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CALORIMETRY STUDIES OF AMMONIA, NITRIC ACID, AND AMMONIUM NITRATE

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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 "X" Facility.

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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:

$$NH_3(\ell) + HNO_3(\ell) \longrightarrow NH_4NO_3(s) \qquad (1)$$

$$HNO_3(\ell) + mix^1 \longrightarrow mix \cdot HNO_3 \qquad (2)$$

$$NH_3(\ell) + dilute\ mix^2 \longrightarrow mix \qquad (3)$$

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

[1] $NH_4NO_3 \cdot (1.68)\ HNO_3$

[2] $NH_4NO_3 \cdot (1.77)\ HNO_3$

Reagents

Concentrated ammonium hydroxide (25.67 wt % NH_3) was standardized by potentiometric titration against standard 1 N HCl. For calorimetric measurements, samples were transferred by syringe into weighed 4-cm^3 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 NH_4NO_3 were filled in the dry box and then flame-sealed under a nitrogen atmosphere. A Karl-Fischer titration of the NH_4NO_3 handled under these conditions showed the presence of less than 0.1% H_2O. An x-ray diffraction pattern of the dried sample was identical to the literature spectrum of NH_4NO_3.

Anhydrous nitric acid was prepared by distillation of 90% HNO_3 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 HNO_3 content of samples used in the study, determined from potentiometric titration against standard 1 N NaOH, was 99.6 + 0.2 wt% HNO_3. As a measure of the extent of reaction with the wall of the calorimeter, HNO_3 samples were analyzed following the calorimetric determination. After correction for the HNO_3 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 NHO3 in contact with the reaction vessel.

The Heat of Reaction of $NH_3(\ell)$ and $HNO_3(\ell)$

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:

$$NH_3 \cdot H_2O(\ell) + HNO_3(\ell) \longrightarrow NH_4NO_3 \cdot H_2O \cdot HNO_3 \qquad (5)$$

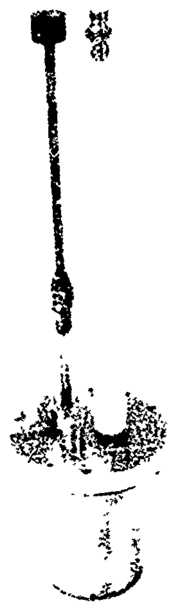

Figure 1. Outside view of calorimeter reaction vessel.

Figure 2. Inside view of calorimeter reaction vessel.

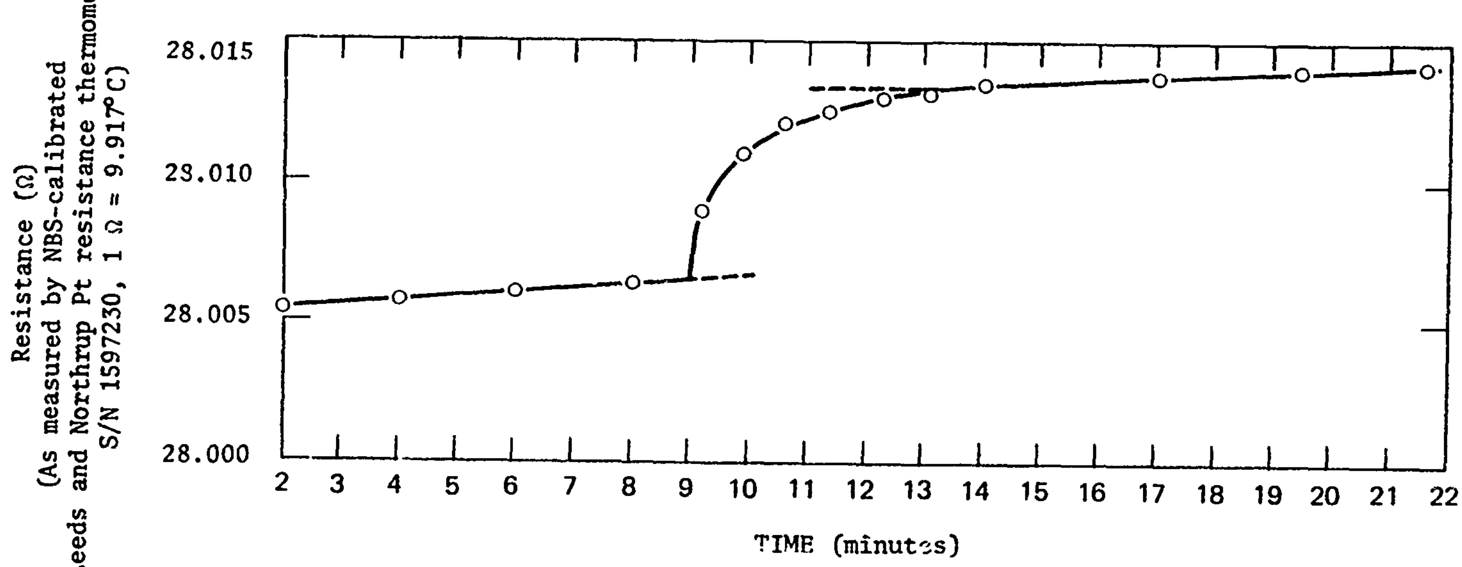

FIGURE 3 HEAT OF SOLUTION OF $NH_4NO_3(s)$ IN 99.6 wt% $HNO_3(\ell)$ (RUN NO. 6)

Figure 3. Heat of solution of $NH_4NO_3(s)$ in 99.6 wt % $HNO_3(\ell)$ (run no. 6).

Table 1. Summary of calorimetric data

Run	System	Reactant Composition: Moles	Reactant Composition: Molality	Run temp. (K)	C_p^* (kcal/ Ω)	ΔT^* (Ω)	Total kcal	kcal/mole
1	NH_4OH/HNO_3	0.0525 NH_3 0.1438 H_2O 1.194 HNO_3	0.70 1.91 -	298.32	32.496	0.0691	2.2455	-42.77
2	NH_4OH/HNO_3	0.0422 NH_3 0.1154 H_2O 1.195 HNO_3	0.56 1.53 -	298.28	31.518	0.0574	1.8091	-42.87
3	NH_4OH/HNO_3	0.0475 NH_3 0.1298 H_2O 1.192 HNO_3	0.63 1.73 -	298.30	31.900	0.0632	2.0161	-42.44
13	NH_4OH/HNO_3	0.0521 NH_3 0.1510 H_2O 1.195 HNO_3	0.69 2.00 -	298.33	31.149	0.0696	2.1680	-41.63
	Average of runs 1, 2, 3, and 13	0.0486 NH_3 0.1350 H_2O 1.194 HNO_3	0.65 1.79 -	298.31		Average Stand Dev. 95% Conf. limit		-42.43 0.56 ± 0.90
4	H_2O/HNO_3	0.2834 H_2O 1.193 HNO_3	3.77 -	298.19	31.580	0.0369	1.1653	- 4.11

*See footnote at end of table.

Table 1. (cont.)

Run	System	Reactant Composition: Moles	Reactant Composition: Molality	Run temp. (K)	C_p^* (kcal/ Ω)	ΔT^* (Ω)	Total kcal	kcal/mole
5	H_2O/HNO_3	0.2082 H_2O 1.197 HNO_3	2.76	298.13	34.059	0.0259	0.8821	- 4.24
9	H_2O/HNO_3	0.1293 H_2O 1.189 HNO_3	1.72	298.08	30.468	0.0118	0.3595	- 2.78
12	H_2O/HNO_3	0.09512 H_2O 0.239 HNO_3	6.32	298.05	31.430	0.0118	0.3709	- 3.90
6	NH_4NO_3/HNO_3	0.0301 NH_4NO_3 1.198 HNO_3	0.40	298.04	32.423	0.0061	0.1978	- 6.58
7	NH_4NO_3/HNO_3	0.0441 NH_4NO_3 1.196 HNO_3	0.59	298.05	31.154	0.0084	0.2617	- 5.93
8	NH_4NO_3/HNO_3	0.0378 NH_4NO_3 1.196 HNO_3	0.50	298.02	30.710	0.0073	0.2242	- 5.93
10	NH_4NO_3/HNO_3	0.0469 NH_4NO_3 0.478 HNO_3	1.56	298.02	28.994	0.0088	0.2551	- 5.44
11	NH_4NO_3/HNO_3	0.0748 NH_4NO_3 0.239 HNO_3	4.97	298.02	31.982	0.0074	0.2367	- 3.16

*See footnote at end of table.

Table 1. (cont.)

Run	System	Reactant Composition: Moles	Molality	Run temp. (K)	C_p^* (kcal/ Ω)	ΔT^* (Ω)	Total kcal	kcal/mole
14	$NH_4NO_3/H_2O/HNO_3$	0.0199 NH_4NO_3 0.0555 H_2O 0.478 HNO_3	0.64 1.78 -	298.04	30.756	0.0039	0.1199	- 6.03
16	NH_4NO_3/HNO_3	0.0500 NH_4NO_3 0.239 HNO_3	3.31	298.01	30.522	0.0070	0.2137	- 4.28
17	NH_4NO_3/HNO_3	0.1427 NH_4NO_3 0.239 HNO_3	9.44	298.00	30.908	0.0077	0.2390	- 1.67

*As measured by NBS-calibrated Leeds and Northrup Pt resistance thermometer, S/N 1597230, 1 Ω = 9.917°C.

To obtain the desired heat of reaction (ΔH_R) of (1), the measured value for (5) was combined with the ΔH_R for the following reactions:

$$NH_3(\ell) + H_2O(\ell) \longrightarrow NH_3 \cdot H_2O \quad (6)$$

$$H_2O(\ell) + HNO_3(\ell) \longrightarrow H_2O \cdot HNO_3 \quad (7)$$

$$NH_4NO_3(s) + H_2O \cdot HNO_3 \longrightarrow NH_4NO_3 \cdot H_2O \cdot HNO_3 \quad (8)$$

Since heats of reaction vary with concentration, it is important to apply ΔH_R values for reactions (6) through (8) that are meassured or calculated at compatible concentrations with (5). For reaction (6), $\Delta H_{R_{298}}$ 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, ΔH_R 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 ΔH_R values for reactions (5) through (8) and Hess' law of constant heat summation, $\Delta H_{R_{298}}$ 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 $\pm$ 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 % HNO_3 used in these measurements is less than 0.5 kcal/mole.

The Heat of Dilution of HNO_3/NH_4NO_3 (56.4/42.6 wt %)

To the best of the investigators' knowledge, the heat of solution of $NH_4NO_3(s)$ 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 $HNO_3(\ell)$ is given in figure 5, and the heat of solution at infinite dilution approaches a value of -6.5 kcal/mole NH_4NO_3.

The heat of dilution of the HNO_3/NH_4NO_3 mix is calculated from the thermochemical cycle shown in table 3. The results (-1.38 kcal/mole HNO_3 (298 K) can also be derived directly from data for the heat

Table 2. Thermochemical cycle for calculating heat of reaction between $NH_3(\ell)$ and $HNO_3(\ell)$

Step	Reaction	ΔH_R (kcal)	Run
1.	$(0.049)NH_3 \cdot (0.135)H_2O + (1.194)HNO_3 \rightarrow (0.049)NH_4NO_3 \cdot (0.135)H_2O \cdot (1.145)HNO_3$	(-42.43)(0.049)=2.079	1,2,3,13
2.	$(0.049)NH_4NO_3 \cdot (0.135)H_2O \cdot (1.145)HNO_3 \rightarrow (0.049)NH_4NO_3 + (0.135)H_2O \cdot (1.145)HNO_3$	(+6.03)(0.049) =+0.295	14
3.	$(0.135)H_2O \cdot (1.145)HNO_3 \rightarrow (0.135)H_2O + (1.145)HNO_3$	(+2.78)(0.135) =+0.375	9
4.	$(0.049)NH_3 + (0.135)H_2O \rightarrow (0.049)NH_3 \cdot (0.135)H_2O$	(-3)(0.049) = -0.147	(ref 3)

SUMMING: $(1.194)HNO_3 + (0.049)NH_3 \rightarrow (.049)NH_4NO_3 + (1.145)HNO_3$

SIMPLIFYING: $(.049)HNO_3 + (.049)NH_3 \rightarrow (.049)NH_4NO_3$ -1.556 (-31.755 kcal/mole)

OR

$HNO_3(\ell) + NH_3(\ell) \rightarrow NH_4NO_3(s)$ -31.755

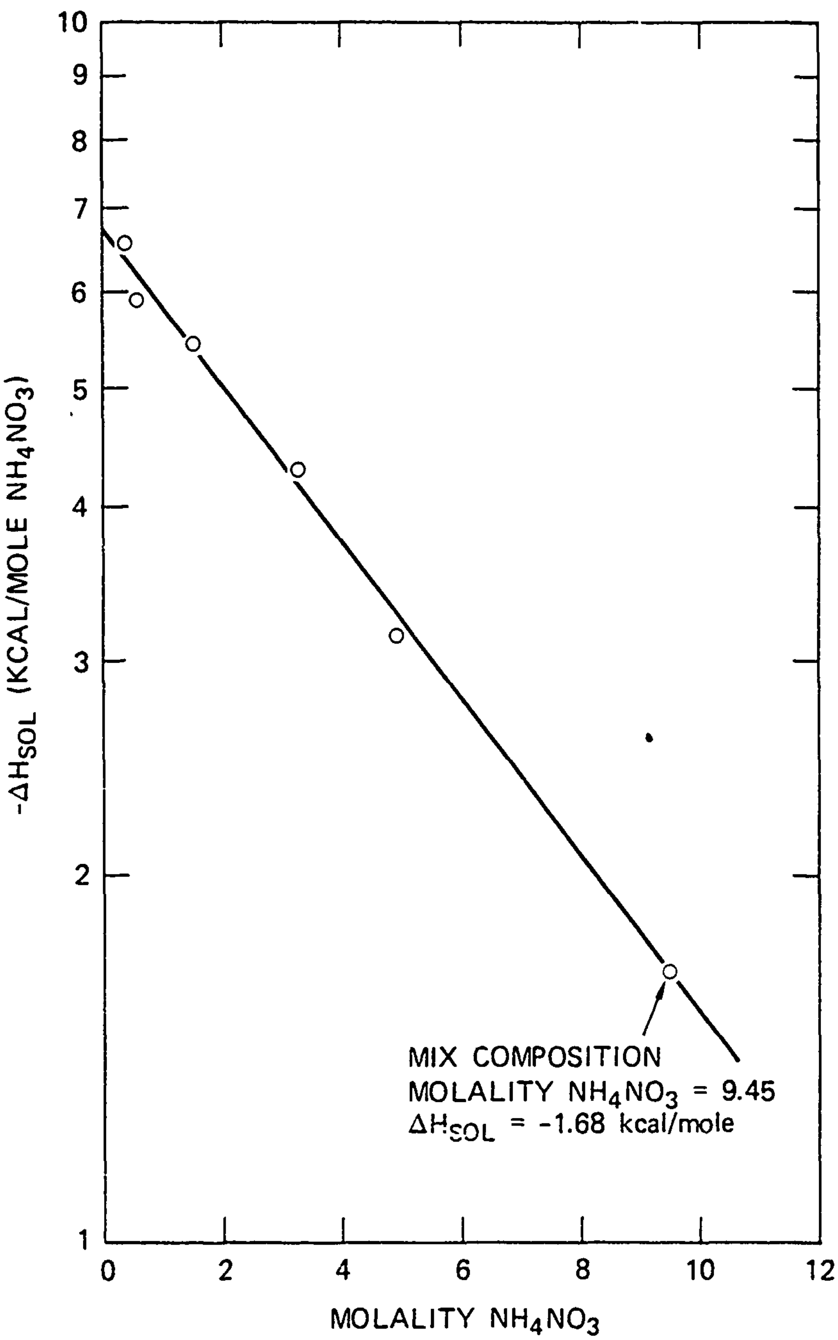

Figure 4. Integral heat of solution of $NH_4NO_3(s)$ in 99.6 wt % $HNO_3(\ell)$ versus molality NH_4NO_3.

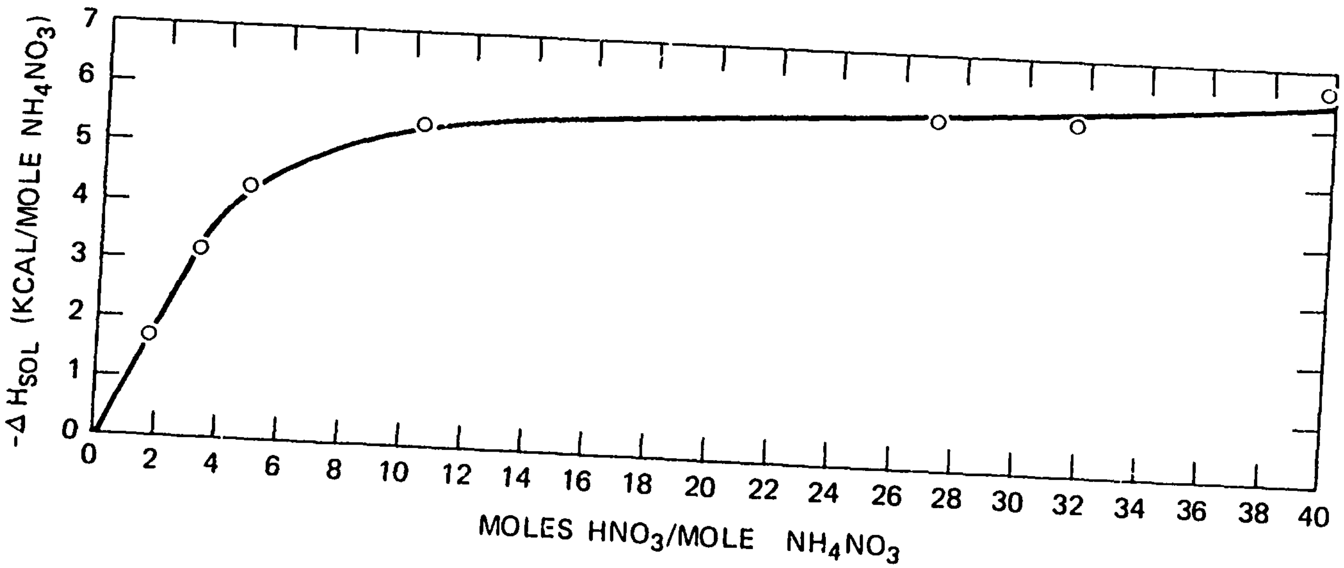

Figure 5. *Integral heat of solution of* $NH_4NO_3(s)$ *in 99.6 wt %* $HNO_3(s)$ *versus moles* HNO_3*/mole* NH_4NO_3.

Table 3. Heat of dilution of mix[a]

Reaction	Molality NH_4NO_3	ΔH_R (kcal) (from fig 4)	
$NH_4NO_3 \cdot (1.68)HNO_3 \rightarrow NH_4NO_3 + (1.68)HNO_3$	(9.45)	+1.68	
$NH_4NO_3 + (1.77)HNO_3 \rightarrow NH_4NO_3 \cdot (1.77)HNO_3$	(8.97)	-1.80	
Sol A $NH_4NO_3 \cdot (1.68)HNO_3 + (0.087)HNO_3 \rightarrow$ Sol B $NH_4NO_3 \cdot (1.77)HNO_3$		-0.12[b]	kcal/mole NH_4NO_3
$(11.49)NH_4NO_3 \cdot (19.31)HNO_3 + HNO_3 \rightarrow (11.49)NH_4NO_3 \cdot (20.31)HNO_3$		-1.38	kcal/mole HNO_3

[a] 1,000 parts mix + 29.51 parts HNO_3.

[b] $\Delta H_R = \Delta H_f$ Sol B - ΔH_f Sol A = -1.80 - (-1.68) = -0.12 (fig 4)

*1000 parts mix + 29.51 parts HNO_3.

Table 4. Heat of formation of NH_4NO_3 solution

Heat of reaction of $NH_3(\ell)$ with dilute mix

System	Step	ΔH_R kcal/mole NH_4NO_3	ΔH_R kcal for reaction
$NH_3 + HNO_3 \rightarrow NH_4NO_3$	1	-31.755	-31.755
$(31.8)NH_4NO_3 + (53.48)HNO_3 \rightarrow (31.8)NH_4NO_3 \cdot (53.48)HNO_3$	2	-1.68	-53.424[a]
$(54.48)HNO_3 \cdot (30.8)NH_4NO_3 \rightarrow (54.48)HNO_3 + (30.8)NH_4NO_3$	3	1.8	+55.440[b]

Overall reaction (sum 1 + 2 + 3)

$NH_3 + (54.48)\ HNO_3 \cdot (30.8)\ NH_4NO_3 \rightarrow (31.8)\ NH_4NO_3 \cdot (53.48)\ HNO_3$	-29.74

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

$\Delta H_R = \Delta H_R$ Step 1 + ΔH_R (mix formation) X (31.8) - ΔH (dilute mix formation) X (30.8).

[a]Product of (-1.68) (31.8)
[b]Product of (1.8) (30.8

Table 5. Heat capacity of mix* at 25.4°C

	C_p system (heat/°C)		C_p mix
Blank	+ mix	ΔC_p	cal/g/°C
3.057	3.120	0.063	0.47

*133.30 g, 43.6 wt % NH_4NO_3/56.2 wt % HNO_3/0.2 wt % H_2O

of solution of $NH_4NO_3(s)$ in $HNO_3(\ell)$. This calculation involves the difference in the heats of formation of NH_4NO_3 dissolved in 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 HNO_3/NH_4NO_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 $NH_3(\ell)$ with a Dilute Mix

The heat of reaction of $NH_3(\ell)$ 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 NH_4NO_3 obtained in table 2 to the heat of dilution of NH_4NO_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 NH_4NO_3 basis. These heats are then multiplied by the number of moles of NH_4NO_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 NH_4NO_3 in the production facility.

Heat Capacity of HNO_3/NH_4NO_3 Mix

The heat capacity of an HNO_3/NH_4NO_3 mix (56.4 Wt % HNO /43.6 wt % NH_4NO_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/°C at 25°C (table 5) is close to that expected for the HNO_3/NH_4NO_3 system, since both components have reported equal heat capacities of about 0.4 cal/g/°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. $$NH_3(\ell) + (54.48)HNO_3\cdot(30.8)NH_4NO_3 \longrightarrow (53.48)HNO_3\cdot(31.8)NH_4NO_3 \quad \Delta H = -29.74\ \frac{\text{kcal}}{\text{gm-mol}}$$

2. $(11.49)NH_4NO_3 \cdot (19.31)HNO_3 + HNO_3 \longrightarrow (11.49)NH_4NO_3 \cdot$

$$(20.31)HNO_3 \quad \Delta H = -1.38 \frac{kcal}{gm\text{-}mol}$$

Also obtained was the heat capacity of the mixture:

43.6 wt % NH_4NO_3

56.2 wt % HNO_3

0.2 wt % H_2O 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.

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