CONTRACTOR REPORT ARLCD-CR-79017

CALORIMETRY STUDIES OF AMMONIA, NITRIC ACID, AND AMMONIUM NITRATE

R. T. REWICK
B. J. GIKIS

SRI INTERNATIONAL
MENLO PARK, CA

I. WEISMAN
PROJECT LEADER, ARRADCOM

OCTOBER 1979

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
LARGE CALIBER WEAPON SYSTEMS LABORATORY
DOVER, NEW JERSEY

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED.
The views, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

Destroy this report when no longer needed. Do not return it to the originator.

The citation in this report of the names of commercial firms or commercially available products or services does not constitute official endorsement or approval of such commercial firms, products, or services by the United States Government.
**Title:** Calorimetry Studies of Ammonia, Nitric Acid, and Ammonium Nitrate

**Authors:** R. T. Rewick, B. J. Sikis, I. Weisman

**Performing Organization:** SRI International

**Contractor Report Number:** ARLCD-CR-79017

**Type of Report & Period Covered:** Final Report

**Program Element, Project, Task Area & Work Unit Numbers:** "X" Facility Project No. 5762528

**Report Date:** OCT 79

**Distribution Statement:** Approved for public release; distribution unlimited.

**Key Words:** Calorimetry, Heat of reaction, Ammonium nitrate, Heat capacity, Nitric acid, Heat of solution, Ammonia, Manufacturing Technology Division (DRDAR-LCM-PE)

**Abstract:** Based on calorimetry studies, basic thermochemical data were obtained for the design of the nitric acid-ammonium nitrate reaction process to be used for the RDX/HMX Facility.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Experimental Details</td>
<td>1</td>
</tr>
<tr>
<td>The Calorimeter</td>
<td>1</td>
</tr>
<tr>
<td>Reagents</td>
<td>2</td>
</tr>
<tr>
<td>The Heat of Reaction of $\text{NH}_3(\ell)$ and $\text{HNO}_3(\ell)$</td>
<td>2</td>
</tr>
<tr>
<td>The Heat of Dilution of $\text{HNO}_3/\text{NH}_4\text{NO}_3$ (56.4/42.6 wt %)</td>
<td>9</td>
</tr>
<tr>
<td>The Heat of Reaction of $\text{NH}_3(\ell)$ with a Dilute Mix</td>
<td>16</td>
</tr>
<tr>
<td>Heat Capacity of $\text{HNO}_3/\text{NH}_4\text{NO}_3$ Mix</td>
<td>16</td>
</tr>
<tr>
<td>Conclusions and Action Taken</td>
<td>16</td>
</tr>
<tr>
<td>References</td>
<td>17</td>
</tr>
<tr>
<td>Distribution List</td>
<td>19</td>
</tr>
</tbody>
</table>
TABLES

1 Summary of calorimetric data
2 Thermochemical cycle for calculating heat of reaction between NH₃(ℓ) and HNO₃(ℓ)
3 Heat of dilution of mix
4 Heat of formation of NH₄NO₃ solution
5 Heat capacity of mix at 25.4°C

FIGURES

1 Outside view of calorimeter reaction vessel
2 Inside view of calorimeter reaction vessel
3 Heat of solution of NH₄NO₃(s) in 99.6 wt % HNO₃(ℓ) (run no. 6)
4 Integral heat of solution of NH₄NO₃(s) in 99.6 wt % HNO₃(ℓ) versus molality NH₄NO₃
5 Integral heat of solution of NH₄NO₃(s) in 99.6 wt % HNO₃(s) versus moles HNO₃/mole NH₄NO₃
INTRODUCTION

The Army is contemplating building another facility (in addition to the one at Holston Army Ammunition Plant (HAAP)) to manufacture RDX and HMX and its compositions. One of the processes in this manufacturing operation is the production of ammonium nitrate in a nitric acid solution. The process contemplated for this new facility has enough differences from the present operation at HAAP that the basic thermochemical data of the following reactions are required; as well as the heat capacity of the mix:

\[
\begin{align*}
\text{NH}_3(\ell) + \text{HNO}_3(\ell) & \rightarrow \text{NH}_4\text{NO}_3(s) \\
\text{HNO}_3(\ell) + \text{mix}^1 & \rightarrow \text{mix} \cdot \text{HNO}_3 \\
\text{NH}_3(\ell) + \text{dilute mix}^2 & \rightarrow \text{mix}
\end{align*}
\]

This report describes the calorimetry work and subsequent calculations to obtain these data.

EXPERIMENTAL DETAILS

The Calorimeter

Figures 1 and 2 show photographs of the calorimeter reaction vessel used for this study. The reaction vessel is constructed from Durimet 20, a stainless steel alloy enriched in Cu and Ni. This alloy is reported in Perry's Chemical Engineering Handbook to be highly resistant to corrosion by 100% nitric acid (51 microns per year at 50°C). Special features of the vessel include a propeller-type stirrer, an ampule holder, and an ampule breaker (plunger device designed to break the ampule). After loading, the reactor vessel is sealed, placed in an insulated Dewar flask, and covered with about 2,700 cm\(^3\) of water. Extending through the styrofoam cap of the Dewar flask are the ampule breaker and stirrer connections, a bath stirrer, a calibration heater, and an NBS-calibrated platinum resistance thermometer. Calorimetric measurements were conducted using well-documented procedures (ref 1) that included the application of the NBS heat-leak correction formulas (ref 2). The results of a typical experiment are shown in figure 3.

\[
\begin{align*}
\text{NH}_4\text{NO}_3 \cdot (1.68) \text{HNO}_3 \\
\text{NH}_4\text{NO}_3 \cdot (1.77) \text{HNO}_3
\end{align*}
\]
Reagents

Concentrated ammonium hydroxide (25.67 wt % NH₃) was standardized by potentiometric titration against standard 1 N HCl. For calorimetric measurements, samples were transferred by syringe into weighed 4-cm³ glass ampules that were flame-sealed, reweighed, and mounted in a fixed position in the sample holder.

Ammonium nitrate (99.5% assay, Mallinckrodt Chemical Company) was dried for several hours at 130°C and then transferred to a dry box through an antechamber that was evacuated to less than 50 microns of Hg. Glass ampules containing NH₄NO₃ were filled in the dry box and then flame-sealed under a nitrogen atmosphere. A Karl-Fischer titration of the NH₄NO₃ handled under these conditions showed the presence of less than 0.1% H₂O. An x-ray diffraction pattern of the dried sample was identical to the literature spectrum of NH₄NO₃.

Anhydrous nitric acid was prepared by distillation of 90% HNO₃ from fuming sulfuric acid (oxides of nitrogen were removed before distillation by treatment with urea). Nitric acid samples stored in sealed polyethylene bottles in the dark at -80°C were transferred by pipette to the calorimeter immediately after thawing to room temperature. The HNO₃ content of samples used in the study, determined from potentiometric titration against standard 1 N NaOH, was 99.6 ± 0.2 wt% HNO₃. As a measure of the extent of reaction with the wall of the calorimeter, HNO₃ samples were analyzed following the calorimetric determination. After correction for the HNO₃ consumed during the reaction of interest, the analysis of the final composition varied less than 1% from the calculated final composition. In addition, no Fe or Ni was detected by atomic absorption analysis of the NH₃ in contact with the reaction vessel.

The Heat of Reaction of NH₃(1) and HNO₃(2)

During a meeting on 2 August 1978 with ARRADCOM, Project Manager of Munitions Production Base Modernization and Expansion; US Army Engineer District, Huntsville, Engineering Division; and SRI it was suggested that direct measurement of reaction (1) would be difficult because of problems of safety, temperature control, and accurate measurement associated with handling liquid ammonia. As an alternative approach, it was proposed to measure the following reaction:

\[ \text{NH}_3 \cdot \text{H}_2\text{O}(1) + \text{HNO}_3(2) \rightarrow \text{NH}_4\text{NO}_3 \cdot \text{H}_2\text{O} \cdot \text{HNO}_3 \]  (5)
Figure 1. Outside view of calorimeter reaction vessel.
Figure 2. Inside view of calorimeter reaction vessel.
Figure 3. Heat of solution of NH₄NO₃(s) in 99.6 wt % H₂O₃(l) (run no. 6).
Table 1. Summary of calorimetric data

<table>
<thead>
<tr>
<th>Run</th>
<th>System</th>
<th>Reactant Composition</th>
<th>Moles</th>
<th>Molality</th>
<th>Run temp. (K)</th>
<th>( C_p^* ) (kcal/( \Omega ))</th>
<th>( \Delta T^* ) (( \Omega ))</th>
<th>Total kcal</th>
<th>kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NH(_4)OH/HNO(_3)</td>
<td>{ 0.0525 NH(_3), 0.1438 H(_2)O, 1.194 HNO(_3) }</td>
<td>0.70</td>
<td>1.91</td>
<td>298.32</td>
<td>32.496</td>
<td>0.0691</td>
<td>2.2455</td>
<td>-42.77</td>
</tr>
<tr>
<td>2</td>
<td>NH(_4)OH/HNO(_3)</td>
<td>{ 0.0422 NH(_3), 0.1154 H(_2)O, 1.195 HNO(_3) }</td>
<td>0.56</td>
<td>1.53</td>
<td>298.28</td>
<td>31.518</td>
<td>0.0574</td>
<td>1.8091</td>
<td>-42.87</td>
</tr>
<tr>
<td>3</td>
<td>NH(_4)OH/HNO(_3)</td>
<td>{ 0.0475 NH(_3), 0.1298 H(_2)O, 1.192 HNO(_3) }</td>
<td>0.63</td>
<td>1.73</td>
<td>298.30</td>
<td>31.900</td>
<td>0.0632</td>
<td>2.0161</td>
<td>-42.44</td>
</tr>
<tr>
<td>13</td>
<td>NH(_4)OH/HNO(_3)</td>
<td>{ 0.0521 NH(_3), 0.1510 H(_2)O, 1.195 HNO(_3) }</td>
<td>0.69</td>
<td>2.00</td>
<td>298.33</td>
<td>31.149</td>
<td>0.0696</td>
<td>2.1680</td>
<td>-41.63</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>{ 0.0486 NH(_3), 0.1350 H(_2)O, 1.194 HNO(_3) }</td>
<td>0.65</td>
<td>1.79</td>
<td>298.31</td>
<td>Average</td>
<td>Stand Dev. 0.56</td>
<td>95% Conf. limit ± 0.90</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>H(_2)O/HNO(_3)</td>
<td>{ 0.2834 H(_2)O, 1.193 HNO(_3) }</td>
<td>3.77</td>
<td></td>
<td>298.19</td>
<td>31.580</td>
<td>0.0369</td>
<td>1.1653</td>
<td>-4.11</td>
</tr>
</tbody>
</table>

*See footnote at end of table.*
Table 1. (cont.)

<table>
<thead>
<tr>
<th>Run</th>
<th>System</th>
<th>Reactant Composition</th>
<th>Run temp. (K)</th>
<th>( C_p^* ) (kcal/( \mu ))</th>
<th>( \Delta T^* ) (( \mu ))</th>
<th>Total kcal</th>
<th>kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( H_2O/\text{HNO}_3 ) {0.2082 ( H_2O ), 1.197 \text{HNO}_3}</td>
<td>298.13</td>
<td>34.059</td>
<td>0.0259</td>
<td>0.8821</td>
<td>- 4.24</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>( H_2O/\text{HNO}_3 ) {0.1293 ( H_2O ), 1.189 \text{HNO}_3}</td>
<td>298.08</td>
<td>30.468</td>
<td>0.0118</td>
<td>0.3595</td>
<td>- 2.78</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>( H_2O/\text{HNO}_3 ) {0.09512 ( H_2O ), 0.239 \text{HNO}_3}</td>
<td>298.05</td>
<td>31.430</td>
<td>0.0118</td>
<td>0.3702</td>
<td>- 3.90</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( \text{NH}_4\text{NO}_3/\text{HNO}_3 ) {0.0301 ( \text{NH}_4\text{NO}_3 ), 1.198 \text{HNO}_3}</td>
<td>298.04</td>
<td>32.423</td>
<td>0.0061</td>
<td>0.1978</td>
<td>- 6.58</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( \text{NH}_4\text{NO}_3/\text{HNO}_3 ) {0.0441 ( \text{NH}_4\text{NO}_3 ), 1.196 \text{HNO}_3}</td>
<td>298.05</td>
<td>31.154</td>
<td>0.0084</td>
<td>0.2617</td>
<td>- 5.93</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( \text{NH}_4\text{NO}_3/\text{HNO}_3 ) {0.0378 ( \text{NH}_4\text{NO}_3 ), 1.196 \text{HNO}_3}</td>
<td>298.02</td>
<td>30.710</td>
<td>0.0073</td>
<td>0.2242</td>
<td>- 5.93</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>( \text{NH}_4\text{NO}_3/\text{HNO}_3 ) {0.0469 ( \text{NH}_4\text{NO}_3 ), 0.478 \text{HNO}_3}</td>
<td>298.02</td>
<td>28.991</td>
<td>0.0088</td>
<td>0.2551</td>
<td>- 5.44</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( \text{NH}_4\text{NO}_3/\text{HNO}_3 ) {0.0748 ( \text{NH}_4\text{NO}_3 ), 0.239 \text{HNO}_3}</td>
<td>298.02</td>
<td>31.982</td>
<td>0.0074</td>
<td>0.2367</td>
<td>- 3.16</td>
<td></td>
</tr>
</tbody>
</table>

*See footnote at end of table.
Table 1. (cont.)

<table>
<thead>
<tr>
<th>Run</th>
<th>System</th>
<th>Reactant Composition</th>
<th>Moles</th>
<th>Molality</th>
<th>Run temp (K)</th>
<th>( C_p^* ) (kcal/Ω)</th>
<th>( \Delta T^* ) (Ω)</th>
<th>Total kcal</th>
<th>kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>( \text{NH}_4\text{NO}_3/\text{H}_2\text{O}/\text{HNO}_3 )</td>
<td>( { \begin{array}{l} 0.0199 \text{ NH}_4\text{NO}_3 \ 0.64 \ 0.0555 \text{ H}_2\text{O} \ 1.78 \ 0.478 \text{ HNO}_3 \ - \end{array} )</td>
<td>298.04</td>
<td>30.756</td>
<td>0.0039</td>
<td>0.1199</td>
<td>-6.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>( \text{NH}_4\text{NO}_3/\text{HNO}_3 )</td>
<td>( { \begin{array}{l} 0.0500 \text{ NH}_4\text{NO}_3 \ 1.31 \ 0.239 \text{ HNO}_3 \ - \end{array} )</td>
<td>298.01</td>
<td>30.522</td>
<td>0.0070</td>
<td>0.2137</td>
<td>-4.28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>( \text{NH}_4\text{NO}_3/\text{HNO}_3 )</td>
<td>( { \begin{array}{l} 0.1427 \text{ NH}_4\text{NO}_3 \ 9.44 \ 0.239 \text{ HNO}_3 \ - \end{array} )</td>
<td>298.00</td>
<td>30.908</td>
<td>0.0077</td>
<td>0.2190</td>
<td>-1.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*As measured by NBS-calibrated Leeds and Northrup Pt resistance thermometer, S/N 1597230, \( 1 \Omega = 9.917^\circ \text{C} \).
To obtain the desired heat of reaction (ΔHR) of (1), the measured value for (5) was combined with the ΔHR for the following reactions:

\[
\begin{align*}
\text{NH}_3(\ell) + H_2O(\ell) & \rightarrow \text{NH}_3\cdot H_2O \quad (6) \\
H_2O(\ell) + HNO_3(\ell) & \rightarrow H_2O\cdot HNO_3 \quad (7) \\
\text{NH}_4NO_3(s) + H_2O\cdot HNO_3 & \rightarrow \text{NH}_4NO_3\cdot H_2O\cdot HNO_3 \quad (8)
\end{align*}
\]

Since heats of reaction vary with concentration, it is important to apply ΔHR values for reactions (6) through (8) that are measured or calculated at compatible concentrations with (5). For reaction (6), ΔHR298 is calculated from literature values (ref 3) to be -3.00 kcal/mole. Similar information for reactions (7) and (8) is either not available or is in concentration ranges that cannot be accurately extrapolated to required laboratory conditions. Therefore, ΔHR was measured for (7) and (8) at the required concentrations for use with (5) and (6) to obtain (1). These reactions are summarized in table 2. Using calculated or measured ΔHR values for reactions (5) through (8) and Hess' law of constant heat summation, ΔHR of reaction (1) was calculated to be -31.755 kcal/mole.

The reliability of the data can be assessed from replicate values obtained for reaction (5). As shown in table 1, the 95% confidence limit of the average value (-42.43 kcal/mole) is ± 0.90 kcal/mole. It is estimated that the error introduced from the water (less than 0.02 mole) contained in the 99.6 wt % HNO3 used in these measurements is less than 0.5 kcal/mole.

The Heat of Dilution of HNO3/NH₄NO₃ (56.4/42.6 wt %)

To the best of the investigators' knowledge, the heat of solution of NH₄NO₃(s) in 99.6 wt % HNO (ℓ) has not been previously reported. The observed exothermic heat of solution is of theoretical interest since the solution of most crystalline materials involves the adsorption of heat. The data appear to fit a straight line on a semilog plot (fig 4), which permits an accurate interpolation between concentrations. In another presentation of the results, the heat of solution per mole of HNO3(ℓ) is given in figure 5, and the heat of solution at infinite dilution approaches a value of -6.5 kcal/mole NH₄NO₃.

The heat of dilution of the HNO₃/NH₄NO₃ mix is calculated from the thermochemical cycle shown in table 3. The results (-1.38 kcal/mole HNO3 (298 K) can also be derived directly from data for the heat
Table 2. Thermochemical cycle for calculating heat of reaction between NH₃(φ) and HNO₃(φ)

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>$\Delta H_r$ (kcal)</th>
<th>Run</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$(0.049)\text{NH}_3 \cdot (0.135)\text{H}_2\text{O} + (1.194)\text{HNO}_3 \rightarrow (0.049)\text{NH}_4\text{NO}_3 \cdot (0.135)\text{H}_2\text{O} \cdot (1.145)\text{HNO}_3$</td>
<td>$-42.43(0.049) = 2.079$</td>
<td>$1, 2, 3, 13$</td>
</tr>
<tr>
<td>2.</td>
<td>$(0.049)\text{NH}_4\text{NO}_3 \cdot (0.135)\text{H}_2\text{O} \cdot (1.145)\text{HNO}_3 \rightarrow (0.049)\text{NH}_4\text{NO}_3 + (0.135)\text{H}_2\text{O} \cdot (1.145)\text{HNO}_3$</td>
<td>$+6.03(0.049) = +0.295$</td>
<td>$14$</td>
</tr>
<tr>
<td>3.</td>
<td>$(0.135)\text{H}_2\text{O} \cdot (1.145)\text{HNO}_3 \rightarrow (0.135)\text{H}_2\text{O} + (1.145)\text{HNO}_3$</td>
<td>$+2.78(0.135) = +0.375$</td>
<td>$9$</td>
</tr>
<tr>
<td>4.</td>
<td>$(0.049)\text{NH}_3 + (0.135)\text{H}_2\text{O} \rightarrow (0.049)\text{NH}_3 \cdot (0.135)\text{H}_2\text{O}$</td>
<td>$-3(0.049) = -0.147$ (ref 3)</td>
<td></td>
</tr>
</tbody>
</table>

**SUMMING:** \[(1.194)\text{HNO}_3 + (0.049)\text{NH}_3 \rightarrow (0.049)\text{NH}_4\text{NO}_3 + (1.145)\text{HNO}_3\]

**SIMPLIFYING:** \[(0.049)\text{HNO}_3 + (0.049)\text{NH}_3 \rightarrow (0.049)\text{NH}_4\text{NO}_3\]

**OR**

\[\text{HNO}_3(φ) + \text{NH}_3(φ) \rightarrow \text{NH}_4\text{NO}_3(φ)\]

$-1.556 \ (-31.755 \ \text{kcal/mole})$
Figure 4. Integral heat of solution of NH₄NO₃(s) in 99.6 wt % HNO₃(ℓ) versus molality NH₄NO₃.
Figure 5. Integral heat of solution of NH₄NO₃(s) in 99.6 wt % HNO₃(s) versus moles HNO₃/mole NH₄NO₃.


Table 3. Heat of dilution of mix

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Molality NH₄NO₃ (kcal)</th>
<th>∆Hₚ (kcal) (from fig 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄NO₃.(1.68)HNO₃ → NH₄NO₃ + (1.68)HNO₃</td>
<td>(9.45)</td>
<td>+1.68</td>
</tr>
<tr>
<td>NH₄NO₃ + (1.77)HNO₃ → NH₄NO₃.(1.77)HNO₃</td>
<td>(8.97)</td>
<td>-1.80</td>
</tr>
<tr>
<td>Sol A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄NO₃.(1.68)HNO₃ + (0.087)HNO₃ → NH₄NO₃.(1.77)HNO₃</td>
<td></td>
<td>-0.12 b kcal/mole NH₄NO₃</td>
</tr>
<tr>
<td>(11.49)NH₄NO₃.(19.31)HNO₃ + HNO₃ → (11.49)NH₄NO₃.(20.31)HNO₃</td>
<td></td>
<td>-1.38 kcal/mole HNO₃</td>
</tr>
</tbody>
</table>

a1,000 parts mix + 29.51 parts HNO₃.
bΔHₚ = ΔHᵢ Sol B - ΔHᵢ Sol A = -1.80 - (-1.68) = -0.12 (fig 4)

*1000 parts mix + 29.51 parts HNO₃.
Table 4. Heat of formation of NH₄NO₃ solution

Heat of reaction of NH₃(ℓ) with dilute mix

<table>
<thead>
<tr>
<th>System</th>
<th>Step</th>
<th>ΔH bulk NH₄NO₃</th>
<th>ΔH for reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃ + HNO₃ → NH₄NO₃</td>
<td>1</td>
<td>-31.755</td>
<td>-31.755</td>
</tr>
<tr>
<td>(31.8)NH₄NO₃ + (53.48)HNO₃ → (31.8)NH₄NO₃ . (53.48)HNO₃</td>
<td>2</td>
<td>-1.68</td>
<td>-53.424 (^a)</td>
</tr>
<tr>
<td>(54.48)HNO₃ . (30.8)NH₄NO₃ → (54.48)HNO₃ + (30.8)NH₄NO₃</td>
<td>3</td>
<td>1.8</td>
<td>+55.440 (^b)</td>
</tr>
</tbody>
</table>

Overall reaction (sum 1 + 2 + 3)

NH₃ + (54.48) HNO₃ . (30.8) NH₄NO₃ → (31.8) NH₄NO₃ . (53.48) HNO₃

The same value can be calculated from the final equation using the relationship:

\[ ΔH_{\text{R}} = ΔH_{\text{R Step 1}} + ΔH_{\text{R (mix formation)}} × (31.8) - ΔH (\text{dilute mix formation}) × (30.8). \]

\(^a\) Product of (-1.68) (31.8)

\(^b\) Product of (1.8) (30.8)
Table 5. Heat capacity of r ix* at 25.4°C

<table>
<thead>
<tr>
<th>C_p system (heat/°C)</th>
<th>ΔC_p</th>
<th>C_p mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>+ mix</td>
<td>ΔC_p</td>
</tr>
<tr>
<td>3.057</td>
<td>3.120</td>
<td>0.063</td>
</tr>
</tbody>
</table>

*133.30 g, 43.6 wt % NH₄NO₃/56.2 wt % HNO₃/0.2 wt % H₂O
of solution of \( \text{NH}_4\text{NO}_3(s) \) in \( \text{HNO}_3(x) \). This calculation involves the difference in the heats of formation of \( \text{NH}_4\text{NO}_3 \) dissolved in \( \text{HNO}_3 \) (fig 4) of the product and the reactant compositions. The importance of this approach is that the heat of dilution or concentration of an \( \text{HNO}_3/\text{NH}_4\text{NO}_3 \) mix over the composition range studied can be calculated directly from figure 4 without recording the separate steps involved. The cycle in table 3 represents the point in the nitric acid-ammonium nitrate reaction process where the nitric acid is added.

The Heat of Reaction of \( \text{NH}_3(x) \) with a Dilute Mix

The heat of reaction of \( \text{NH}_3(x) \) with a dilute mix (molality = 8.97) to generate the normal mix (molality = 9.45) is calculated from the thermochemical cycle shown in table 4. The result (-29.74 kcal/mole) is obtained by first adding the heat of reaction for the formation of \( \text{NH}_4\text{NO}_3 \) obtained in table 2 to the heat of dilution of \( \text{NH}_4\text{NO}_3 \) in nitric acid to obtain the normal mix composition. These are represented by steps 1 and 2 in table 4. Finally, the heat of dilution of ammonium nitrate in nitric acid to obtain the dilute mix must be added as in step 3. Figure 4 is used to obtain the required heats for steps 2 and 3 on a mole of \( \text{NH}_4\text{NO}_3 \) basis. These heats are then multiplied by the number of moles of \( \text{NH}_4\text{NO}_3 \) involved as shown in the chemical equations of steps 2 and 3. The algebraic sum of the respective heats gives the overall heat of reaction, and the chemical sum of equations 1, 2, and 3 gives the overall reaction involved. This reaction will take place in the reactor generating \( \text{NH}_4\text{NO}_3 \) in the production facility.

Heat Capacity of \( \text{HNO}_3/\text{NH}_4\text{NO}_3 \) Mix

The heat capacity of an \( \text{HNO}_3/\text{NH}_4\text{NO}_3 \) mix (56.4 Wt % \( \text{HNO}_3 \)/43.6 Wt % \( \text{NH}_4\text{NO}_3 \)) was determined experimentally from the difference in heat capacity of the empty reaction vessel and the vessel containing a weighed quantity of the mix. The result of 0.45 cal/g/^\circ C at 25^\circ C (table 5) is close to that expected for the \( \text{HNO}_3/\text{NH}_4\text{NO}_3 \) system, since both components have reported equal heat capacities of about 0.4 cal/g/^\circ C.

CONCLUSIONS AND ACTION TAKEN

The following heat of reaction data pertinent to the design of a nitric acid-ammonium nitrate reaction process for the RDX/HMX facility were obtained:

1. \[
\text{NH}_3(x) + (54.48)\text{HNO}_3 \cdot (30.8)\text{NH}_4\text{NO}_3 \rightarrow (53.48)\text{HNO}_3 \cdot (31.8)\text{NH}_4\text{NO}_3 \Delta H = -29.74 \text{ kcal/g-mol}
\]
2. \[(11.49)\text{NH}_4\text{NO}_3\cdot(19.31)\text{HNO}_3 + \text{HNO}_3 \rightarrow (11.49)\text{NH}_4\text{NO}_3\cdot(20.31)\text{HNO}_3\] \[\Delta H = -1.38 \text{ kcal/g-mol}\]

Also obtained was the heat capacity of the mixture:

43.6 wt % NH\(_4\)NO\(_3\)

56.2 wt % HNO\(_3\)

0.2 wt % H\(_2\)O

0.47 cal/g/°C

These data were forwarded to the U. S. Army Engineer District, Huntsville, Alabama, for their design of the NA/AN process to be used in the manufacture of RDX/HMX.

REFERENCES


DISTRIBUTION LIST

Commander
US Army Armament Research and Development Command
ATTN: DRDAR-LCM-PE (4)
     DRDAR-LCM-P
     DRDAR-LCM-E (2)
Dover, NJ 07801

Project Manager for Munition Production
Base Modernization and Expansion
US Army Materiel Development and Readiness Command
ATTN: DRCPM-PBM-EE (4)
Dover, NJ 07801

US Army Engineer District, Huntsville
ATTN: Engineering Division, HNDED-ME (3)
     HNDED-PM (2)
P.O. Box 1600 West Station
Huntsville, AL 35807

Commander
Holston Army Ammunition Plant
ATTN: SARHO-E (3)
Kingsport, TN 37662

Director
US Army Industrial Base Engineering Activity
ATTN: DRXIB-MT (2)
Rock Island, IL 61299

Ralph M. Parsons Company
ATTN: K. Lewis (5)
100 West Walnut Street
Pasadena, CA 91124

SRI International
ATTN: B. Gikis (5)
     R. Rewick (5)
     Dr. D. D. Cubicciotti (3)
333 Ravenswood Avenue
Menlo Park, CA 94025