 °C/min compared with an onset temperature of 136 °C and a maximum self-heat rate of 5 °C/min for a recently received or “new” sample.

Figure 4.12. HA industrial sample stability test at 100 °C.
Table 4.9
Average pressure generated for the 100 ℃ HA industrial sample stability test

<table>
<thead>
<tr>
<th>Sample g.</th>
<th>Time hr</th>
<th>Initial psia</th>
<th>Final pressure psia</th>
<th>Ave. (dP/dt) psia/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.28</td>
<td>72.0</td>
<td>27</td>
<td>56</td>
<td>0.40</td>
</tr>
<tr>
<td>2.22</td>
<td>73.5</td>
<td>28</td>
<td>54</td>
<td>0.34</td>
</tr>
</tbody>
</table>

3.5. *Estimation of the heat of decomposition*

Earlier in this chapter, a value for the overall heat of decomposition reaction of -28 Kcal/mol (-3.55 KJ/g) was obtained using a novel approach to correct for the evaporation of the solvent. The APTAC does not measure heat release itself, so a more accurate way to obtain heat of reaction is from a flux calorimeter. Figure 4.13 presents the heat flux for HA industrial sample measured in a Setaram C 80 II calorimeter. The integration under the curve yields -29.8 Kcal/mol (-3.78 KJ/g), which is in close agreement with the value estimated using the APTAC. This fact stresses the importance of considering the heat of vaporization effect commonly overlooked in adiabatic calorimetry.
3.6. **Analytical results**

H₂ and N₂ were detected in the gas sample by GC. Both samples with and without air contained the same chromatographic peaks. EI-FTMS performed in the gas sample showed the presence of mainly N₂ and N₂O with a small amount of NO. To measure the relative composition of the gas phase EI-FTMS was used primarily, the relative quantification of H₂ was by GC, since EI-FTMS is not able to detect H₂. Table 4.10 presents a summary of the analytical results for the gaseous products of HA thermal decomposition.

![Figure 4.13. Heat flux generated by HA industrial sample decomposition. Research in collaboration with the National Research Institute for Fire and Disaster (NRIFD), Tokyo, Japan.](image)
Table 4.10
Analytical results for gaseous products of HA decomposition

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Replicas</th>
<th>N₂ % mol</th>
<th>NO % mol</th>
<th>N₂O % mol</th>
<th>H₂ % mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA air, 3</td>
<td>2</td>
<td>65 ± 4</td>
<td>6 ± 2</td>
<td>28 ± 3</td>
<td>1 ± 0.1</td>
</tr>
<tr>
<td>HA air, 5</td>
<td>2</td>
<td>75 ± 6</td>
<td>3 ± 3</td>
<td>20 ± 3</td>
<td>2 ± 0.1</td>
</tr>
<tr>
<td>HA vac, 3</td>
<td>2</td>
<td>68 ± 8</td>
<td>4 ± 4</td>
<td>27 ± 4</td>
<td>1 ± 0.5</td>
</tr>
<tr>
<td>HA vac, 5</td>
<td>2</td>
<td>83 ± 14</td>
<td>2.95 ± 3</td>
<td>14 ± 11</td>
<td>0.05 ± 0.01</td>
</tr>
</tbody>
</table>

Table 4.11 presents the analytical results of the gas phase analysis for samples run with air and in vacuum. It can be seen from the table that there is practically no difference in the gaseous product composition for samples run in the two different environments.

Table 4.11
Comparison of analytical results for gaseous products of HA decomposition for samples run with air and in vacuum

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Replicas</th>
<th>N₂ % mol</th>
<th>NO % mol</th>
<th>N₂O % mol</th>
<th>H₂ % mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA air</td>
<td>2</td>
<td>70 ± 7</td>
<td>4 ± 2</td>
<td>24 ± 6</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>HA vacuum</td>
<td>2</td>
<td>76 ± 10</td>
<td>3 ± 1</td>
<td>20.7 ± 9</td>
<td>0.3 ± 0.5</td>
</tr>
</tbody>
</table>

A titration method was used to confirm the presence of ammonia in the final liquid phase, and the water content was determined by Karl Fischer moisture method. The presence of ammonia in the liquid phase was also confirmed by its characteristic odor.

Table 4.12 contains a summary of the analysis performed in the liquid residues.
Table 4.12
Liquid phase residue analysis for HA samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Ammonia mass %</th>
<th>Water mass %</th>
<th>Liquid residue accounted for mass %</th>
<th>Liquid residue unaccounted for mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA air, 1</td>
<td>1.8</td>
<td>96.4</td>
<td>98.2</td>
<td>1.8</td>
</tr>
<tr>
<td>HA air, 3</td>
<td>8</td>
<td>88.1</td>
<td>96.1</td>
<td>3.9</td>
</tr>
<tr>
<td>HA vac, 1</td>
<td>0.7</td>
<td>97.5</td>
<td>98.2</td>
<td>1.8</td>
</tr>
<tr>
<td>HA vac, 2</td>
<td>0.8</td>
<td>98.1</td>
<td>98.9</td>
<td>1.1</td>
</tr>
</tbody>
</table>

It can be seen from Table 4.12 that the main liquid remains of the thermal decomposition of HA are ammonia and water with a maximum of ~5 wt.% of the liquid mass unaccounted for, which can be due to analytical error.

Table 4.13 shows the difference between the liquid residues for samples run in air and in vacuum. The apparent marked difference between the ammonia values for the samples run in air (4.9 mass%) and in vacuum (0.8 mass%) is compensated by a larger standard deviation for samples in air compared to that of the samples run in vacuum. It can be assumed that within the experimental error there is no difference on liquid remains composition for samples run in air or in vacuum.
Table 4.13
Comparison of analytical results for liquid remains of HA decomposition for samples run with air and in vacuum

<table>
<thead>
<tr>
<th>Sample</th>
<th>Replicas</th>
<th>Ammonia mass %</th>
<th>Water mass %</th>
<th>Liquid residue accounted for mass %</th>
<th>Liquid residue unaccounted for mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA air</td>
<td>2</td>
<td>4.9 ± 4.4</td>
<td>92.3 ± 5.9</td>
<td>97.2</td>
<td>2.8</td>
</tr>
<tr>
<td>HAvacuum</td>
<td>2</td>
<td>0.8 ± 0.1</td>
<td>97.8 ± 0.4</td>
<td>98.6</td>
<td>1.5</td>
</tr>
</tbody>
</table>

3.7. Overall HA decomposition reaction under runaway conditions

Because no significant differences were observed in the overall HA decomposition reaction run with or without air, it can be assumed that the oxidation path given in Equation 4.2 is not significant.

The production of $N_2$ and $N_2O$ during the runaway indicates that both Equation 4.3 and 4.4 are important during the runaway, irrespective of the basic pH of the sample and sample remains. This is expected since during the runaway the increased temperature can activate a wider spectrum of reactions.

Based on our experimental observations the overall HA decomposition reaction can be described by the following Equations:

$$xNH_2OH_{\text{liq}} \rightarrow yNH_3_{\text{gas}} + 7N_2_{\text{gas}} + 2.4N_2O_{\text{gas}} + 0.4NO_{\text{gas}} + zH_2O_{\text{gas/liq}} + 0.2H_2_{\text{gas}}$$

(4.5)
where the coefficients for $N_2$, $N_2O$, NO and $H_2$ in Equation 4.5 were selected arbitrarily to maintain the composition in the gas phase consistent with the experimental observations. After that, three atomic material balances (N, O, and H) produced a linear system of three Equations and three unknowns and provided values for the coefficients $x$, $y$ and $z$ by solving the following equation:

$$
\begin{bmatrix}
1 & -1 & 0 \\
3 & -3 & -2 \\
1 & 0 & -1
\end{bmatrix}
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix} =
\begin{bmatrix}
19.2 \\
0.4 \\
2.8
\end{bmatrix}
$$

(4.6)

The coefficients for the HA thermal decomposition overall reaction based on the experimental evidence are then:

$$
31.4NH_2OH_{liq} \longrightarrow 122NH_3_{gas} + 7N_2_{gas} + 2.4N_2O_{gas} + 0.4NO_{gas} + 28.6H_2O_{gas/lq} + 0.2H_2_{gas}
$$

(4.7)

The fractional nature of the coefficients is due to their experimental roots. It is important to note than any linear combination of these coefficients is acceptable and also consistent are slight deviations in the actual coefficients (based on experimental measurements of the gas phase composition). Calculation of the theoretical heat of decomposition is complicated due to uncertainties in the heat of formation value for hydroxylamine in liquid state (-25.5 Kcal/mol [121] or –21.7 Kcal/mol[120]).
Computational chemistry calculations done by other members of our group yielded \(-11.2 \pm 0.5\) Kcal/mol for heat of formation of hydroxylamine in the gas phase which, using the heat of vaporization of 11.4 Kcal/mol as reported in [122], yields a heat of formation for hydroxylamine in the liquid phase of \(-22.6\) Kcal/mol (which is consistent with the data available in the literature). The value of the theoretical heat of decomposition will vary depending on the reference states assumed, which for water can be liquid or gas.

Table 4.14 presents calculations for the theoretical heat of decomposition of hydroxylamine based on Equation 4.7 and compares it to the experimental values.

<table>
<thead>
<tr>
<th>Δ(H^o_{\text{NH}_2\text{OH}}) Kcal/mol</th>
<th>Reference for water</th>
<th>(ΔH^o_{\text{rxn}}) Kcal/mol</th>
<th>% Error based on APTAC (-28 Kcal/mol)</th>
<th>% Error based on Flux calorimeter (-29.8 Kcal/mol)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>-25.5</td>
<td>gas</td>
<td>-29.6</td>
<td>5</td>
<td>0.7</td>
</tr>
<tr>
<td>-25.5</td>
<td>liq</td>
<td>-39.2</td>
<td>29</td>
<td>24</td>
</tr>
<tr>
<td>-21.7</td>
<td>gas</td>
<td>-33.4</td>
<td>16</td>
<td>11</td>
</tr>
<tr>
<td>-21.7</td>
<td>liq</td>
<td>-43</td>
<td>35</td>
<td>31</td>
</tr>
</tbody>
</table>

*Value obtained in collaboration with the NRIFD, Japan

As it can be seen from Table 4.14, the error percentage varies between 5 and 31%. The least difference between theoretical and experimental error is obtained when a gas reference state for water is used along with a \(ΔH^o_{\text{NH}_2\text{OH}}\) of \(-25.5\) Kcal/mol.
4. Conclusions

In glass cells, HA decomposes exothermically with an onset temperature of ~117 °C. The overall decomposition reaction was modeled with first order kinetics with an activation energy of 28.5 ± 2 Kcal/mol. In the thermal decomposition of HA solutions under runaway conditions, $T_{on}$, $T_{max}$, $\Delta P_{max}$, non-condensable pressure, $t_{MR}$, $E_a$, and reaction order are observed not to be significantly affected by the presence of air above the sample. So the detected oxidation products (NO, N$_2$O) are formed primarily by oxygen available within the hydroxylamine molecule. Similar heat rates and pressure rates were measured under air and vacuum conditions. This result shows that an attempt to pacify HA runaway reactions by handling hydroxylamine under oxygen free atmospheres will not result in milder decomposition reactions.

During a HA runaway or process upset, the integrity of glass lined equipment may be compromised since, as shown by our results, glass may dissolve. Another important process safety related result is that the heat produced by the runaway reaction vaporized a solvent with a large heat of vaporization that tempered the reaction. If hydroxylamine is used in another solvent with a lower heat of vaporization, the temperature and pressure increase will be higher.

The HA runaway reaction can be classified as a hybrid system since the pressure at the maximum temperatures is generated mostly by vapor pressure of water with some
noncondensable gas products. Stability tests for the industrial sample (HA with stabilizers) show that at 100 °C the decomposition reaction generates ~ 0.4 psi/hr of vapor. Approximately 0.426 moles of noncondensable gas per mol of pure hydroxylamine are produced during the runaway. The detected gas phase HA decomposition products under runaway conditions for samples run with and without air are approximately 70 mol% N₂, 24 mol % N₂O, 4 mol % NO, and 2 mol % H₂. Ammonia is detected in the liquid residue.

Based on the quantitative analysis of the gas phase decomposition products, the following overall decomposition reaction was determined:

\[
3.14NH₂OH_{\text{aq}} \rightarrow 1.22NH₃_{\text{gas}} + 7N₂_{\text{gas}} + 2.4N₂O_{\text{gas}} + 0.4NO_{\text{gas}} + 28.6H₂O_{\text{gas}} + 0.2H₂_{\text{gas}}
\]

This reaction gives a theoretical heat of reaction of –29.6 Kcal/mol, which is consistent with the –28 Kcal/mol estimated in this work.


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CHAPTER V

THERMAL DECOMPOSITION OF HYDROXYLAMINE IN THE PRESENCE OF METALS*

1. Background

In 1865 Lossen discovered hydroxylamine by reducing ethyl nitrate with tin (granular) and hydrochloric acid \([127]\). Divers [127] divided metals into two groups depending on the products that they formed when contacted with free nitric acid: metals such as copper, mercury, silver, and bismuth, which produce nitrous acid, metal nitrate and water form the first group and metals like tin, zinc, cadmium, magnesium, aluminium, lead, iron, or alkali metals, which produce ammonia form the second group. Some of the metals in the second group can produce hydroxylamine. This information may be useful to rationalize the thermal behavior of hydroxylamine upon contacting metal surfaces since hydroxylamine is considered to be an intermediate in the reduction of nitric oxide \([128]\) to ammonia:

\[
NO \longrightarrow NH_2OH \longrightarrow NH_3 \tag{5.1}
\]

Thus it can be hypothesized that metals in the second group are more likely to decompose hydroxylamine faster although, to the best of our knowledge, information regarding reaction behavior in terms of exothermic activity, self-heat rates, or pressure generation to prove this hypothesis is not available.

Soon after the discovery of hydroxylamine, some literature describing the chemical reactions of hydroxylamine with various materials was published. Presented here is a summary of the available literature regarding hydroxylamine reactions with metals. None of these articles gave the slightest clue of a possible violent gas-producing reaction when hydroxylamine contacts metals.

In 1883, Divers [127] presented the following reaction when hydroxylamine contacts tin:

$$NH_3O + SnO \rightarrow NH_3 + SnO_2$$  \hspace{1cm} (5.2)

At this time the structural formula of hydroxylamine had not been elucidated, which explains its representation as $NH_3O$ instead of $NH_2OH$ in Equation 5.2. Divers also noted that sodium amalgam readily converts hydroxylamine into ammonia but it does not act on hydroxyamidosulphonate [129].

Due to its importance in the photography industry, it is not a surprise that some of the effects of catalysis upon the oxidation products of hydroxylamine were discovered in the
Kodak laboratories [30]. The Kodak research group concluded that when hydroxylamine is contacted with mercurous nitrate, mainly \( \text{N}_2\text{O} \) is produced, but when silver is introduced as a catalyst, \( \text{N}_2 \) is the main product. This article suggests a difference between the oxidation products and the catalytic decomposition products of hydroxylamine (although it does not identify the latter and ammonia was not mentioned in the paper). The author proposed that hydroxylamine is absorbed in silver losing one electron and that the absorbed intermediate produces \( \text{N}_2 \):

\[
\begin{align*}
\text{Ag}^+ + \text{NH}_2\text{O}^- & \rightarrow \text{Ag} + \text{NH}_2\text{O}^\cdot \\
2\text{NH}_2\text{O}^\cdot & \rightarrow \text{N}_2 + 2\text{H}_2\text{O}
\end{align*}
\]  

(5.3)

(5.4)

Whereas in the absence of catalyst, \( \text{N}_2\text{O} \) is produced via the nitroxyl intermediate:

\[
\begin{align*}
\text{Hg}_2^{++} + \text{NH}_2\text{OH} & \rightarrow 2\text{Hg} + \text{NOH} + 2\text{H}^+
\end{align*}
\]  

(5.5)

\[
\begin{align*}
2\text{NOH} & \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}
\end{align*}
\]  

(5.6)

Davies and Kustin [31] studied the reaction of Manganese III with hydroxylamine in acid media at 25°C and determined that nitrate (\( \text{NO}_3^- \)) is the main product of the oxidation reaction. The authors proposed the following mechanism:

\[
\begin{align*}
\text{Mn}^{3+} + \text{NH}_3\text{OH}^+ & \rightarrow \text{Mn}^{2+} + \text{NH}_2\text{O}^\cdot + 2\text{H}^+
\end{align*}
\]  

(5.7)
The authors recognized the possibility of forming N\textsubscript{2} due to a reaction similar to 5.4 but discarded that reaction from the mechanism, since only small amounts of N\textsubscript{2} were detected.

Later Honig and Kustin\cite{132} studied the oxidation reaction of hydroxylamine by silver (II) in perchlorate media. NO\textsubscript{3}\textsuperscript{-} was assumed to be the main oxidation product and no gas products were detected. It is important to note that the apparatus used had the capability to detect only N\textsubscript{2} and O\textsubscript{2}. There is a possibility of N\textsubscript{2}O being formed (since the reaction proceeded in acid media, see Equation 4.4) and not detected.

The reaction of cobalt (III) with hydroxylamine was studied\cite{133} and the following mechanism was suggested:

\[
\text{MnOH}^{2+} + \text{NH}_3\text{OH}^+ \rightarrow \text{Mn}^{2+} + \text{NH}_2\text{O} \cdot + \text{H}_3\text{O}^+ \quad (5.8)
\]

\[
2\text{H}_2\text{O} + 5\text{Mn}^{3+} + \text{NH}_2\text{O} \cdot \rightarrow 5\text{Mn}^{2+} + \text{NO}_3^- + 6\text{H}^+ \quad (5.9)
\]

\[
\text{NH}_2\text{OH} + 2\text{Co}^{3+} \rightarrow 2\text{Co}^{2+} + \text{HNO} + 2\text{H}^+ \quad (5.10)
\]

\[
2\text{HNO} + 4\text{Co}^{3+} + \text{H}_2\text{O} \rightarrow 4\text{Co}^{2+} + \text{N}_2\text{O}_3 + 4\text{H}^+ \quad (5.11)
\]
Therefore, the overall reaction is:

\[ 8\text{Co}^{3+} + 2\text{NH}_2\text{OH} + \text{H}_2\text{O} \rightarrow 8\text{Co}^{2+} + \text{N}_2\text{O}_3 + 8\text{H}^+ \]  \hspace{1cm} (5.12)

and

\[ \text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2 \]  \hspace{1cm} (5.13)

No gas products were detected. One year later, a slightly different mechanism was proposed by the same group [134]. The authors discovered that different reaction products were produced depending on relative initial quantities of hydroxylamine and cobalt (III). When hydroxylamine was in excess, a colorless gas was produced (the authors assumed that it was nitrogen), and when cobalt (III) was in excess, the oxidation proceeded as far as nitrate:

\[ \text{Co}^{3+} \rightleftharpoons \text{CoOH}^{2+} + \text{H}^+ \]  \hspace{1cm} (5.14)

\[ \text{CoOH}^{2+} + \text{NH}_3\text{OH}^+ \rightarrow \text{Co(II)} + \text{NH}_2\text{O} \cdot + \text{H}^+ + \text{H}_2\text{O} \]  \hspace{1cm} (5.15)

\[ \text{Co}^{3+} + \text{NH}_3\text{OH}^+ \rightarrow \text{Co(II)} + \text{NH}_2\text{O} \cdot + 2\text{H}^+ \]  \hspace{1cm} (5.16)

\[ 2\text{NH}_2\text{O} \cdot \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \]  \hspace{1cm} (5.17)

\[ \text{Co}^{2+} + \text{Co}^{3+} \rightleftharpoons (\text{Co}^{3+}\text{H}_2\text{OCO}^{2+}) \]  \hspace{1cm} (5.18)

\[ (\text{Co}^{3+}\text{H}_2\text{OCO}^{2+}) + \text{NH}_2\text{O} \cdot \rightarrow 2\text{Co(II)} + \text{HNO} + \text{H}^+ \]  \hspace{1cm} (5.19)
All reaction mechanisms presented here are similar because they were mainly created by analogy. As an example, this later mechanism was proposed even when the N₂ was not measured. As mentioned before, none of this literature suggested a possible violent reaction of hydroxylamine in the presence of metals.

This chapter presents valuable data regarding hazard posed by the thermal decomposition of hydroxylamine free base in contact with some metal surfaces and iron ion. Onset temperatures, maximum temperature, maximum pressure, noncondensable pressure, heat rate as a function of temperature, pressure rate as a function of temperature, temperature vs. pressure, and time to maximum rate are among the useful contributions of this chapter. To the best of our knowledge none of this information has ever been reported. In fact, some references may be misleading, for example the “Chemical risk analysis. A practical handbook” [135] states that hydroxylamine does not have a dangerous reaction with transition metals, metal halides (FeCl₃ for example) or metal oxides contrary to our observations.

\[ HNO + 4Co(III) + 2H₂O \rightarrow NO_3^- + 4Co(II) + 5H^+ \] (5.20)
2. Experimental details

2.1. Samples

2.1.1. Hydroxylamine samples

Two sources of 50 wt.% hydroxylamine/water were used in the present study: Aldrich hydroxylamine 99.999% 50 wt.% solution in water, catalog No. 46,780-4, and hydroxylamine 50 wt.% solution in water with added stabilizers, supplied by an industrial source (HA-ind). The Aldrich hydroxylamine samples featured a nominal high purity and contained no added stabilizers. All HA samples were used in the received condition without further analysis or purification.

2.1.2. Ferric oxide solution

For some experiments reported in this chapter, a suspension of ferric oxide (Fe$_2$O$_3$) was prepared using iron III oxide 99.998% from Aldrich catalog number 25,572-6, formula weight 159.69, and 70.3 % Fe concentration. The water used was Aldrich reagent grade catalog number 32,007-2. A dark red 90 ppm suspension, since ferric oxide or rust is not greatly soluble in water, was prepared.

2.1.3. Ferric ion solution

A 90.8 ppm ferric ion solution, Fe$^{3+}$, was made using ammonium iron III sulfate dodecahydrate 99.99+% [NH$_4$Fe(SO$_4$)$_2$*12H$_2$O, Aldrich catalog no. 43152-4] and Aldrich reagent grade water catalog number 32,007-2. The physical appearance of the
solution was yellowish. The same source for the ferric ion was used in the experiments performed at the NRIFD, Tokyo, Japan.

2.1.4. Ferrous ion solutions

A 90 ppm ferrous ion, Fe$^{2+}$ solution was prepared using iron II sulfate hydrate 99.999% (FeSO$_4$·$n$H$_2$O, Aldrich catalog number 45027-8) which contains 21.4% iron by titration and Aldrich reagent grade water catalog number 32,007-2. The physical appearance of the solution was greenish. The solutions of Fe$^{2+}$ are known to oxidize in the presence of Fe$^{3+}$, so special care was taken to use the solution as quickly as possible. During the time that the experiments were run, no visible signs of Fe$^{3+}$ formation were observed, such that the solution remained greenish and no precipitates were formed (Fe$^{3+}$ sulfates and hydrates are brown). Ammonium iron (II) sulfate hexahydrate (Fe(NH$_4$)$_2$(SO$_4$)$_2$·6H$_2$O) was the ferrous ion source used in the experiments performed at NRIFD, Tokyo, Japan.

2.2. Apparatus

Most of the data presented in this chapter were collected with an APTAC calorimeter using the adiabatic mode, some data about the HA heat of reaction was collected with a flux calorimeter (Setaram C 80 II) at NRIFD as described in Chapter III.
2.3. Analytical methods

For the analytical measurements of the gas phase, a three Tesla Fourier Transform Mass Spectrometer (FTMS), also known as Ion Cyclotron Resonance Mass Spectrometry (ICR-MS), and a gas chromatograph (GC) were used, as described in Chapter III.

Liquid products were analyzed for ammonia using a titration with NaOH and for water using the Karl Fisher method. Atomic Absorption (AA) identified presence of a bluish ammonia-copper complex.

2.4. Experimental method

The experiments reported here were performed in a closed cell environment with air above the sample. The heat-wait-search routine was used as described in Chapter III. HA samples were transferred to sample cells using disposable plastic pipettes. Sample masses were obtained by weight differences. Because of the relative small amounts of sample, no stirring was used during the APTAC runs. A sample thermocouple with a Teflon-coated sheath was used to prevent the metal surface from contacting the sample. An inconel-sheath thermocouple without Teflon coating was used in some experiments discussed below.

Experimental runs were performed in spherical sample cells of 130 cm$^3$ nominal volume and of borosilicate glass, stainless steel 316 (SS), stainless steel 316 coated with silica (SS-Sa), titanium (Ti), and titanium coated with silica (Ti-Sa). It was presumed that
glass cells provided a neutral environment without significant catalysis for the HA decomposition reaction. Reactivity with respect to the other materials (SS, SS-Sa, Ti, Ti-Sa) was tested by using the corresponding cells.

Experiments were performed to test the effect of carbon steel (composed primarily of iron, 97 - 99 %, graphite, < 2 %), which is a common industrial contaminant that is found in nails, wire, or structural components. A piece of carbon steel nail with a surface area to sample volume ratio (SVR) of approximately 0.024 mm$^{-1}$ was introduced into the sample after the sample was weighed in a glass cell.

For the ferric and ferrous ion experiments, approximately 1 ml of the ion solution (~90 ppm) was introduced to the glass cell containing the sample once the experiment was running and the 30 °C search period had begun. This allowed the recording of the thermal activity as soon as the ion solution contacted the sample.

To carry out the experiments described above, the APTAC tube heater assembly was modified with a second 1/8” hole so an approximately 30 cm-long metal needle could be introduced through it (see Chapter III for details). The needle was connected to a glass precision syringe in which a volume of 1 ml of iron solution was contained.
2.5. *Uncertainties*

Most of the experimental uncertainties were discussed in Chapter IV. The only additional uncertainty is the one regarding the injection of the ion solution. To measure this uncertainty, a water injection was made in exactly the same way as the iron solution injections. The injected mass was 0.99 g., which is equal to the target value (1 g.) within the balance uncertainty (± 0.01 g.).

3. **Results and discussion**

3.1. *Inconel sheath thermocouple*

As summarized in Table 5.1, two heat-wait-search experiments of HA with stabilizers (HA-ind) using a thermocouple with an inconel sheath without Teflon coating and three tests using a Teflon coated thermocouple demonstrated the catalytic effect of the inconel sheath material as a catalyst in the HA decomposition reaction. The thermocouple sheath was approximately 2 mm beneath the liquid surface yielding a SVR of 0.0015 ± 0.0002 mm⁻¹. Although the area of contact was very small, the onset temperature was lowered by 11°C, and the self-heat rates at 120, 135, and 150 °C were higher compared with results using the Teflon coated thermocouple.
Table 5.1
Effect of inconel sheath thermocouple on onset temperature for HA-ind samples

<table>
<thead>
<tr>
<th>Thermocouple</th>
<th>Replicas</th>
<th>Average $T_{on}$, °C</th>
<th>$dT / dt_{120^\circ C}$ °C/min</th>
<th>$dT / dt_{135^\circ C}$ °C/min</th>
<th>$dT / dt_{150^\circ C}$ °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inconel sheath</td>
<td>2</td>
<td>122</td>
<td>0.05</td>
<td>0.11</td>
<td>0.38</td>
</tr>
<tr>
<td>Teflon coated sheath</td>
<td>3</td>
<td>133</td>
<td>0.03</td>
<td>0.08</td>
<td>0.22</td>
</tr>
</tbody>
</table>

3.2. *Nail test*

A nail of carbon steel was added to each of two kinds of samples resulting in SVR values of $0.022 \pm 0.002$ mm$^{-1}$ and $0.024 \pm 0.002$ mm$^{-1}$ just prior to closing the sample cells at the beginning of an experiment. Because it was assumed in this study that glass and Teflon do not significantly participate in the HA decomposition reaction, a glass cell and a Teflon-coated sample thermocouple were used to ensure that the only significant catalytic material was the nail. The effect of a nail on the HA reaction is observed in Figure 5.1, which displays the self-heat rate as a function of temperature for HA of both types in tests with and without a nail. The presence of the nail resulted in greatly lowered onset temperatures, from 133-136 °C to below 50 °C, increased self-heat rates, and increased maximum self-heat rates from no greater than 5 °C/min to 13 °C/min (HA) and 31 °C/min (HA-ind). These tests demonstrate that the decomposition reaction of HA with and without stabilizers is strongly catalyzed by carbon steel (primarily iron metal).
Following the tests, the sample and nail remains were visually inspected. HA with stabilizers had a very intense blue color and the nail had changed from gray to black, and HA without stabilizers had a bluish color and there was no apparent difference in the nail color. Table 5.2 presents a summary of the experiments in which metal surfaces were in contact with hydroxylamine.
Table 5.2  
Effects of heterogeneous catalysis experiments on HA thermal decomposition

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Cell material</th>
<th>Sample material</th>
<th>SVR a</th>
<th>T on</th>
<th>dT/dt max</th>
<th>Liquid residue</th>
<th>Solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-ind</td>
<td>Glass</td>
<td>2.21</td>
<td>NA</td>
<td>133</td>
<td>1.7</td>
<td>Bluish</td>
<td>NA b</td>
</tr>
<tr>
<td>HA-ind + nail</td>
<td>Glass</td>
<td>2.41</td>
<td>0.022</td>
<td>&lt; 50</td>
<td>31</td>
<td>Intense blue</td>
<td>Black c</td>
</tr>
<tr>
<td>HA-ind + inconel</td>
<td>Glass</td>
<td>2.26</td>
<td>0.001</td>
<td>122</td>
<td>11</td>
<td>Bluish</td>
<td>NA b</td>
</tr>
<tr>
<td>HA-ind</td>
<td>SS</td>
<td>2.20</td>
<td>0.45</td>
<td>&lt; 50</td>
<td>9</td>
<td>Slightly blue</td>
<td>Reddish</td>
</tr>
<tr>
<td>HA-ind</td>
<td>Ti</td>
<td>2.23</td>
<td>0.45</td>
<td>&lt; 50</td>
<td>13</td>
<td>Intense blue</td>
<td>White</td>
</tr>
<tr>
<td>HA-ind</td>
<td>SS-Sa</td>
<td>2.11</td>
<td>0.46</td>
<td>&lt; 50</td>
<td>9</td>
<td>Clear</td>
<td>White</td>
</tr>
<tr>
<td>HA</td>
<td>Glass</td>
<td>2.25</td>
<td>NA</td>
<td>136</td>
<td>4</td>
<td>Teal</td>
<td>NA b</td>
</tr>
<tr>
<td>HA + nail</td>
<td>Glass</td>
<td>2.25</td>
<td>0.024</td>
<td>&lt; 50</td>
<td>13</td>
<td>Slightly blue</td>
<td>Gray c</td>
</tr>
<tr>
<td>HA</td>
<td>SS</td>
<td>2.27</td>
<td>0.44</td>
<td>&lt; 50</td>
<td>71</td>
<td>Bluish</td>
<td>Reddish</td>
</tr>
<tr>
<td>HA</td>
<td>Ti</td>
<td>2.18</td>
<td>0.45</td>
<td>&lt; 50</td>
<td>100</td>
<td>Bluish</td>
<td>White</td>
</tr>
<tr>
<td>HA</td>
<td>SS-Sa</td>
<td>2.22</td>
<td>0.44</td>
<td>&lt; 50</td>
<td>17</td>
<td>Slightly blue</td>
<td>Yellowish</td>
</tr>
<tr>
<td>HA</td>
<td>Ti-Sa</td>
<td>2.28</td>
<td>0.44</td>
<td>&lt; 50</td>
<td>79</td>
<td>Clear</td>
<td>Greenish</td>
</tr>
</tbody>
</table>

a  Ratio of metal surface contact area to sample volume  
b  No residue observed  
c  Nail color after the test. No residue was detected on the cell surface

3.3. Tests in a stainless steel sample cell

The effect of a stainless steel (SS) sample cell on the HA decomposition reaction was measured in experiments with HA with and without stabilizers for a SVR of 0.45 ± 0.01 mm⁻¹. As shown in Table 5.2 and Figures 5.2 and 5.3, the HA with stabilizers exhibited a smaller maximum self-heat rate than the HA without stabilizers. This result is in contrast to the carbon steel nail test in which the HA with stabilizers exhibited the larger self-heat rate. The experimental reproducibility was lower in the SS
and the other metal cell experiments, because a small change in sample weight changes the surface area of catalyst, which directly affects the reaction and self-heat rate. As listed in Table 5.2, the sample remains in the SS cell for HA with and without stabilizers were bluish in color, and a reddish residue was attached to the cell. A possibly identity for this reddish residue is iron hydroxide FeO(OH) since this compound has brown color. It is well known that the iron III salts are yellow or brown, so it appears that hydroxylamine acted as a oxidation agent and changed some iron metal from Fe$^0$ to Fe$^{3+}$ while reducing to ammonia.

![Figure 5.2](image-url)

Figure 5.2. Decomposition reaction of HA with stabilizers (HA-ind) in various test cell materials. -Sa indicates coated with silica.
3.4. Tests in titanium sample cells

The onset temperatures and maximum self-heat rates of HA with stabilizers in three titanium sample cell tests with various sample sizes and $\phi$ factors are shown in Table 5.3. Because of the relatively large amounts of sample used in two of these experiments, the maximum self-heat rates generated by the decomposition reactions (1,907 and 943 °C/min) were beyond the APTAC’s capability to track the reactions in the adiabatic mode (adiabatic tracking for temperatures rises up to 400 °C/min). Figure 5.2 shows that HA with stabilizers in titanium sample cells exhibited a slightly greater self-heat rate than in stainless steel cells between 100-150 °C. As seen in Table 5.2 and Figure 5.3, the self-heat rates of HA without stabilizers in SS and Ti cells are similar. As listed in Table 5.2, the sample remains in the titanium cell for HA with and
without stabilizers were bluish in color, and a white solid residue was observed on the cell surface. A possible identity for this white precipitate is titanium dioxide (TiO₂).

Similarly as with SS the hydroxylamine acted as an oxidation agent changing some of the Ti metal, Ti⁰, to Ti⁴⁺ while reducing to ammonia.

Table 5.3
Effect of sample size for HA-ind samples in Ti cells

<table>
<thead>
<tr>
<th>Sample</th>
<th>~φ</th>
<th>Onset temp., T_on</th>
<th>dT/dt_max</th>
</tr>
</thead>
<tbody>
<tr>
<td>g.</td>
<td>°C</td>
<td>°C/min</td>
<td></td>
</tr>
<tr>
<td>2.23</td>
<td>3.6</td>
<td>&lt; 50</td>
<td>13</td>
</tr>
<tr>
<td>6.20</td>
<td>1.9</td>
<td>41</td>
<td>943</td>
</tr>
<tr>
<td>7.24</td>
<td>1.8</td>
<td>41</td>
<td>1907</td>
</tr>
</tbody>
</table>

3.5. Test in silica coated sample cells

In an attempt to provide a neutral environment in metal cells for the HA decomposition reaction, cells of Ti and SS were coated with silica (SiO₂) by chemical vapor deposition. The results of these experiments are summarized in Table 5.2 and in Figures 5.2 and 5.3, where it is apparent that the sample cell surfaces were not fully pacified by the coating process. As shown in Figure 5.3, the self-heat rates for sample without stabilizers were reduced but were still much greater than the rates in glass cells. For the HA-industrial sample with stabilizers, shown in Figure 5.2, no reduction in self-heat rate was observed. Figure 5.2 shows also that HA with stabilizers in Ti-Sa sample cells exhibited a somewhat larger self-heat rate than in SS-Sa cells between 100-150 °C. As shown in
Figure 5.3, the HA without stabilizers in a Ti-Sa cell exhibited two major exotherm peaks with maximum self-heat rates of 12 and 79 °C/min. The sample remains in the silica coated cells for HA with and without stabilizers had varying appearances, which are listed in Table 5.2.

3.6. *Exothermal activity above 200 °C in metal cells*

With the exception of HA without stabilizers in a Ti-Sa cell, all samples tested in metal cells exhibited major exothermic activity only below 200 °C. From 200 to 300 °C only small self-heat rates, generally < 1 °C/min, were observed in the sample sizes tested. The HA without stabilizers sample in a titanium cell exhibited a more energetic but still mild second exotherm with a maximum self-heat rate of 6 °C/min in this temperature range. This mild exothermic activity from 200 to 300 °C is not shown in Figures 5.2 and 5.3.

3.7. *HA thermal decomposition in the presence of iron ion*

Due to the scarcity of data regarding hydroxylamine hazardous behavior in the presence of ferrous or ferric ion, a minor incident occurred in the laboratory during the first ferrous ion experiment. A sample of 8 g. of HA was placed in a cell and 1 ml of a 16,000 ppm Fe²⁺ solution (from iron II sulfate hydrate) was added. A brown precipitate formed and, immediately after that, a violent reaction that created a bubbling system with very little vapor-liquid disengagement took place. At the end of the reaction the
sample cell was practically empty. Even though the hot reaction mass was dispersed as far as 2 m., no one was injured since a full face shield, a laboratory coat and gloves were always worn when handling hydroxylamine. Figure 5.4 shows the sample cell after this experiment where the spots on the balance are reaction products (the reaction products consisted in a dark brownish suspension). Under these particular conditions the cell remained intact but a ruptured cell could result from a higher concentration of iron ion, which will increase the pressure generation rate, or a closed cell experiment since the pressure generated inside the sample cell will create a huge pressure differential across the sample cell wall which most probably will lead to the mechanical failure of the glass sample cell. The dark brown or blackish precipitate is characteristic of Fe\textsuperscript{3+} compounds and can be either ferric oxide (Fe\textsubscript{2}O\textsubscript{3}) or iron hydroxide FeO(OH). Either way the reaction involved the oxidation of Fe\textsuperscript{2+} to Fe\textsuperscript{3+}, and because the brown color was present a few seconds before the reaction became violent, this iron oxidation may be the first step in the reaction.
A similar experiment as the one described above was repeated inside a fume hood under controlled conditions so this violent reaction could be recorded by a digital camera. To slow down the reaction the final HA/iron II solution contained only 197 ppm Fe$^{2+}$. Figures 5.5 through 5.10 are frames of that videotaped experiment.
Figure 5.5. HA + 197 ppm Fe$^{2+}$ experiment. Time, 0 s.

Figure 5.6. HA + 197 ppm Fe$^{2+}$ experiment. Time, 2 s.

Figure 5.7. HA + 197 ppm Fe$^{2+}$ experiment. Time, 10 s.
Figure 5.8. HA + 197 ppm Fe$^{2+}$ experiment. Time, 18 s.

Figure 5.9. HA + 197 ppm Fe$^{2+}$ experiment. Time, 20 s.

Figure 5.10. HA + 197 ppm Fe$^{2+}$ experiment. Time, 41 s.
It can be seen from Figures 5.6 and 5.7 that the reaction starts with the production of a precipitate, so the bottom part of the beaker is not reacting yet. The reaction front moves quickly down the beaker releasing heat, evaporating the solvent, and producing colorless gases. The violence of the reaction can be appreciated from Figures 5.8 and 5.9 where the reaction mixture is a bubbling system exiting the beaker. Figure 5.10 shows that the reaction stops only when all the HA has been consumed and only a small amount of precipitate remains in the beaker.

Some experiments where the reactants were premixed and then tested with the calorimeter resulted in poor reproducibility and are not included in this dissertation. An important qualitative observation from these preliminary experiments was the clearly marked presence of two maximums in both the heat rate and pressure rate data. These two peaks can be attributed to two different reactions, the first one forming the precipitate. After these experiments it became clear that, to obtain accurate measurements of the thermal decomposition of HA when in contact with iron ion, the injection of the latter should be made once the apparatus has begun to record data.
3.7.1. Ferric ion experiments

3.7.1.1. Fe₂O₃

It was important to test the catalytic effect of rust (ferric oxide, Fe₂O₃), since it is a common industrial contaminant. Table 5.4 presents a summary of the experiments with ferric oxide. It is important to note that rust is not very soluble in water, so its catalytic effect is not expected to be very significant.

Table 5.4
HA decomposition in the presence of ferric oxide data summary

<table>
<thead>
<tr>
<th>Identification</th>
<th>[Fe₂O₃] ppm</th>
<th>Initial a g. ± 0.01</th>
<th>Final g. ± 0.01</th>
<th>Liquid residue</th>
<th>Solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃, 10</td>
<td>10.0</td>
<td>9.03 6.33</td>
<td>Slightly green</td>
<td>White fluffy</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃, 200</td>
<td>199.7</td>
<td>9.01 6.80</td>
<td>Slightly blue</td>
<td>White fluffy</td>
<td></td>
</tr>
</tbody>
</table>

a Initial HA sample plus 1 ml of Fe₂O₃ solution
φ = 2

Open literature information was used to suggest an identity for the white residue [136]. Given the species involved in the reaction there are few commonly known options for an iron containing precipitate and those are presented in Table 5.5. Although Table 5.5 was expected to be comprehensive, there exist some uncommon higher oxidation states of iron (Fe⁴⁺, Fe⁶⁺) [137] that may be missing. Since the precipitate was white and not gray a better identity for it is Fe(OH)₂.
Table 5.5
Iron compounds containing at least one of the following atoms: oxygen, hydrogen and nitrogen

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>Silver</td>
</tr>
<tr>
<td>Iron hydroxide</td>
<td>FeO(OH)</td>
<td>Brown, blackish</td>
</tr>
<tr>
<td>Iron (II) hydroxide</td>
<td>Fe(OH)₂</td>
<td>Pale green, white</td>
</tr>
<tr>
<td>Iron (II) nitrate</td>
<td>Fe(NO₃)₂6H₂O</td>
<td>Green</td>
</tr>
<tr>
<td>Iron (III) nitrate</td>
<td>Fe(NO₃)₃6H₂O</td>
<td>Slightly purple</td>
</tr>
<tr>
<td>Iron nitride</td>
<td>Fe₂N</td>
<td>Gray</td>
</tr>
</tbody>
</table>

Table 5.6 presents a summary of the measured parameters for the decomposition of HA in the presence of 10 and 200 ppm of iron oxide. As can be seen from this table, the onset temperature decreased by 9 °C when the iron oxide concentration increased 20 times. The time to maximum rate was reduced significantly (around 4.7 times) for the sample with the highest concentration of catalyst. As expected, only the dynamic parameters $T_{on}$, $T_{max}$, $P_{max}$, and $t_{MR}$ (those that depend on the self heating rate) were affected by the amount of contaminant. The static parameters $\Delta T_{adb}$ and noncondensable pressure remained unchanged.
Table 5.6
HA decomposition in the presence of ferric oxide decomposition parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{on}$ °C</th>
<th>$T_{max}$ °C</th>
<th>$\Delta T_{ad}$ °C</th>
<th>$P_{max}$ psia</th>
<th>Non-condensables psia</th>
<th>$t_{MR}$ min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$, 10</td>
<td>111</td>
<td>284</td>
<td>173</td>
<td>1269</td>
<td>109</td>
<td>223</td>
</tr>
<tr>
<td>Fe$_2$O$_3$, 200</td>
<td>102</td>
<td>279</td>
<td>176</td>
<td>1187</td>
<td>109</td>
<td>51</td>
</tr>
</tbody>
</table>

$\phi = 2$

3.7.1.2. **HA homogeneous catalysis**

It was hypothesized that homogeneous catalysis (ions in solution) produces a more violent reaction than heterogeneous catalysis due to a higher ion availability. To test for a difference in the reaction due to the oxidation state of iron, Fe$^{3+}$ and Fe$^{2+}$ solutions were prepared. Table 5.7 presents a summary of the experiments performed using ferric and ferrous ion solutions.
Table 5.7
HA decomposition in the presence of iron ion data summary

<table>
<thead>
<tr>
<th>Identification</th>
<th>[Fe ion] ppm</th>
<th>Initial&lt;sup&gt;a&lt;/sup&gt; g. ± 0.01</th>
<th>Final g. ± 0.01</th>
<th>Liquid residue</th>
<th>Solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 3+, 1</td>
<td>10.1</td>
<td>9.03</td>
<td>7.50</td>
<td>Slightly blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 3+, 2</td>
<td>10.0</td>
<td>9.10</td>
<td>7.53</td>
<td>Blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 3+, 3</td>
<td>10.1</td>
<td>9.03</td>
<td>7.52</td>
<td>Blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 3+, 4</td>
<td>10.0</td>
<td>9.05</td>
<td>7.45</td>
<td>Blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 3+, 5</td>
<td>10.1</td>
<td>9.03</td>
<td>7.46</td>
<td>Blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 2+, 1</td>
<td>10.0</td>
<td>9.02</td>
<td>7.25</td>
<td>Blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 2+, 2</td>
<td>10.0</td>
<td>9.01</td>
<td>7.32</td>
<td>Blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 2+, 3</td>
<td>10.8</td>
<td>9.01</td>
<td>7.44</td>
<td>Blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 2+, 4</td>
<td>9.9</td>
<td>9.06</td>
<td>7.42</td>
<td>Slightly blue</td>
<td>Brown</td>
</tr>
<tr>
<td>Fe 2+, 5</td>
<td>9.9</td>
<td>9.08</td>
<td>7.46</td>
<td>Blue</td>
<td>Brown</td>
</tr>
</tbody>
</table>

<sup>a</sup> Initial HA sample plus 1 ml of the respective iron ion solution

The blue residue is explained by copper contamination from the tube heater assembly, since an analysis for one of the samples (Fe3+, 5) revealed 100 ppm of copper. It seems that the same precipitate is formed irrespective of the initial oxidation state of the iron ion. Iron hydroxide is suggested as a possible identity for this precipitate based on the information presented in Table 5.5. Table 5.8 presents the decomposition parameters measured for the HA decomposition when in contact with ferrous and ferric ions. It can be seen that the decomposition behavior was the same within the experimental error irrespective of the initial oxidation state of the ion for all the reported parameters. It is
important to note that the reaction started immediately after the injection of the ion solution.

Table 5.8
HA decomposition parameters in the presence of iron ion

<table>
<thead>
<tr>
<th>Ion</th>
<th>Runs</th>
<th>T&lt;sub&gt;on&lt;/sub&gt; °C</th>
<th>T&lt;sub&gt;max&lt;/sub&gt; °C</th>
<th>ΔT&lt;sub&gt; adb&lt;/sub&gt; °C</th>
<th>P&lt;sub&gt;max&lt;/sub&gt; psia</th>
<th>Non-condensable psi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 3+</td>
<td>5</td>
<td>Immediate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>257 ± 3</td>
<td>227 ± 3</td>
<td>951 ± 29</td>
<td>105 ± 2</td>
</tr>
<tr>
<td>Fe 2+</td>
<td>5</td>
<td>Immediate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>260 ± 2</td>
<td>230 ± 2</td>
<td>970 ± 24</td>
<td>103 ± 2</td>
</tr>
</tbody>
</table>

<sup>a</sup> Onset of the reaction was observed few seconds after addition of ion solution

Although only 10 ppm of Fe<sup>2+</sup> or Fe<sup>3+</sup> was used, the dramatic effect of the contaminant can be appreciated from Figure 5.11. The vertical line in the plot represents the injection point, where the time has been normalized so time = 0 represents the injection time. For comparison, the plot also includes the experiments run with ferric oxide and without any contaminant (HA).
Figure 5.11. Temperature vs. time profile for HA decomposition in the presence of iron ion.

Figure 5.12 presents a similar temperature vs. time plot, but the time scale has been modified to show the initial 40 min after injection. It can be seen that there is no difference between experiments run with ferric and ferrous ion and that the reaction starts immediately after injection.
Figure 5.12. Temperature vs. time profile for HA decomposition in the presence of iron ion for 40 minutes following injection.

As shown in Figure 5.13, the pressure data follows the temperature data for the decomposition of HA with iron ion. The higher pressure acquired by the Fe$_2$O$_3$ experiments is due to vapor pressure at higher temperature since all experiments presented in this plot have a very similar noncondensable pressure.
Figure 5.13. Pressure vs. time profile for HA decomposition in the presence of iron ion.

The presence of two well defined exothermic behaviors are clearly shown in the heat and pressure rates of Figure 5.14 and 5.15, respectively. The good data reproducibility is also presented in these plots. The initial injection of the iron ion triggers the first reaction, which liberates enough thermal energy to heat the reaction mixture to the onset temperature of the second exotherm. A summary of some important parameters deduced from Figures 5.14 and 5.15 are presented in Table 5.9.
Figure 5.14. Heat rate plot for HA decomposition in the presence of iron ion.

Figure 5.15. Pressure rate plot for HA decomposition in the presence of iron ion.
Table 5.9
Heat and pressure rates for HA decomposition in the presence of iron ion

<table>
<thead>
<tr>
<th>Ion</th>
<th>Replicas</th>
<th>φ</th>
<th>(dT/dt&lt;sub&gt;max&lt;/sub&gt;)&lt;sup&gt;1&lt;/sup&gt; °C/min</th>
<th>(dT/dt&lt;sub&gt;max&lt;/sub&gt;)&lt;sup&gt;2&lt;/sup&gt; °C/min</th>
<th>(dP/dt&lt;sub&gt;max&lt;/sub&gt;)&lt;sup&gt;1&lt;/sup&gt; Psia/min</th>
<th>(dP/dt&lt;sub&gt;max&lt;/sub&gt;)&lt;sup&gt;2&lt;/sup&gt; Psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 3+</td>
<td>5</td>
<td>2</td>
<td>24 ± 16</td>
<td>35 ± 3</td>
<td>12 ± 9</td>
<td>252 ± 33</td>
</tr>
<tr>
<td>Fe 2+</td>
<td>5</td>
<td>2</td>
<td>27 ± 12</td>
<td>38 ± 3</td>
<td>16 ± 13</td>
<td>286 ± 24</td>
</tr>
</tbody>
</table>

<sup>1</sup> First exotherm
<sup>2</sup> Second exotherm

A few flux calorimetry experiments were performed in collaboration with the NRIFD, Tokyo, Japan to measure the heat released when HA comes in contact with ferric or ferrous ion. It is important to note that the flux calorimeter used was not modified to support an injection during a experiment, so the HA and the ion solution had to be mixed immediately before starting the experiment and, in doing so, part of the heat generated was not measured by the apparatus. Another drawback of these experiments is that, since the reaction begins immediately after mixing the HA and the ion solution, there was no opportunity to obtain a base line. As a result, the heat flux integration was more difficult and included higher uncertainty. Figure 5.16 and Table 5.10 present the determined values.
Figure 5.16. Heat flux for HA decomposition alone and in the presence of iron ions. Data obtained in collaboration with the NRIFD, Tokyo, Japan.

As seen in Figure 5.16 and Table 5.10 all of the decomposition reactions feature three heat flow peaks, which represent three reactions. For the HA decomposition the main exothermic reaction is the third one, which exhibits an onset temperature around 110 °C in agreement with our APTAC experiments. For the ferric and ferrous ion, the greater heat flux corresponds to the first reaction. The total amount of heat released is similar for all three reactions.

Table 5.10
Estimated heat of reaction for the HA decomposition in presence of iron ions. Work in collaboration with the NRIFD

<table>
<thead>
<tr>
<th>Sample</th>
<th>$-\Delta H_{\text{ex}}$ KJ/g</th>
<th>Peak 1 %</th>
<th>Peak 2 %</th>
<th>Peak 3 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>3.78</td>
<td>15.5</td>
<td>9.3</td>
<td>75.2</td>
</tr>
<tr>
<td>HA + Fe$^{3+}$</td>
<td>3.53</td>
<td>79.2</td>
<td>8.3</td>
<td>12.5</td>
</tr>
<tr>
<td>HA + Fe$^{2+}$</td>
<td>3.99</td>
<td>83.8</td>
<td>7.2</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Table 5.11 presents a summary of some of the visual experiments performed. These experiments are useful to test for violent reactions, color of precipitate, and gas evolution. As can be seen from Table 5.11, it seems that the same precipitate is obtained when mixing Fe$^{3+}$ with ammonia or hydroxylamine, although the reaction with ammonia is not violent. Some Fe$^{3+}$ was used to test for possible unreacted hydroxylamine remaining in the liquid residue, but no traces of HA were detected since there was no apparent violent reaction. Mixing HA with ammonia does not generate any apparent reaction.

The difference of HA reactivity towards homogeneous (ion in solution) and heterogeneous (metal surface in suspension) catalysis is clearly seen in the visualization experiments of Table 5.11 since mixing HA with a suspension of Fe$_2$O$_3$ does not generate any apparent reaction in contrast to the experiment between HA and ferrous or ferric ion where a very violent reaction is observed. As shown in the table, mixing HA with ferrous or ferric ion will not produce the same result.
Table 5.11
Summary of visualization experiments

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA 5 ml + 1 ml of 1,800 ppm Fe₂O₃</td>
<td>No apparent reaction</td>
</tr>
<tr>
<td>HA 5 ml + 1 ml of 1,622 ppm Fe²⁺</td>
<td>Very violent reaction with boiling of the reacting mixture. Brown precipitate formed</td>
</tr>
<tr>
<td>HA 5 ml + 1 ml of 8,991 ppm Fe³⁺</td>
<td>Very violent reaction and very dark precipitate formed, probably Fe₂O₃</td>
</tr>
<tr>
<td>Liquid residue of Fe₂O₃, 200 + 1ml of 8,991 ppm Fe³⁺</td>
<td>No violent reaction, only change in color due to formation of brown precipitate that does not mix. So no traces of HA left</td>
</tr>
<tr>
<td>5 ml of NH₄OH + 1 ml of 8,991 ppm Fe³⁺</td>
<td>No violent reaction, only change in color due to formation of brown precipitate that does not mix. Same behavior as above</td>
</tr>
<tr>
<td>Liquid residue of HA, air ³ + 1ml of 8,991 ppm Fe³⁺</td>
<td>No violent reaction, only change in color due to formation of brown precipitate that does not mix. Same behavior as above. No hydroxylamine left</td>
</tr>
<tr>
<td>1 ml NH₄OH + 1 ml HA</td>
<td>No indication of a reaction at all</td>
</tr>
</tbody>
</table>

3.8. Analytical results

Table 5.12 presents a summary of the relative composition of gas products for the decomposition of HA in the presence of iron ions. It is interesting to note that the “catalyst” affected the relative composition of the gas mixture, except for the experiments with ferric oxide. Without the iron ions the gas phase was roughly 70-30 mol% N₂/N₂O compared with the approximately 50-50 mol% N₂/N₂O reported in
Table 5.12. The gas phase is also more diversified with O₂, NH₃, and water aside from the N₂, NO, N₂O, and H₂ for the HA decomposition without the iron ions.

Table 5.12
Gas phase analytical results for HA decomposition in presence of iron ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rep</th>
<th>NH₃ % mol</th>
<th>H₂O % mol</th>
<th>N₂ % mol</th>
<th>NO % mol</th>
<th>O₂ % mol</th>
<th>N₂O % mol</th>
<th>H₂ % mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA + Fe₂O₃</td>
<td>1</td>
<td>0.6</td>
<td>0</td>
<td>66.5</td>
<td>3.0</td>
<td>0.3</td>
<td>27</td>
<td>2.6</td>
</tr>
<tr>
<td>HA + Fe³⁺</td>
<td>2</td>
<td>2.1 ± 0.3</td>
<td>0.2 ± 0.3</td>
<td>44.8 ± 1.4</td>
<td>5.9 ± 0.1</td>
<td>0.5 ± 0.1</td>
<td>46.2 ± 1.5</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>HA + Fe²⁺</td>
<td>2</td>
<td>1.7 ± 0.4</td>
<td>0.3 ± 0.3</td>
<td>45.6 ± 0.4</td>
<td>5.4 ± 0.1</td>
<td>0.5 ± 0.2</td>
<td>46.1 ± 1</td>
<td>0.4 ± 0.1</td>
</tr>
</tbody>
</table>

As shown in Table 5.13, analysis of the liquid phase yields compositions similar to that for the HA experiments with ~7 wt.% ammonia and ~92 wt.% water.

Table 5.13
Liquid phase analytical results for HA decomposition in presence of iron ions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rep</th>
<th>Ammonia wt.%</th>
<th>Water wt.%</th>
<th>Unaccounted wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA + Fe₂O₃</td>
<td>1</td>
<td>6.8</td>
<td>90.7</td>
<td>2.5</td>
</tr>
<tr>
<td>HA + Fe³⁺</td>
<td>2</td>
<td>8.2 ± 0.5</td>
<td>90.2 ± 0.8</td>
<td>1.6 ± 1.1</td>
</tr>
<tr>
<td>HA + Fe²⁺</td>
<td>2</td>
<td>5.1 ± 3.7</td>
<td>94.0 ± 4.4</td>
<td>0.9 ± 0.6</td>
</tr>
</tbody>
</table>
4. Conclusions

The HA decomposition reaction rate is enhanced by metals. Inconel with a surface to sample volume of 0.0015 mm\(^{-1}\) reduced the onset temperature of the industrial HA (with stabilizers) by 11°C, and a 0.022 mm\(^{-1}\) surface to volume ratio of a carbon steel nail increased the self-heat rate of HA with stabilizers by a factor of ~15. In both SS and Ti sample cells, the maximum self-heat rate of the HA with stabilizers was lowered by a factor of ~8 compared to the HA without stabilizers. Silica coating did not pacify metal surfaces, and in all the tested metal cells, uncoated and coated with silica, the onset temperatures were less than 50°C for each sample of HA with and without stabilizers. Most of the exothermic activity for the sample sizes employed was below 200°C, but HA without stabilizers in a Ti-Sa cell exhibited a second major exotherm above 200°C with a maximum self-heat rate of 79°C/min. These results demonstrate that HA decomposition in air and in contact with metal surfaces, uncoated or coated with silica, is a complex reacting system.

If HA comes in contact with iron ion (Fe\(^{3+}\) or Fe\(^{2+}\)), even in concentrations as small as 197 ppm and at ambient temperatures, it will react violently producing a bubbling system with very little vapor-liquid disengagement. A great amount of energy (3.99 KJ/g) will be released, in a very short period of time, which will result in boiling of the reaction mass. Rust will cause heterogeneous catalysis of the reaction, which is not as violent as iron homogeneous catalysis, where even 10 ppm of iron ion will produce
enough energy to trigger the complete decomposition of hydroxylamine if the system is kept adiabatic.

Homogeneous catalysis of HA takes place in two well defined exothermic reactions, the first being more aggressive than the second. The HA decomposition product distribution is affected by iron ion presence with an increase in the relative amount of N₂O produced.


130 T. H. James, Effect of catalysis upon the oxidation products of hydroxylamine, Journal of the American chemical society, 64 (4) (1942) 731-734.


136 David R. Lide, CRC handbook of chemistry and physics, 75th edn., CRC press, Boca Raton, Florida, 1995, p. 4-64

CHAPTER VI
HYDROXYLAMINE HYDROCHLORIDE STUDIES

1. Background

Hydroxylamine Hydrochloride (oxammonium hydrochloride or hydroxylammonium chloride) is one of the preferred forms of hydroxylamine derivatives since it is more stable than hydroxylamine free base (solid hydroxylamine is unstable at room temperature). New applications for hydroxylamine hydrochloride are constantly been developed [138]. One common method to determine possible hazards posed by a substance is from the number of reported incidents in which the substance has been involved. A widely used source of incident information involving chemicals is Bretherick’s Handbook of Chemical Hazard and in its 1999 edition [139], only one laboratory incident involving hydroxylamine hydrochloride is reported.

The pH of hydroxylamine hydrochloride solutions is quite low, and even a 0.2 molar solution (~1.4 mass %) has a pH of 3.2 in contrast to HA solutions, which have a pH of 11. This difference in acidity may lead to stabilization of the hydroxylammonium ion $NH_3OH^+$ (protonated hydroxylamine species), which may explain the difference in thermal behavior between hydroxylamine and hydroxylamine hydrochloride. In basic media the hydroxylammonium ion may not even exist [140], and in acid media
hydroxylammonium ion may be the dominant species. Equation 6.1 has a pKb of 8.13 and Equation 6.2 has a pKa of 6.04.

\[ \text{NH}_3\text{OH} \leftrightarrow \text{NH}_2^+ + \text{OH}^- \text{ in alkaline solutions} \quad (6.1) \]

\[ \text{NH}_3\text{OH}^+ \leftrightarrow \text{NH}_2\text{OH} + \text{H}^+ \text{ in acid solutions} \quad (6.2) \]

Mitchell \cite{41} studied the reaction of hydroxylamine hydrochloride and ferric ion and proposed the following reaction:

\[ 4\text{Fe}^{3+} + 2\text{NH}_3\text{OH}^+ \leftrightarrow 4\text{Fe}^{2+} + 6\text{H}^+ + \text{N}_2\text{O} + \text{H}_2\text{O} \quad (6.3) \]

Nevertheless, to the best of our knowledge, literature information about the thermal stability of hydroxylamine hydrochloride solutions alone or in the presence of metals does not exist; therefore the information presented in this chapter is of great value.

2. Experimental details

2.1. Samples

Two kinds of samples were used: industrial hydroxylamine and hydroxylamine hydrochloride 99.9999 wt.% from Aldrich catalog No. 37992-1. Both solid samples were used to prepare ~35 wt.% solutions in water since this concentration is of particular industrial interest. The industrial sample was prepared with water provided also by the
company, and Aldrich reagent grade water catalog No. 32,007-2 (less than 0.01 ppm of heavy metals) was used to dissolve the Aldrich hydroxylamine hydrochloride.

Prepared were a 35.02 wt.% industrial hydroxylamine hydrochloride/industrial water solution, which from now on will be identified as “HH-ind” and a 35.05 wt.% hydroxylamine/water solution, which from now on will be identified as “HH”. The physical appearance of these solutions was clear and homogeneous like pure water. The solution was stored in a laboratory refrigerator near 10 °C and was used without chemical analysis.

2.2. Apparatus

The experiments described in this chapter were performed with an APTAC, which is described in Chapter III. The data gathered in this chapter are of particular value due to the difficulty of performing the experiments, because the high temperatures combined with the highly corrosive nature of the HH decomposition products destroyed stainless steel tubing rendering the standard configuration of the apparatus useless.

As described in Chapter III, the standard tube heater assembly of the apparatus had to be redesigned to accommodate a 1/16” sample thermocouple coated with Teflon and to minimize gas decomposition product contact with the APTAC tubing. Hastelloy C-276 tubing was used to construct this redesigned tube heater assembly due to its higher
corrosion resistance to hydrogen chloride, which is assumed to be one of the decomposition products.

2.3. Analytical methods

For the analytical measurements of the gas phase, a three Tesla Fourier Transform Mass Spectrometer (FTMS) also known as Ion Cyclotron Resonance Mass Spectrometry (ICR-MS) and a gas chromatograph (GC) were used as discussed in Chapter III.

Liquid products were analyzed for ammonia using a titration with NaOH and were analyzed for water using the Karl Fisher method.

2.4. Experimental method

The experiments reported here were performed in a closed cell environment with air above the sample. The heat-wait-search routine was used (see Chapter III for details). HA samples were transferred to sample cells using disposable plastic pipettes. Sample masses were obtained by weight differences. Because of the relative small amounts of sample, no stirring was used during the APTAC runs. A sample thermocouple with a Teflon-coated sheath and a total diameter of ~1/16” was used to follow the exothermic behavior until completion without thermocouple failure. Attempts to use 0.02” diameter thermocouples in different fashions (coated with Teflon, coated with SiO₂, or protected with a glass sheath) failed. Also, the Teflon coat prevents the thermocouple metal
surface from contacting the sample, which may be catalyzed by metals as in the case of hydroxylamine free base.

Experimental runs were performed in spherical sample cells of 130 cm$^3$ nominal volume and of borosilicate glass, stainless steel 316 (SS), and titanium (Ti). It was presumed that glass cells provided a neutral environment without significant catalysis for the HH and HH-ind decomposition reaction. Reactivity with respect to the other materials (SS and Ti) was tested by using the corresponding cells.

Experiments were performed to test the effect of carbon steel (composed primarily of iron, 97 - 99 %, graphite, < 2 %), which is a common industrial contaminant that is found in nails, wire, or structural components. A piece of carbon steel nail with a surface area to sample volume ratio (SVR) of approximately 0.024 mm$^{-1}$ was introduced into the sample after the sample was weighed in a glass cell.

2.5. Uncertainties

The experimental uncertainties were discussed in Chapter IV.
3. Results and discussion

3.1. HH experiments in glass cells

A summary of the experiments performed in glass cells is presented in Table 6.1. As shown in the table, there is a small difference of less than 0.5 g. between the initial and final sample weight, which is a first indication of the low noncondensable pressure produced. Given the species involved in the reaction, a colorless liquid phase was expected (NH₄OH and NH₄Cl are possible decomposition products and both are colorless). The emerald green color of the final sample solution may be a result of small dissolution of the black Teflon thermocouple material due to the extremely corrosive conditions developed during the experiments.

Table 6.1
HH decomposition data summary

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Initial g. ± 0.01</th>
<th>Final g. ± 0.01</th>
<th>Liquid residue</th>
<th>Solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH-ind, 1</td>
<td>3.26</td>
<td>3.05</td>
<td>Emerald green</td>
<td>No residue</td>
</tr>
<tr>
<td>HH-ind, 2</td>
<td>3.41</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Brown&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>HH-ind, 3</td>
<td>3.33</td>
<td>3.07</td>
<td>Emerald green</td>
<td>No residue</td>
</tr>
<tr>
<td>HH, 1</td>
<td>3.38</td>
<td>3.09</td>
<td>Emerald green</td>
<td>No residue</td>
</tr>
<tr>
<td>HH, 2</td>
<td>3.32</td>
<td>2.48</td>
<td>Emerald green</td>
<td>No residue</td>
</tr>
<tr>
<td>HH, 3</td>
<td>3.31</td>
<td>NA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Emerald green</td>
<td>No residue</td>
</tr>
</tbody>
</table>

<sup>a</sup> A leak developed at the final part of the experiment
<sup>b</sup> Not measured
The experimental screening temperature range was 50 to 250 °C, and for this range only one mild exotherm was detected. A summary of the measured decomposition parameters is presented in Table 6.2, which shows that the onset temperature for the industrial and Aldrich or characterized sample is not different within the experimental error \( T_{on} = 155.4 \) and 145.4 °C respectively). The same is true for the other experimental measurements reported in Table 6.2. The noncondensable pressure generated is relatively low (16 for the industrial samples and 25 for the characterized samples). The presence of industrial stabilizer seems to have had no effect on the thermally induced decomposition of HH-ind solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Runs</th>
<th>( T_{on} ) °C</th>
<th>( T_{max} ) °C</th>
<th>( \Delta T_{adb} ) °C</th>
<th>( P_{max} ) psia</th>
<th>Non cond. psia</th>
<th>tMR min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH-ind</td>
<td>3</td>
<td>155.4 ± 7.1</td>
<td>190.7 ± 9.8</td>
<td>35 ± 12</td>
<td>106 ± 42</td>
<td>16 ± 2.2</td>
<td>201 ± 154</td>
</tr>
<tr>
<td>HH</td>
<td>3</td>
<td>145.4 ± 9.7</td>
<td>184.9 ± 8.3</td>
<td>40 ± 4</td>
<td>99 ± 17</td>
<td>25 ± 8.6</td>
<td>101 ± 40</td>
</tr>
</tbody>
</table>

The reported uncertainties are one standard deviation of the experimental replicas \( \phi = 3.8 ± 0.2 \)

Figure 6.1 presents the heat rate versus temperature curves for the experiments reported in Table 6.1. A summary of the Figure 6.1 data is presented in Table 6.3. The experiments run with the industrial sample present good reproducibility with the exception of the third industrial replica (HH-ind, 3). The experiments run with the well-characterized sample do not overlap as do the experiments with the industrial sample. The slightly different measurements can be explained by the low HH (and HH-ind)
decomposition heat rates, which are close to the APTAC detection limit. The heat and pressure generation rates are quite low and average 0.6 °C/min and 1.5 psia/min respectively.

Figure 6.1. HH decomposition self-heat rate with (HH-ind) and without (HH) stabilizers. \( \phi = 3.8 \pm 0.2 \).

Table 6.3
HH thermal decomposition rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \frac{dT}{dt}_{\text{max}} )</th>
<th>( \frac{dP}{dt}_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH-ind</td>
<td>0.6 ± 0.4</td>
<td>1.5 ± 0.4</td>
</tr>
<tr>
<td>HH</td>
<td>0.6 ± 0.4</td>
<td>1.5 ± 0.8</td>
</tr>
</tbody>
</table>

\( \phi = 3.8 \pm 0.2 \)
Figure 6.2 presents the pressure rate data vs. temperature for the experiments, and summary of the maximum pressure rates is presented in Table 6.3. Figure 6.2 parallels the behavior of the heat rate vs. temperature data presented in Figure 6.1. As can be seen from Table 6.3, there are not detectable differences in the maximum temperature and pressure rates attained by the two sample types.

![Figure 6.2. HH decomposition pressure rate with (HH-ind) and without (HH) stabilizers. $\phi = 3.8 \pm 0.2.$](image)

Figure 6.3 presents a pressure plot of the mixture before and during the decomposition for both kinds of samples, and the vapor pressure data of the solvent (water) for comparison. It can be seen from this plot that the pressure created by the
noncondensable components is minimal when compared to the vapor pressure of the solvent. This tempered behavior for the thermal decomposition of HH systems information is useful for process and pressure relief designs.

![Figure 6.3. HH vapor pressure data.](image)

A kinetic model for the overall thermal decomposition of the HH was developed using the procedure described in Chapter II and a summary of the results is presented in Table 6.4. The complex nature of the HH decomposition is demonstrated by the obtained reaction order of 0.5 shown in Figure 6.4. The fractional reaction order indicates that several reactions are involved in the HH thermal decomposition. It is important to note that the best fitted overall reaction order was not always 0.5, instead it
ranged between 0.3 and 0.8 with 0.5 the most common best fit for the model for the two sample types.

Table 6.4
Calculated kinetic parameters for the HH linearized model

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ea</th>
<th>( \ln(\alpha [A]_{on}^{-1}/\text{min}^{-1}) )</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH-ind</td>
<td>24±4</td>
<td>23±5</td>
<td>0.5±0.3</td>
</tr>
<tr>
<td>HH</td>
<td>25±2</td>
<td>25±3</td>
<td>0.5±0.1</td>
</tr>
</tbody>
</table>

Figure 6.4. Overall reaction order for “HH-ind, 1”.

The Arrhenius plot for the first half of the decomposition reaction is shown in Figure 6.5, which shows that the activation energies (given by the slope of the curves)
are similar for all the experiments. The calculated activation energy for the HH decomposition is $\sim 25 \pm 2$ Kcal/mol.

Figure 6.5. Arrhenius plot for the first half of the HH and “HH-ind” decomposition reactions.

In the experiments reported in this chapter, the sample plus sample cell system was maintained at nearly adiabatic conditions. Because some of the heat generated is absorbed by the sample cell, the effect of the sample size is important when analyzing data from calorimetry and has to be considered when designing pilot or commercial scale processes. Some experiments run with various HH-ind sample sizes are shown in Table 6.5 and Figure 6.6. It can be shown from Figure 6.6 that even at thermal inertia
factors close to unity the maximum heat rate is 11 °C/min, which is relatively mild. As a comparison the maximum heat rate for HA is ~ 469 °C/min for a thermal inertia factor of 1.37.

Table 6.5

<table>
<thead>
<tr>
<th>φ</th>
<th>T_{on}</th>
<th>T_{max}</th>
<th>dT/dt_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>145.8</td>
<td>243.2</td>
<td>11.0</td>
</tr>
<tr>
<td>2</td>
<td>154.1</td>
<td>195.9</td>
<td>1.0</td>
</tr>
<tr>
<td>3.7</td>
<td>161.4</td>
<td>198.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Figure 6.6. Effect of thermal inertia on the self heat rate of HH-ind decomposition.
A nonlinear parameter estimation was performed using the ChemInform software for the \( \phi = 1.6 \) experiment, and the kinetic parameters for the power law model are summarized in Table 6.6. The calculated model parameters are similar to the ones obtained by the linearized method at a \( \phi = 3.7 \) which increases the confidence in the model because different sample sizes give similar kinetic models. The excellent agreement between the simulated and the experimental data for the nonlinear parameter estimation is presented in Figure 6.7.

Figure 6.7. Simulation of temperature vs. time plot for HH-ind, \( \phi = 1.6 \).

Table 6.6
Summary of power law kinetic parameters for Figure 6.7

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \phi )</th>
<th>( \text{Ea (Kcal/mol)} )</th>
<th>( p )</th>
<th>( \ln(\alpha [A]^p) ) / min(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH-ind</td>
<td>1.6</td>
<td>30.6</td>
<td>0.74</td>
<td>30</td>
</tr>
</tbody>
</table>
3.2. *Hydroxylamine hydrochloride 100 % thermal decomposition*

The fact that HH (35 mass % hydroxylamine/water solutions) did not react very aggressively gave us confidence to test the thermal decomposition of solid 100% hydroxylamine hydrochloride (available from Aldrich) under runaway conditions. Table 6.7 presents a summary of the measured parameters.

<table>
<thead>
<tr>
<th>Table 6.7</th>
<th>Solid 100 % hydroxylamine hydrochloride decomposition parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass g.</td>
<td>$T_{on}$ °C</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------</td>
</tr>
<tr>
<td>1.22</td>
<td>112.1</td>
</tr>
</tbody>
</table>

It can be seen from Table 6.7 that even for solid hydroxylamine hydrochloride the onset temperature is higher than 100 °C. Even though the initial moles of solid hydroxylamine hydrochloride are practically the same as for the HH experiments reported in Table 6.2 (0.0175 moles) the noncondensable pressure is four times higher, which indicates that part of the gas products are soluble. One possible decomposition product is HCl which is very soluble (82.3 g in 100 ml of water solubility). Figure 6.8 presents the temperature and pressure data over time for solid hydroxylamine hydrochloride thermal decomposition. As can be seen in Figure 6.8, the profiles do not change slope very drastically, which indicates a mild exothermic activity. The heat and pressure rates
shown in Figure 6.9 also indicate a mild exothermic activity with 0.54 °C/min maximum heat rate and 1.28 psi/min maximum pressure rate. The residue after the reaction was a greenish solid.

Figure 6.8. Temperature and pressure profiles for 100 % hydroxylamine hydrochloride thermal decomposition.
3.3. Nail test

Figure 6.10 presents the heat rate vs. temperature data generated when a carbon steel nail (composed primarily of iron, 97-99%, graphite < 2%) was added to 3.2 g of HH-ind. The onset temperature dropped from 155 to 54 °C and the maximum heat rate increased from 0.58 to 11.4 °C/min. The addition of carbon steel catalyzed the decomposition as indicated by an increase in the heat rate of almost 20 times. At the end of the experiment, the nail was completely dissolved and the liquid residue was green. The measured parameters are summarized in Table 6.8.
Table 6.8
Decomposition parameters for HH-ind plus nail

<table>
<thead>
<tr>
<th>Mass g.</th>
<th>$T_{on}$ °C</th>
<th>$T_{max}$ °C</th>
<th>$P_{max}$ psia</th>
<th>Non cond. psia</th>
<th>$dT/dt_{max}$ °C/min</th>
<th>$dP/dt_{max}$ psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>54.3</td>
<td>144.9</td>
<td>82.8</td>
<td>26.2</td>
<td>11.4</td>
<td>12.79</td>
</tr>
</tbody>
</table>

Figure 6.10. Effect of carbon steel (nail) on the HH-ind decomposition reaction in glass cells.

3.4. Effect of Ti and SS on the thermal decomposition of HH

The catalytic effect of stainless steel and Ti were measured using 130 cm$^3$ cells of the corresponding material in a similar fashion as for the HA experiments. Stainless steel catalyzed the HH decomposition reaction to a lesser extent than carbon steel. Ti has a low effect in the heat rate. Ti is a weak catalyst for the HH decomposition in contrast to that for the hydroxylamine free base where the Ti and SS catalyzed the decomposition
similarly. Table 6.9 presents a summary of the relevant details for these experiments, and the heat rate vs. temperature plot is presented in Figure 6.11.

Table 6.9
Measured parameters for the HH decomposition in various test cell materials

<table>
<thead>
<tr>
<th>Cell material</th>
<th>Mass g.</th>
<th>$T_{on}$ $^\circ$C</th>
<th>$\frac{dT}{dt}_{max}$ $^\circ$C/min</th>
<th>Solid residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>3.34</td>
<td>55.1</td>
<td>0.57</td>
<td>White</td>
</tr>
<tr>
<td>SS</td>
<td>3.36</td>
<td>90.2</td>
<td>4.1</td>
<td>Black</td>
</tr>
<tr>
<td>Glass</td>
<td>3.32</td>
<td>144.5</td>
<td>0.45</td>
<td>None</td>
</tr>
</tbody>
</table>

Figure 6.11. Decomposition reaction of HH in various test cell materials.

Although the experiment run in a Ti cell has a lower onset temperature, the heat rate is low for all the temperature range in contrast to the experiment run in SS which has an onset temperature 35 $^\circ$C higher than the Ti experiment but, after that, the heat rate
rapidly increases to a maximum of 4.4 °C/min at ~120 °C. The maximum rate for the experiment run in SS is approximately ten times greater than that of the experiment run in glass, and the temperature at which this maximum rate is observed is approximately 47 °C lower. The Ti and SS residues are probably TiO₂ and Fe₂O₃ or FeCl₃, respectively.

3.5. Analytical results

Only Aldrich samples were analyzed to avoid uncertainties due to the presence of unknown stabilizers in the industrial samples. One liquid sample was analyzed (HH, 3) and the result of this analysis is presented in Table 6.10. The gas phase of the hydroxylamine hydrochloride (solid) was analyzed using EI-FTMS and the gas phase of “HH, 3” was analyzed using a GC. Based on the analysis of the gas phase samples, it is probable that the relative amounts of the decomposition products of hydroxylamine hydrochloride solid and HH are similar. Because there is a considerable amount of H₂ (detected by GC but not by EI-FTMS) in the gas phase, both analytical techniques were used to determine a probable relative composition of the gas phase, which is presented in Table 6.11.
Table 6.10
Liquid phase residue analysis for HH samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ammonia mass %</th>
<th>Water mass %</th>
<th>Total mass %</th>
<th>Unaccounted for mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH, 3</td>
<td>4.1</td>
<td>72.4</td>
<td>76.5</td>
<td>23.5</td>
</tr>
</tbody>
</table>

Table 6.11
Proposed gas phase decomposition products for HH

<table>
<thead>
<tr>
<th>Sample</th>
<th>N₂ mol %</th>
<th>NO mol %</th>
<th>O₂ mol %</th>
<th>N₂O mol %</th>
<th>H₂ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH</td>
<td>64.8</td>
<td>0.9</td>
<td>16.8</td>
<td>8.5</td>
<td>9.0</td>
</tr>
</tbody>
</table>

4. Conclusions

The HH and HH-ind decomposition reaction, which is represented approximately by 0.5 order power law kinetics, proceeds at low rates at temperatures near ambient. This reaction is exothermic with energy releases corresponding to a heating rate (for sample plus cell) of 0.1 °C/min near 145 °C. Reaction rates, as predicted from the Arrhenius expression, escalate rapidly at higher temperatures with greater rates of energy release.

The HH decomposition products are extremely corrosive at temperatures above 100 °C. One probable corrosive decomposition product is hydrochloric acid, which at room temperature is very soluble in water. The solubility characteristics of HCl explain the corrosive nature of the decomposition products at elevated temperatures and also why
HCl was not detected in the gas phase decomposition products, which are mainly N\textsubscript{2} and O\textsubscript{2} with small quantities of N\textsubscript{2}O and H\textsubscript{2}, and a trace amount of NO. The liquid phase residue contains 4.1 mass\% ammonia and 72.4 mass\% water. The 23.5 mass\% balance of the liquid phase was probably HCl.

The decomposition reaction of HH is catalyzed by stainless steel, carbon steel and, in a lesser extent, by Ti metal. One industrial concern is the integrity of the metal equipment in the event of a runaway reaction due to the extremely corrosive nature of the decomposition products. As discussed earlier in this chapter, the nail was dissolved at the end of the experiment and the SS sample cell was perforated. It is probable that part of the exotherm during these experiments was due to the reaction between HCl and SS, which produces H\textsubscript{2} and FeCl\textsubscript{3} \[142\]. FeCl\textsubscript{3} is a probable identity for the black solid residue in the SS experiment.

The data presented in this chapter are extremely valuable, and to the best of our knowledge no thermal stability data for hydroxylamine hydrochloride solutions (or solid) have been previously reported. This can be explained by the necessity of using glass test cells, which renders the other thermal safety adiabatic calorimeters (such as the ARC) inadequate to perform these experiments.


140 Ayres, Analisis quimico cuantitativo, Ediciones del Castillo, Mexico, D.F., p.704.


CHAPTER VII

HYDROXYLAMINE SULFATE STUDIES

1. Background

Lossen [128] first prepared hydroxylamine sulfate by evaporating hydroxylamine hydrochloride in the presence of sulfuric acid and extracting the mixture with alcohol. Hydroxylamine sulfate decomposition reactions are believed to be either:

\[
4(NH_2OH)_2H_2SO_4 \rightarrow 4(NH_4)_2HSO_4 + N_2 + 2NO + 6H_2O \quad (7.1)
\]

or

\[
3(NH_3OH)_2SO_4 \rightarrow (NH_4)_2SO_4 + 2SO_2 + 2N_2O + 8H_2O \quad (7.2)
\]

Hydroxylammonium sulfate [hydroxylamine sulfate or oxammonium sulfate, \((H_2NOH)\_2H_2SO_4]\) is the most common form of hydroxylamine used in industry. It is normally sold as a solution or colorless monoclinic crystals. The commercially available solutions are 25 wt.\%, which is close to the maximum solubility limit at room temperature, and are transported in stainless steel containers. The main industrial application of hydroxylamine sulfate is the production of cyclohexanone oxime or caprolactam. Hydroxylamine sulfate is also used as a reducing agent in photography, in
synthetic and analytical chemistry, to purify aldehydes and ketones, and as an antioxidant for fatty acids and soaps.

Information about hydroxylamine sulfate thermal stability is scarce with the exception of a DTA study, which reports for the solid an onset temperature above 138°C accompanied by gas evolution [79].

This chapter reports thermal stability data for solid hydroxylamine sulfate and for 25 wt.% hydroxylamine sulfate/water solutions (HS). At present, this information is not available in the open literature and can contribute to process control strategies and safer ways to handle hydroxylamine sulfate.

2. Experimental details

2.1. Samples

The sample tested was hydroxylamine sulfate 99.999% available from Aldrich catalog number 37991-3. Aldrich reagent water catalog number 32,007-2 was used to prepare 25 ± 0.2 wt. % solutions (HS), since this concentration is close to the hydroxylamine sulfate solubility limit at room temperature. The physical appearance of the solution was clear, homogeneous, and odorless.
2.2. **Apparatus**

The experiments described in this chapter were performed in an APTAC, which is described in Chapter III. The data gathered in this chapter are of particular value due to the difficulty of performing the experiments, since the high temperatures combined with the highly corrosive nature of the HS decomposition products may destroy stainless steel tubing rendering the standard configuration of the apparatus useless.

As described in Chapter III, the standard tube heater assembly of the apparatus had to be redesigned to accommodate a 1/16” sample thermocouple coated with Teflon and to minimize contact of corrosive gas decomposition products with the APTAC tubing. Hastelloy C-276 was used to construct this redesigned tube heater assembly due to its higher corrosion tolerance to sulfuric acid, which was assumed to be one of the HS decomposition products.

2.3. **Analytical methods**

Liquid products were analyzed for ammonia using a titration with NaOH and for water using the Karl Fisher method.

2.4. **Experimental method**

The experiments reported here were performed in a closed cell environment with air above the sample. The heat-wait-search routine was used (see Chapter III for details). HA samples were transferred to sample cells using disposable plastic pipettes. Sample
masses were obtained by weight differences. When small sample sizes were used it was not feasible to use a stirrer, but when sample size permitted (sample more than 30 g) a 300-rpm stirring rate was programmed. A sample thermocouple with a Teflon-coated sheath and a total diameter of ~1/16” was used to follow the exothermic behavior until completion without thermocouple failure. The Teflon coat also prevents the thermocouple metal surface from contacting the sample, which may be catalyzed by metals as in the case of hydroxylamine free base.

Experimental runs were performed in spherical sample cells of 130 cm³ nominal volume and of borosilicate glass, stainless steel 316 (SS), and titanium (Ti). It was presumed that glass cells provided a neutral environment without significant catalysis for the HS decomposition reaction. Reactivity with respect to the other materials (SS and Ti) was tested by using the corresponding cells.

2.5. Uncertainties

The experimental uncertainties were discussed in Chapter IV.
3. Results and discussion

3.1. HS experiments in glass

A summary of the HH experiments run in glass cells is presented in Table 7.1. For all experiments reported in Table 7.1 the sample remains were crystal clear with a pH of less than 1.0. The residues did not smell like ammonia, since the ammonia produced was probably in the form of odorless ammonium sulfate [(NH₄)₂SO₄]. There was a maximum mass loss of around 6% for the “HS, 1” experiment.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial g.</th>
<th>Final g.</th>
<th>Liquid Residue</th>
<th>Solid Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS, 1</td>
<td>4.45</td>
<td>4.20</td>
<td>Crystal clear</td>
<td>No residue</td>
</tr>
<tr>
<td>HS, 2</td>
<td>4.33</td>
<td>4.20</td>
<td>Crystal clear</td>
<td>No residue</td>
</tr>
</tbody>
</table>

The experimental screening temperature range was from 50 °C to 220 °C, and for these temperatures only one mild exotherm was detected. A temperature and pressure vs. time profile is presented in Figure 7.1, where the change in slope for the pressure profile is observed to be more drastic than that for the temperature profile indicating noncondensable gas production.
Table 7.2 presents a summary of the measured parameters for the experiments presented in Table 7.1. A relatively high onset temperature of 152 °C was detected and the $\Delta T_{adb}$ was only 33.5 °C.

Table 7.2
Measured HS decomposition parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Runs</th>
<th>$T_{on}$ °C</th>
<th>$T_{max}$ °C</th>
<th>$\Delta T_{adb}$ °C</th>
<th>$P_{max}$ psia</th>
<th>Non cond. psia</th>
<th>$t_{MR}$ min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>2</td>
<td>151.8 ± 14</td>
<td>185.3 ± 2</td>
<td>34 ± 15</td>
<td>188 ± 10</td>
<td>10.6 ± 0.4</td>
<td>326 ± 93</td>
</tr>
</tbody>
</table>

$\phi = 2.4 \pm 0.2$

Figures 7.2 and 7.3 present the heat rate and pressure rate data for the experiments listed in Table 7.1. Table 7.3 presents the maximum values for the heat and pressure rates of Figures 7.2 and 7.3, respectively. As shown, the rates are quite low and close to the
APTAC detection limit capabilities, which may explain the data scatter, especially for the “HS, 2” experiment.

Table 7.3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\frac{dT}{dt}_{\text{max}}$ $^\circ\text{C}/\text{min}$</th>
<th>$\frac{dP}{dt}_{\text{max}}$ psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>0.11 ± 0.02</td>
<td>0.32 ± 0.06</td>
</tr>
</tbody>
</table>

$\phi = 2.4 \pm 0.2$

Figure 7.2. HS thermal decomposition self-heat rate. $\phi \sim 2.4 \pm 0.2$. 
Since there was such a small exothermic activity, an experiment was performed using
the maximum workable amount of HS sample. The summarized data for this experiment
are presented in Table 7.4. As predicted by theory, the onset temperature did not change
considerably and the adiabatic temperature rise was practically the same as what one
would predict from the experiments presented in Table 7.2 \[\phi_1/\phi_2 \Delta T_{\text{adf1}} = 73.1\] vs. 73.4
measured]. As shown in Table 7.4 and Figure 7.4 the maximum heat generation rate
was very low even for a thermal inertia factor close to unity.
Table 7.4
HS decomposition parameters. “HS, 3”, $\phi = 1.1$

<table>
<thead>
<tr>
<th>Initial g.</th>
<th>Final g.</th>
<th>$T_{\text{on}}$ °C</th>
<th>$T_{\text{max}}$ °C</th>
<th>$\Delta T_{\text{adb}}$ °C</th>
<th>$P_{\text{max}}$ psia</th>
<th>Non cond.</th>
<th>$t_{\text{MR}}$ min</th>
<th>$\text{dT/d}t_{\text{max}}$ °C/min</th>
<th>$\text{dP/d}t_{\text{max}}$ psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.20</td>
<td>39.141</td>
<td>152.4</td>
<td>225.8</td>
<td>73.4</td>
<td>647.3</td>
<td>144.9</td>
<td>303</td>
<td>0.62</td>
<td>5.385</td>
</tr>
</tbody>
</table>

Figure 7.4. HS heat rate at two different thermal inertia factors.

The low thermal inertia experiment was utilized to obtain the overall decomposition kinetic parameters for a power law model (see Chapter II for details). As shown in Figure 7.5, the best fit is obtained when a reaction order of two is used. The high dependence on the hydroxylamine sulfate concentration may be related to the fact that each hydroxylamine sulfate molecule contains two hydroxylamine free base molecules. A summary of the kinetic parameters is shown in Table 7.5, which shows, as expected, a high activation energy of 43 Kcal/mol.
Figure 7.5. HS thermal decomposition Arrhenius plot for different reaction orders.

Table 7.5
Calculated kinetic parameters for HS overall decomposition reaction

<table>
<thead>
<tr>
<th>Model</th>
<th>$E_a$ (Kcal/mol)</th>
<th>$\ln(\alpha [A]_0^{p-1} / \text{min}^{-1})$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power law kinetics</td>
<td>43.0</td>
<td>43.0</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 7.6 presents a vapor pressure plot for the experiments presented in Table 7.1 and also for the experiment performed at a thermal inertia factor of 1.1 (HS, 3). The hybrid nature of the decomposition is clearly seen in the vapor pressure data for the “HS, 3” experiment, where the pressure starts to deviate from the vapor pressure of the solvent soon after the reaction onset.
3.2. *Solid hydroxylamine sulfate thermal decomposition*

In an experiment using 1.58 g. of solid 100% hydroxylamine sulfate, a very violent reaction occurred in which shortly following the onset temperature at 144 °C, the pressure increased violently and the sample cell was reduced to finely divided pieces of glass. Figure 7.7 presents the temperature and pressure profiles for this experiment and Figure 7.8 the heat and pressure rates. As can be seen from Figure 7.8, the maximum heat rate was ~500 °C/min and the maximum pressure rate was ~5,200 psi/min just before the cell ruptured.
Figure 7.7. Temperature and pressure profiles for hydroxylamine sulfate solid.

Figure 7.8. Heat and pressure rates for hydroxylamine sulfate solid.
3.3. *HS decomposition in presence of metals*

Several experiments were performed in SS and Ti sample cells with sample sizes ranging from 3.3 to 5.0 g., but no appreciable exothermic behavior was detected. It can be concluded from these experiments that Ti and SS metal do not catalyze the HS decomposition reaction or at least not to a significant extent consistent with the fact that HS is transported in SS containers without problems.

3.4. *Analytical results*

One liquid sample was analyzed and the results of the analysis are presented in Table 7.6. In the analysis of the liquid phase 16 mass% was unaccounted for, which may be sulfuric acid since the residue had a very low pH of 1. The ammonia may have been in the form of ammonium sulfate since the residue did not have the aroma of ammonia.

| Table 7.6 |
| HS liquid residue analysis |

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ammonia wt. %</th>
<th>Water wt. %</th>
<th>Total wt. %</th>
<th>Unaccounted for wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS, 3</td>
<td>1.8</td>
<td>82.0</td>
<td>83.8</td>
<td>16.2</td>
</tr>
</tbody>
</table>
4. Conclusions

HS exhibits a mild exothermic decomposition reaction beginning at 150 °C. SS and Ti metals do not catalyze the decomposition reaction in a significant fashion. The decomposition reaction generates ~ 0.8 moles of noncondensable gas per initial mole of hydroxylamine sulfate.

The hydroxylamine solid is stable at temperatures below 100 °C and at 144 °C the onset of a violent decomposition reaction with pressure generation rates greater than 5,200 psi/min was measured.
1. Background

Hydroxylamine-o-sulfonic acid is synthesized by treating hydroxylammonium salt with chlorosulfonic acid. The main uses of hydroxylamine-o-sulfonic acid are as an intermediate for amination or formation of heterocycles. Unlike the derivatives presented in previous chapters, the hydroxylamine free base molecule is modified by substitution of SO$_3$H for the hydrogen originally attached to the oxygen atom. Therefore, the hydroxylamine-o-sulfonic acid molecular formula is:

\[ HO - S - O - NH_2 \]  

(8.1)

This hydroxylamine derivative is far less common than the hydroxylammonium salts and information about its thermal stability as a solid or in solution is nonexistent. This chapter presents thermal stability data for pure hydroxylamine-o-sulfonic acid and for 35 wt.% aqueous solutions, which have not been reported previously.
2. Experimental details

2.1. Samples

Samples of 99.999% hydroxylamine-o-sulfonic acid were obtained from Aldrich, catalog number 48097-5. Aldrich reagent water, catalog number 32,007-2, was used to prepare $35 \pm 0.1$ wt.% solutions (HOSA), since this concentration was used for the hydroxylamine hydrochloride samples. The physical appearance of the solution was clear, homogeneous, and odorless.

2.2. Apparatus

The experiments described in this chapter were performed in an APTAC, which is described in Chapter III. The data gathered in this chapter are of particular value due to the difficulty of performing the experiments, since the high temperatures combined with the highly corrosive nature of HOSA (initial sample pH was 1) may destroy the stainless steel tubing and render the standard configuration of the apparatus useless.

As described in Chapter III, the standard tube heater assembly of the apparatus was redesigned to accommodate a 1/16” sample thermocouple coated with Teflon and to minimize gas decomposition product contact with the APTAC tubing. Hastelloy C-276 was used to construct this redesigned tube heater assembly due to its high corrosion tolerance.
2.3. *Analytical methods*

Liquid products were analyzed for ammonia using a titration with NaOH and for water using the Karl Fisher method.

2.4. *Experimental method*

The experiments reported here were performed in a closed cell environment with air above the sample. The heat-wait-search routine was used, as described on Chapter III. HA samples were transferred to sample cells using disposable plastic pipettes. Sample masses were obtained by weight differences. When small sample sizes were used it was not feasible to use a stirrer, but when sample size permitted (sample more than 20 g) a 500-rpm stirring rate was programmed. A sample thermocouple with a Teflon-coated sheath and a total diameter of ~1/16” was used to follow the exothermic behavior until completion without thermocouple failure. The Teflon coat also prevents the thermocouple metal surface from contacting the sample, which may be catalyzed by metals as in the hydroxylamine free base case.

Experimental runs were performed in spherical sample cells of 130 cm³ nominal volume and of borosilicate glass, stainless steel 316 (SS), and titanium (Ti). It was presumed that glass cells provided a neutral environment without significant catalysis for the HOSA decomposition reaction. Reactivity with respect to the other materials (SS and Ti) was tested by using the corresponding cells.
2.5. Uncertainties

The experimental uncertainties were discussed in Chapter IV.

3. Results and discussion

3.1. HOSA experiments in glass

A summary of HOSA experiments performed in glass cells is presented in Table 8.1.

The initial and final sample pH was close to one. The source of the yellowish color for the second sample was probably corrosion products from the top of the tube heater assembly. The residues did not smell like ammonia.

Table 8.1
HOSA decomposition experiments data summary

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial g. ± 0.1</th>
<th>Final g. ± 0.01</th>
<th>Liquid Residue</th>
<th>Solid Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOSA, 1</td>
<td>3.37</td>
<td>3.05</td>
<td>Crystal clear</td>
<td>No residue</td>
</tr>
<tr>
<td>HOSA, 2</td>
<td>3.31</td>
<td>2.89</td>
<td>Yellowish</td>
<td>No residue</td>
</tr>
</tbody>
</table>

The temperature range screened was from 50 to 210 °C, and for this range two mild exothermic processes were detected. As shown in Figure 8.1, there was no stabilization at 50 °C, but the temperature kept on increasing due to exothermic behavior. The second
exotherm started around 150 °C. Figure 8.1 also shows that the pressure generated in the first exotherm is almost imperceptible.

![Temperature and pressure vs. time profile for HOSA. φ = 2.4.](image)

Table 8.2 presents a summary of the measured parameters for the experiments presented in Table 8.1. The lower exotherm is not presented in this table since the apparatus was not able to detect the initial part of the exotherm. An inspection of the raw data shows that the first exotherm starts at around 50 °C and ends at about 90 °C with a maximum heat rate of approximately 1.4 °C/min. As shown in Table 8.2, the second exotherm has a long induction period that is reflected in a time to maximum rate, t_MR of 328 min. The adiabatic temperature rise is 40 °C (as with the first exotherm). The noncondensable
pressure for the combined first and second exotherm as reported in Table 8.2 is

\[ \sim 13 \text{ psia}. \]

### Table 8.2
Measured HOSA decomposition parameters for the second exothermic behavior

<table>
<thead>
<tr>
<th>Sample</th>
<th>Runs</th>
<th>( T_{\text{on}} ) °C</th>
<th>( T_{\text{max}} ) °C</th>
<th>( \Delta T_{\text{adb}} ) °C</th>
<th>( P_{\text{max}} ) psia</th>
<th>Non cond. psia</th>
<th>( t_{\text{MR}} ) min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOSA</td>
<td>2</td>
<td>159.8 ± 14</td>
<td>198.3 ± 5</td>
<td>39 ± 9</td>
<td>191 ± 22</td>
<td>13 ± 3</td>
<td>328 ± 51</td>
</tr>
</tbody>
</table>

\(^a\) The noncondensables pressure is for the overall system (first and second exotherms combined).

\[ \phi = 2.4 \pm 0.02 \]

Figures 8.2 and 8.3 present the heat rate and pressure rate data for the experiments presented in Table 8.1. The maximum heat and pressure rates for the first and second exothermic behaviors are summarized in Table 8.3. As can be seen from Figure 8.2, only the last part of the first exothermic activity was detected. Although, the first exotherm has a heat rate 10 times greater than the second one, both exothermic activities can be considered mild.

### Table 8.3
HOSA thermal decomposition rates

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{\text{on}}^1 ) °C</th>
<th>( T_{\text{on}}^2 ) °C</th>
<th>( \frac{dT}{dt}_{\text{max}}^1 ) °C/min</th>
<th>( \frac{dP}{dt}_{\text{max}}^1 ) psia/min</th>
<th>( \frac{dT}{dt}_{\text{max}}^2 ) °C/min</th>
<th>( \frac{dP}{dt}_{\text{max}}^2 ) psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOSA</td>
<td>&lt; 50</td>
<td>160</td>
<td>1.41 ± 0.67</td>
<td>0.23 ± 0.11</td>
<td>0.14 ± 0.11</td>
<td>0.33 ± 0.32</td>
</tr>
</tbody>
</table>

\[ \phi = 2.4 \pm 0.02 \]

\(^1\) First exotherm

\(^2\) Second exotherm
Figure 8.2. HOSA thermal decomposition self-heat rate. $\phi = 2.4 \pm 0.02$.

Figure 8.3. HOSA thermal decomposition pressure rate. $\phi = 2.4 \pm 0.02$. 
As shown in Figures 8.2 and 8.3, the first exotherm has higher heat rates but lower pressure rates. The pressure rates are mild for both reactions and the combined effect of the two exothermic activities produces only 13 psia of noncondensable pressure.

Since there was little exothermic activity for the samples presented in Table 8.1, a sample (HOSA, 3) was run using the maximum workable sample size, and a summary of this experiment is presented in Table 8.4. It can be seen from this table that, although the thermal inertia factor is close to one, the second exothermic activity remains mild at 0.35 °C/min, which is 2.5 times greater than for the experiments run at \( \phi =2.4 \). The onset datum reported in Table 8.4 is surprising, since a similar or lower onset temperature than that reported in Table 8.2 for larger \( \phi \) was expected. Instead, an onset temperature 45 °C higher was measured. The “HOSA, 3” experiment also presented a first exothermic activity beginning before 50 °C with an approximate maximum heat rate value of 1.6 °C/min, which is close to the ~ 1.4 °C/min for the experiments run at \( \phi =2.4 \).

<table>
<thead>
<tr>
<th>Initial g.</th>
<th>Final g.</th>
<th>( T_{on} ) °C</th>
<th>( T_{max} ) °C</th>
<th>( \Delta T_{ad} ) °C</th>
<th>( P_{max} ) psia</th>
<th>Non cond. psia</th>
<th>tMR min</th>
<th>( dT/dt_{max} ) °C/min</th>
<th>( dP/dt_{max} ) psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.81</td>
<td>23.69</td>
<td>&lt;50° 204.8</td>
<td>267.6</td>
<td>63</td>
<td>764.8</td>
<td>107.8</td>
<td>346</td>
<td>1.58° 0.35</td>
<td>3.35</td>
</tr>
</tbody>
</table>

\( ^1 \) First exotherm
\( \phi =1.2 \)
Figure 8.4 presents the measured heat rate for experiments run at the two thermal inertia factors. Inconsistent with theory, the first exothermic activity was not modified by the thermal inertia factor and the second exotherm was measured at higher temperatures when the thermal inertia factor was lower. In either case the exothermic activity was very low, less than 2 °C/min, and self heat rates of that low magnitude are difficult to measure, which may explain the deviations from theory.

![Graph showing heat rate vs. temperature for different thermal inertia factors.](image)

**Figure 8.4.** HOSA heat rate at different thermal inertia factors.

The low thermal inertia experiment was used to calculate the kinetics for the second exotherm (the only one that was fully measured) and the results are presented in Figure 8.5 and Table 8.5. As shown in Table 8.5, the activation energy for the second overall reaction is approximately 31 Kcal/mol. The second exotherm in this figure is in
fact composed of several reactions and that explains the fractional reaction order and the non-linearity in the low temperature range of the Arrhenius plot shown in Figure 8.5.

![Arrhenius plot for different reaction orders](image)

Figure 8.5. HOSA second exotherm thermal decomposition Arrhenius plot for different reaction orders.

<table>
<thead>
<tr>
<th>Model</th>
<th>$E_a$ (Kcal/mol)</th>
<th>$\ln(\alpha [A]_{on}^{-1})$ / min$^{-1}$</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power Law</td>
<td>31</td>
<td>25</td>
<td>0.7</td>
</tr>
</tbody>
</table>

The vapor pressure data are presented in Figure 8.6. As shown in this figure, there is no large deviation from the vapor pressure of the solvent. Based on the noncondensable pressure generated, the HOSA can be classified as a hybrid system.
Figure 8.6. Vapor pressure data for HOSA thermal decomposition. HOSA, 1 and 2, $\phi \sim 2.4$, HOSA, 3, $\phi \sim 1.2$.

3.2. *Solid hydroxylamine sulfate thermal decomposition*

An experiment using pure hydroxylamine-o-sulfonic acid was run, and a summary of the measured parameters is presented in Table 8.6. The maximum heating rate was only 10.4 °C/min. The non-condensable pressure is low and is consistent with the values obtained for the HOSA experiments since the ratio of noncondensable psi to grams of pure hydroxylamine-o-sulfonic acid is 12.4 for the experiment run with 24.8 g. of HOSA and 12.2 for the pure solid.
Table 8.6
Measured decomposition parameters for pure hydroxylamine-o-sulfonic acid thermal decomposition

<table>
<thead>
<tr>
<th>Initial g.</th>
<th>Final g.</th>
<th>T_{on} °C</th>
<th>T_{max} °C</th>
<th>ΔT_{adb} °C</th>
<th>P_{max} psia</th>
<th>Non cond.</th>
<th>t_{MR} min</th>
<th>dT/dt_{max} °C/min</th>
<th>dP/dt_{max} psia/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.58</td>
<td>1.27</td>
<td>71.5</td>
<td>259.1</td>
<td>188</td>
<td>74.3</td>
<td>19.3</td>
<td>980.7</td>
<td>10.4</td>
<td>3.077</td>
</tr>
</tbody>
</table>

Figure 8.7 shows the temperature and pressure profiles for pure hydroxylamine-o-sulfonic acid. As shown in this plot the decomposition of the solid has a long induction period, and the exotherm starts to change slope dramatically at a temperature of approximately 150 °C. Figure 8.8 presents the heat and pressure rates as functions of temperature, and several reactions can be presumed to construct the unusual shape of the heat rate and pressure rate data.

Figure 8.7. Temperature and pressure profiles for solid hydroxylamine-o-sulfonic acid.
3.3. HOSA thermal decomposition reaction in the presence of metals

3.3.1. Nail test

Figure 8.9 presents the heat rate vs. temperature data generated when a carbon steel nail (composed primarily of iron, 97-99 %, graphite < 2%) was added to 3.33 g. of HOSA. It can be seen that only a mild exothermic activity starting below 50 °C was recorded by the apparatus. It is most probable that a significant portion of the exotherm was not recorded, since as soon as the nail came in contact with the HOSA, bubbles were formed around the nail and by the time the experiment began, the temperature inside the sample cell was already 54 °C. At the end of the experiment the nail was completely dissolved and a greenish solution was left in the reaction cell. The measured parameters are
summarized in Table 8.7. Nevertheless, one should keep in mind that most likely the main part of the exotherm occurred before data recording began.

![Graph showing heat rate and temperature for HOSA and HOSA with nail](image)

Figure 8.9. Effect of carbon steel (nail) on the HOSA decomposition reaction in glass cells.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>(T_{on}) (°C)</th>
<th>(T_{max}) (°C)</th>
<th>(P_{max}) (psia)</th>
<th>Non cond. (psia)</th>
<th>(dT/dt_{max}) (°C/min)</th>
<th>(dP/dt_{max}) (psia/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.333</td>
<td>&lt; 50</td>
<td>97</td>
<td>33.4</td>
<td>6.3</td>
<td>0.14</td>
<td>0.07</td>
</tr>
</tbody>
</table>
The catalytic effect of stainless steel (SS) and Ti was measured using 130 cm³ cells made out of the corresponding material in a similar fashion as for the HA experiments. Table 8.8 presents a summary of details for these experiments, and the heat rate vs. temperature plot is presented in Figure 8.10. As shown the first exothermic activity is clearly catalyzed by SS and to a lesser extent by Ti. The second exotherm onset temperature is decreased in SS, and when the experiments are run in Ti the second exotherm disappears. At the end of the experiment, the SS sample cell was leaking from the bottom indicating that the reacting mixture is extremely corrosive to SS.

Table 8.8
Measured parameters for HOSA decomposition in various test cell materials

<table>
<thead>
<tr>
<th>Cell Material</th>
<th>Mass (g)</th>
<th>dT/dt max (°C/min)</th>
<th>dP/dt max (psia/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>3.31</td>
<td>3.1</td>
<td>0.6</td>
</tr>
<tr>
<td>SS</td>
<td>3.37</td>
<td>27.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>
3.4. Analytical results

One liquid sample was analyzed, and the results of the analysis are presented in Table 8.9. In the analysis of the liquid phase there is 39 mass% unaccounted for, and this product may be sulfuric acid since the residue had a very low pH of 1. The ammonia may be in the form of ammonium sulfate since the residue did not smell like ammonia.

Table 8.9
HOSA liquid residue analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ammonia wt %</th>
<th>Water wt %</th>
<th>Total wt %</th>
<th>Unaccounted for wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOSA, 2</td>
<td>1.9</td>
<td>59.0</td>
<td>60.9</td>
<td>39.1</td>
</tr>
</tbody>
</table>
4. Conclusions

HOSA has a complex overall thermal decomposition reaction, which presents two separate exothermic activities, the first one more aggressive than the second with an approximate self heat rate of 1.4 °C/min. The decomposition of the pure solid hydroxylamine-o-sulfuric acid is relatively mild presenting an onset temperature of around 71 °C and a maximum heat rate of 10 °C/min. Ti and specially SS catalyze the first exothermic behavior, and HOSA will react exothermically with carbon steel upon contact, even at room temperature. The moles of noncondensable products generated per mol of hydroxylamine-o-sulfonic acid are approximately 0.47.
CHAPTER IX

COMPARISON OF THE THERMAL BEHAVIOR FOR SOME MEMBERS OF
THE HYDROXYLAMINE FAMILY

1. Background

This chapter presents a comparison of the thermal behavior of the hydroxylamine compounds presented in Chapters IV through VIII. All the experiments presented in this chapter have been discussed in previous chapters. Nevertheless the tables and figures in this chapter allow straightforward comparison among the hydroxylamine family members.

Comparisons presented in this chapter include HA, HH, HS, and HOSA solutions and also solid hydroxylamine hydrochloride [H₂NOH*HCl], hydroxylamine sulfate [(H₂NOH₂(H₂SO₄)], and hydroxylamine o-sulfonic acid [H₂NOSO₃H]. Thermal behavior of aqueous solutions in the presence of Ti and SS metal surfaces also are compared. The effect of carbon steel as a nail contaminant added to the solutions also is presented.
2. HA, HH, HS, and HOSA thermal decomposition behavior in glass

Table 9.1 presents a compilation of measured parameters based on an initial solute mass of approximately 1.1 g. With the exception of HOSA first exothermic activity, HA has the lowest onset temperature. Analysis of Table 9.1 shows that, in the event of a runaway, HA will pose the greatest risk, since it is able to generate higher temperature, pressure, and noncondensable pressure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{on}$ ($^\circ$C)</th>
<th>$T_{max}$ ($^\circ$C)</th>
<th>$\Delta T_{adb}$ ($^\circ$C)</th>
<th>$P_{max}$ (psia)</th>
<th>Non cond. (psia)</th>
<th>$t_{MR}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>136 ± 1</td>
<td>207 ± 6</td>
<td>71 ± 7</td>
<td>338 ± 41</td>
<td>44 ± 5</td>
<td>87 ± 35</td>
</tr>
<tr>
<td>HH</td>
<td>145 ± 10</td>
<td>185 ± 8</td>
<td>40 ± 4</td>
<td>99 ± 17</td>
<td>25 ± 9</td>
<td>101 ± 40</td>
</tr>
<tr>
<td>HS</td>
<td>152 ± 14</td>
<td>185 ± 2</td>
<td>34 ± 15</td>
<td>188 ± 10</td>
<td>10.6 ± 0.4</td>
<td>325 ± 93</td>
</tr>
<tr>
<td>HOSA</td>
<td>&lt;50$^1$, 160 ± 14</td>
<td>90$^1$, 198 ± 5</td>
<td>40$^1$, 40 ± 9</td>
<td>191 ± 22</td>
<td>13 ± 3</td>
<td>328 ± 51</td>
</tr>
</tbody>
</table>

$^1$ Refers to the first HOSA exothermic activity

A summary of the heat and pressure rates is presented in Table 9.2. Information in Table 9.1 qualitatively suggests that hydroxylamine free base will release a greater amount of energy per unit mass, since the adiabatic temperature increase was higher even when a significant amount of the released heat was consumed to vaporize the solvent and reach a greater equilibrium vapor pressure. With the additional information presented in Table 9.2, it is evident that not only the heat released per unit mass of hydroxylamine is greater, but also that it is liberated faster. The rate of energy release is
a critical issue when evaluating thermal hazard; after all, a runaway is created when the heat produced by the reaction cannot be removed fast enough by the cooling system.

Table 9.2
Thermal decomposition rates for some hydroxylamine family members

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \frac{dT}{dt}_{\text{max}} ) °C/min</th>
<th>( \frac{dP}{dt}_{\text{max}} ) psi/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>4.5 ± 1.0</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>HH</td>
<td>0.59 ± 0.38</td>
<td>1.51 ± 0.76</td>
</tr>
<tr>
<td>HS</td>
<td>0.11 ± 0.02</td>
<td>0.32 ± 0.06</td>
</tr>
<tr>
<td>HOSA</td>
<td>1.41 ± 0.67</td>
<td>0.33 ± 0.32</td>
</tr>
</tbody>
</table>

The heat rate vs. temperature behavior is presented in Figure 9.1, which shows that the studied members of the hydroxylamine family exhibit exothermic activity between ~ 100 and 220 °C. For this range of temperature, HA presents the most aggressive reaction with a heat rate 7.6 times greater than that of HH, which presents the second most aggressive reaction. HOSA has its first and most violent exothermic activity beginning at ~ 50 °C with a maximum heat rate of ~ 1.4 °C/min.
Figure 9.1. Measured heat rates for some hydroxylamine family members.

Figure 9.2 presents the pressure rate for the solutions studied. As shown in this graphic, HA has the greatest pressure rate followed by HH, HOSA, and HS in that order. It is important to note that although HOSA was second in the heat generation rate, it is not second with respect to the pressure generation rate. This observation can be explained by the fact that the most aggressive exothermic behavior for HOSA occurs at low temperatures, where the solvent vapor pressure is low and the produced heat is utilized to heat the sample instead of vaporizing the solvent. The pressure generation rate for HA is more than 13 times greater than that of HH.
3. Solid hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-o-sulfonic acid thermal behavior

The thermal analysis of pure hydroxylamine hydrochloride, hydroxylamine sulfate, and hydroxylamine-o-sulfonic acid produced surprising results, since the least reactive solution, HS, turned out to be the most reactive solid. HS solutions presented maximum heat and pressure rates of only 0.62 °C/min and 5.39 psi/min, respectively, even when 40 g. of HS (10 g. of hydroxylamine sulfate) was tested. As shown in the temperature and pressure profiles of Figures 9.3 and 9.4, respectively, hydroxylamine sulfate has a
dramatically different behavior when compared to hydroxylamine hydrochloride and hydroxylamine-o-sulfonic acid. It is important to note that solid 100% hydroxylamine was not tested, and, most probably, it would have resulted in an even more violent reaction than the hydroxylamine sulfate, since 100% hydroxylamine is known to decompose violently at room temperature.

Figure 9.3. Temperature profile for some hydroxylamine family members. Solid 100% concentration.
Figure 9.4. Pressure profile for some hydroxylamine family members. Solid 100% concentration.

Table 9.3 presents a summary of the decomposition parameters for the studied solids. It can be seen from this table that the hydroxylamine sulfate has the highest reaction onset temperature. This observation stresses the importance of experimental work to test for reactivity, since there is no correlation between reaction onset temperature and rate of energy release.
Table 9.3
Measured parameters for some hydroxylamine family members. Solid 100 % concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (g)</th>
<th>T_{on} (°C)</th>
<th>T_{max} (°C)</th>
<th>P_{max} (psia)</th>
<th>Noncond (psia)</th>
<th>dT/dt_{max} (°C/min)</th>
<th>dP/dt_{max} (psi/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxylamine hydrochloride</td>
<td>1.22</td>
<td>112</td>
<td>187</td>
<td>139</td>
<td>80.9</td>
<td>0.54</td>
<td>1.28</td>
</tr>
<tr>
<td>Hydroxylamine sulfate</td>
<td>1.58</td>
<td>144</td>
<td>NM¹</td>
<td>NM¹</td>
<td>NM¹</td>
<td>&gt; 500</td>
<td>&gt;5,20</td>
</tr>
<tr>
<td>Hydroxylamine-o-sulfonic acid</td>
<td>1.58</td>
<td>71.5</td>
<td>259</td>
<td>74</td>
<td>19</td>
<td>10.4</td>
<td>3.07</td>
</tr>
</tbody>
</table>

¹ NM Not measured due to cell rupture

Figures 9.5 and 9.6 present the heat and pressure rates for the studied solids. It can be seen that solid hydroxylamine-o-sulfonic acid has a far more aggressive heat and pressure generation rates than that of hydroxylamine hydrochloride solid. This is another example of the importance of experimental work, since behavior in solution cannot be predicted by solid behavior.
Figure 9.5. Heat rate for some hydroxylamine family members. Solid 100% concentration.
Figure 9.6. Pressure rate for some hydroxylamine family members. Solid 100% concentration.

4. HA, HH, HS, and HOSA behavior in the presence of metals

4.1. Nail test

Figure 9.7 presents the heat rates produced when a similar piece of carbon steel in the form of a nail was added to HA, HH, and HOSA. Carbon steel catalyzed the three solutions, and the apparent low heat generation of HOSA can be misleading, since, as presented in Chapter VIII, HOSA started to react as soon as the nail contacted the solution, so most of the exothermic behavior was not measured. In fact, based on what was observed in the laboratory it is safe to assume that HOSA reacted more aggressively when contacting the nail than HH and HA. HA and HH had similar reaction rates but
the HA reaction proceeded for a longer period of time. In the case of HH and HOSA, the measured heat rates included not only the decomposition reaction, but also the reaction between the acid media and the carbon steel, since in both cases the nail was completely dissolved at the end of the experiment.

Figure 9.7. Heat rate for hydroxylamine solutions with and without carbon steel in the form of a nail.
4.2. *Test in stainless steel (SS) and titanium (Ti) sample cells*

Table 9.4 presents a summary of the maximum heat rates attained by HA, HH, and HOSA in glass, SS, and Ti test cells. HS data are not included in the table, since, as stated in Chapter VII, no appreciable exothermic behavior was detected for those experiments. Table 9.4 presents also the ratio of maximum heat rate in a metal cell to maximum heat rate in glass. As can be seen in the table, SS catalyses HA decomposition as much as Ti does. For the HH decomposition, there is a significant difference between SS and Ti; Ti has almost a null catalytic effect, whereas SS increases the maximum rate almost 7 times. For HOSA, SS increases the maximum heating rate 19 times and Ti increases the maximum heating rate 2 times.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass</th>
<th>SS</th>
<th>Ti</th>
<th>SS</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>4</td>
<td>77</td>
<td>100</td>
<td>19.3</td>
<td>25</td>
</tr>
<tr>
<td>HH</td>
<td>0.6</td>
<td>4.1</td>
<td>0.6</td>
<td>6.9</td>
<td>1</td>
</tr>
<tr>
<td>HOSA</td>
<td>1.4</td>
<td>27</td>
<td>3.1</td>
<td>19.1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 9.4
Maximum heat rate obtained for HA, HH, and HOSA in different test cell materials
Figure 9.8 presents the heat rate vs. temperature for the samples in various test cell materials. It can be seen that the effect of SS metal upon contact with HA, HH, or HOSA is to increase the heat rates.

![Graph showing heat rate vs. temperature for different samples in various materials.](image)

**Figure 9.8.** Effect of SS in the decomposition reaction of various hydroxylamine solutions.

Figure 9.9 presents the effect of Ti in the decomposition reaction of various hydroxylamine solutions. It can be seen from this graphic that, except for HA, the effect of Ti in the thermal decomposition is not so drastic as for SS. Ti is known for its inert qualities so it was surprising to observe the result that Ti catalyses the HA decomposition reaction.
Figure 9.9. Effect of Ti in the decomposition reaction of various hydroxylamine solutions.

5. Kinetic comparison

Table 9.5 presents the activation energy and reaction order obtained when a power law kinetic model was applied to the exothermic behavior of the various hydroxylamine solutions studied. The least reactive substance, HS, has the highest overall activation energy, but the more reactive solution, HA, has a higher activation energy than HH. The HA activation energy (28.5 Kcal/mol) is lower than the energy required to break the H₂N—OH (61.3 Kcal/mol) so correlations based on weakest bond breakage as a way to
predict reactivity can not be applied to the HA system. The higher dependence of HS decomposition rate on concentration represented by a reaction order of two may be due to the presence of two hydroxylamine free base molecules in each hydroxylamine sulfate molecule.

Table 9.5
Comparison of kinetic parameters for various members of the hydroxylamine family

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$ Kcal/mol</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>28.5</td>
<td>1</td>
</tr>
<tr>
<td>HH</td>
<td>25</td>
<td>0.5</td>
</tr>
<tr>
<td>HS</td>
<td>43</td>
<td>2</td>
</tr>
<tr>
<td>HOSA</td>
<td>31</td>
<td>0.7</td>
</tr>
</tbody>
</table>

6. Comparison of the analytical results

Gas phase analyses were performed only in HA and HH samples, and the results are presented in Table 9.6. As expected, the HH sample produced more hydrogen. The concentration of nitrogen in the gas phase remained almost the same for HA and HH, but the $N_2O$ concentration was lower in the HH sample. The HH sample produced oxygen that was not measured in the HA decomposition gaseous products.
Table 9.6
Gas phase analysis for HA and HH

<table>
<thead>
<tr>
<th>Sample</th>
<th>N₂ mol %</th>
<th>NO mol %</th>
<th>O₂ mol %</th>
<th>N₂O mol %</th>
<th>H₂ mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>70</td>
<td>4</td>
<td>-</td>
<td>24</td>
<td>2</td>
</tr>
<tr>
<td>HH</td>
<td>64.8</td>
<td>0.9</td>
<td>16.8</td>
<td>8.5</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 9.7 presents the results for the analysis of the liquid phase residues for the various hydroxylamine derivatives. As shown in the table, all of them produced ammonia. HA and HH had a higher ammonia mass% than that of HS and HOSA. For HA the unaccounted for mass% was only 2.8 but for HH and HOSA it was over 20 mass%.

Table 9.7
Comparison of liquid phase analysis for various hydroxylamine solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ammonia Mass %</th>
<th>Water Mass %</th>
<th>Unaccounted Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA</td>
<td>7.9</td>
<td>92.3</td>
<td>2.8</td>
</tr>
<tr>
<td>HH</td>
<td>4.1</td>
<td>72.4</td>
<td>23.5</td>
</tr>
<tr>
<td>HS</td>
<td>1.8</td>
<td>82</td>
<td>16.2</td>
</tr>
<tr>
<td>HOSA</td>
<td>1.9</td>
<td>59</td>
<td>39.1</td>
</tr>
</tbody>
</table>
CHAPTER X
CONCLUSIONS

In glass cells, HA decomposes exothermically with an onset temperature of ~117 °C. The overall decomposition reaction was modeled with first order kinetics with an activation energy of 28.5 ± 2 Kcal/mol. In the thermal decomposition of HA solutions under runaway conditions, $T_{on}$, $T_{max}$, $\Delta P_{max}$, non-condensable pressure, $t_{MR}$, $E_a$, and reaction order were observed not to be significantly affected by the presence of air above the sample. Therefore, the detected oxidation products (NO, N$_2$O) are formed primarily by oxygen available within the hydroxylamine molecule. Similar heat rates and pressure rates were measured under air and vacuum conditions. This result suggests that an attempt to pacify HA runaway reactions by handling hydroxylamine under oxygen free atmospheres will not result in milder decomposition reactions.

During a HA runaway or process upset, the integrity of glass lined equipment may be compromised, since, as shown by our results, glass may dissolve. Another important process safety-related result is that the heat produced by the runaway reaction vaporized a solvent with a large heat of vaporization that tempered the reaction. If hydroxylamine is used in another solvent with a lower heat of vaporization, the temperature and pressure increase will be higher.
The HA runaway reaction can be classified as a hybrid system, since the pressure at the maximum temperatures is generated mostly by the vapor pressure of water with some noncondensable gas products. Stability tests for the industrial sample (HA with stabilizers) show that at 100 °C the decomposition reaction generates ~ 0.4 psi/hr of vapor. Approximately 0.426 moles of noncondensable gas per mol of pure hydroxylamine are produced during the runaway reaction. The detected gas phase HA decomposition products under runaway conditions for samples run with and without air were, approximately, 70 mol% N₂, 24 mol % N₂O, 4 mol % NO, and 2 mol % H₂. Ammonia was detected in the liquid residue.

Based on the quantitative analysis of the gas phase decomposition products, the following overall decomposition reaction was determined:

$$31.4 \text{NH}_2\text{OH}_{\text{aq}} \rightarrow 122 \text{NH}_3\text{gas} + 7 \text{N}_2\text{gas} + 2.4 \text{N}_2\text{O}_{\text{gas}} + 0.4 \text{NO}_{\text{gas}} + 28.6 \text{H}_2\text{O}_{\text{gas}} + 0.2 \text{H}_2\text{gas}$$

This reaction gives a theoretical heat of reaction of −29.6 Kcal/mol, which is consistent with the −28 Kcal/mol estimated in this work.

The HA decomposition reaction is enhanced by metals. Inconel with a surface to sample volume ratio of 0.0015 mm⁻¹ reduced the onset temperature of the industrial HA (with stabilizers) by 11°C, and a carbon steel nail with a 0.022 mm⁻¹ surface to sample
volume ratio increased the self-heat rate of HA with stabilizers by a factor of ~ 15. In both SS and Ti sample cells, the maximum self-heat rate of the HA with stabilizers was lowered by a factor of ~ 8 compared to the HA without stabilizers. Silica coating did not pacify metal surfaces, and in all the tested metal cells, uncoated and coated with silica, the onset temperatures were less than 50 °C for each of HA with and without stabilizers. Most of the exothermic activity for the sample sizes employed was below 200 °C, but HA without stabilizers in a Ti-Sa cell exhibited a second major exotherm above 200 °C with a maximum self-heat rate of 79 °C/min. These results demonstrate that HA decomposition in air and in contact with metal surfaces, uncoated or coated with silica, is a complex reacting system, and the decomposition products depend on the participating surfaces.

If HA is in contact with iron ion (Fe^{3+} or Fe^{2+}), even in concentrations as small as 197 ppm and at ambient temperatures, it will react violently to produce a bubbling system with very little vapor-liquid disengagement. A great amount of energy will be released in a very short period of time, which will result in boiling of the reaction mass. Rust will catalyze the reaction heterogeneously, but the reaction is not as violent as with homogeneous catalysis by iron, where even 10 ppm of iron ion will trigger the complete adiabatic decomposition of hydroxylamine.
The homogeneous catalysis of HA takes place in two well-defined exothermic reactions, with the first one more aggressive than the second one. The decomposition products of HA are affected by the iron ion presence, which increases the relative amount of N₂O produced.

The HH and HH-ind decomposition reaction, which is represented approximately by 0.5 order power law kinetics, proceeds at low rates at temperatures near ambient. This reaction is exothermic with energy releases corresponding to a heating rate (for sample plus cell) of 0.1 °C/min near 145 °C. The HH decomposition products are extremely corrosive at temperatures above 100 °C, and approximately 0.496 mol of noncondensable gas per mol of hydroxylamine hydrochloride are produced. One possible corrosive decomposition product is hydrochloric acid, which at room temperature is very soluble in water. The solubility characteristics of HCl explain the corrosive nature of the decomposition products at elevated temperatures and also why HCl was not detected in the gas phase decomposition products, which are mainly 64.8 mol% N₂ and 16.8 mol% O₂ with 8.5 mol% N₂O, 9 mol% H₂ and a trace amount, 0.9 mol%, of NO. The liquid phase residue contains 4.1 mass% ammonia and 72.4 mass% water. The rest of the liquid phase is probably HCl.

The decomposition reaction of HH is catalyzed by stainless steel, carbon steel, and to a lesser extent, by Ti metal. One industrial concern should be the integrity of metal equipment in the event of a runaway due to the extremely corrosive nature of the
decomposition products. It is probable that part of the exotherm during these experiments was due to the reaction between HCl and SS, which produces H₂ and FeCl₃. FeCl₃ is then a probable identity for the black solid residue in the SS experiment.

HS has a mild exothermic decomposition reaction beginning at 150 °C. SS and Ti metals do not catalyze the decomposition reaction in a significant fashion. The decomposition reaction generates around 0.789 moles of noncondensable gas per initial mol of hydroxylamine sulfate. The hydroxylamine sulfate solid is stable at temperatures below 100 °C, and at 144 °C, the onset of a violent decomposition reaction was detected where pressure generation rates close to 5,500 psi/min were measured before the cell ruptured and turned into finely divided pieces of glass.

HOSA has a complex overall thermal decomposition reaction, which presents two separate exothermic activities, the first one more aggressive than the second with an approximate self heat rate of 1.4 °C/min. The moles of noncondensable products generated per mol of hydroxylamine-o-sulfonic acid are approximately 0.468. The decomposition of the pure solid hydroxylamine-o-sulfuric acid is mild, presenting an onset temperature of around 71 °C and a maximum heat rate of 10 °C/min. Ti and specially SS catalyze the first exothermic behavior, and HOSA will react exothermically with carbon steel upon contact, even at room temperature.
A comparison of the thermal decomposition behavior of the members of the hydroxylamine family reveals that the greatest heat and pressure risk is posed by HA. Also HA is the member of the family that is catalyzed more readily by metals even by Ti, which is normally considered to be an inert material.

Prior to the accident that destroyed the Concept Sciences plant, the final step in their routine production of HA from hydroxylamine sulfate was vacuum distillation at 50 °C, which is well below the temperatures for significant decomposition rates of HA in glass cells reported in this work. The presence of metal contaminants or significantly higher temperatures, however, can lead to greatly increased decomposition rates. Decomposition or reaction rate data and the effect of catalysts are essential for safe design, storage, use, and handling of potentially hazardous chemicals. Therefore, the availability of information such as described in this work, use of the information in industrial procedures, and training of plant personnel can help to promote the design of safe and economic processes employing these chemicals.
REFERENCES


[94] Interpretation of the infrared spectra of the solid hydroxylammonium halides. The Journal of Chemical Physics 30 (1959) 1124-1130.


[117] Karl Wieghardt, Gabriele Backes-Dahmann, Wolfgang Swiridoff, Johannes Weiss, Reaction between hydroxylamine and molybdate (VI): preparation of the complexes $[\text{Mo(NO)(CN)}_3]^2^-$, $[\text{Mo(NO)(H}_2\text{NO)}_\text{Cl}_4]^2^-$, and $[\text{Mo(NO)(H}_2\text{NO)}(\text{N}_3)_\text{4}]^2^-$, crystal structure of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Mo(NO)}(\text{H}_2\text{NO})(\text{N}_3)_\text{4}]^*\text{H}_2\text{O}$, Inorganic Chemistry, 22 (1983) 1221-1224.


## APPENDIX A

### PROPERTIES OF HYDROXYLAMINE

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical appearance</td>
<td>White-colorless</td>
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</tr>
<tr>
<td></td>
<td>Odor less</td>
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</tr>
<tr>
<td></td>
<td>Solid crystals</td>
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<tr>
<td>Melting Point</td>
<td>33.05 °C</td>
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<tr>
<td></td>
<td>32.05 °C</td>
<td>[123]</td>
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<tr>
<td>Boiling Point</td>
<td>56-57 °C @ 22 mm Hg</td>
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<tr>
<td></td>
<td>70 °C @ 60 mm Hg</td>
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<tr>
<td></td>
<td>142 °C @ 760 mm Hg (extrapolated)</td>
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<tr>
<td>Vapor pressure</td>
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<tr>
<td></td>
<td>5.3 mm Hg @ 32 °C</td>
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</tr>
<tr>
<td></td>
<td>10 mm Hg @ 47.2 °C</td>
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</tr>
<tr>
<td></td>
<td>40 mm Hg @ 64.6 °C</td>
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</tr>
<tr>
<td></td>
<td>100 mm Hg @ 77.5 °C</td>
<td>[123]</td>
</tr>
<tr>
<td></td>
<td>400 mm Hg @ 99.2 °C</td>
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</tr>
<tr>
<td>Density of solid</td>
<td>1.2255 g/ml @ 0 °C</td>
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</tr>
<tr>
<td>Density of liquid</td>
<td>1.204 g/ml @ 33 °C</td>
<td>[123]</td>
</tr>
<tr>
<td></td>
<td>1.2255 gr/ml @ 0 °C</td>
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<tr>
<td>Specific gravity of vapor</td>
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<td>(calculated)</td>
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<tr>
<td>Heat of formation, solid</td>
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<td>Free energy of formation</td>
<td>-5.6 kcal/mol @ 25 °C</td>
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<tr>
<td>Heat of fusion</td>
<td>3.94 kcal/mol @ 32.05 °C</td>
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<td>Property</td>
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<tr>
<td>Heat of sublimation</td>
<td>15.34 kcal/mol @ 0 and 32 °C</td>
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<td>Heat of solution</td>
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<td>Heat of hydrolysis</td>
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<td>Heat of vaporization</td>
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<td>Entropy for gas, calculated</td>
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<tr>
<td>PKβ</td>
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<td>Flash point</td>
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<td>Refractive index of isotropic phase</td>
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<td>Heat of formation liquid</td>
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<td>-21.7 Kcal/mol</td>
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<tr>
<td>Heat of formation gas</td>
<td>-10.2 Kcal/mol</td>
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</table>
VITA

Lizbeth Olivia Cisneros Treviño was born in Mexico in 1973. She received her Bachelor of Science degree in chemical engineering from the Instituto Tecnologico y de Estudios Superiores de Monterrey (ITESM), Mexico, in 1994. She worked for 2.5 years before obtaining a Fulbright scholarship to pursue her Ph.D. in chemical engineering at Texas A&M University. Her permanent address is Saltillo 916 Col. Chapultepec, San Nicolas de los Garza, N.L., Mexico.