

## Full Paper

## Determination of Urea Nitrate and Guanidine Nitrate Vapor Pressures by Isothermal Thermogravimetry

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## Abstract

Since the bombing of Pan Am Flight 103 over Lockerbie, Scotland in 1988, detection of military explosives has received much attention. Only in the last few years has detection of improvised explosives become a priority. Many detection methods require that the particulate or vapor be available. Elsewhere we have reported the vapor pressures of peroxide explosives triacetone triperoxide (TATP), diacetone diperoxide (DADP), and 2,4,6-trinitrotoluene (TNT). Herein we examine the vapor signatures of the nitrate salts of urea and guanidine (UN and GN, respectively), and compare them to ammonium nitrate (AN) and TATP using an isothermal thermo-gravimetric method. The vapor signatures of the nitrate salts are assumed to be the vapor pressures of the neutral parent base and nitric acid. Studies were performed at elevated temperatures (80–120 °C for UN, 205–225 °C for GN, 100–160 °C for AN, and 40–59 °C for TATP), enthalpies of sublimation calculated and vapor pressures extrapolated to room temperature. Reported vapor pressure values (in Pa) are as follows:

GN	≪ UN	< AN	≪ TATP
$2.66 \times 10^{-18}$	$3.94 \times 10^{-5}$	$5.98 \times 10^{-4}$	24.8

**Keywords:** Ammonium Nitrate, Energetic Salts, Guanidine Nitrate, Urea Nitrate, Vapor Pressure

## 1 Introduction

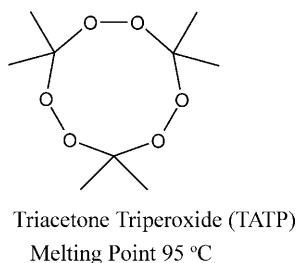
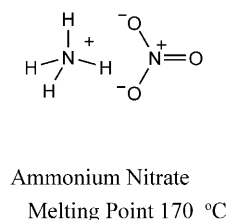
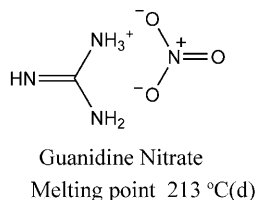
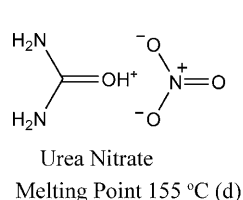
Chemical detection of explosives requires a detection signature produced by vapor or particulates. Vapor pressure is a strong indicator of the potential for detection. For most solids, including most explosives, vapor pressures are exceedingly low at ambient temperature, making direct determinations difficult or impossible. While modern explosive detectors claim to be able to detect vapors directly under ambient conditions they are limited in their ability to quantify the information even under controlled experimental conditions. A widely used laboratory approach to obtain ambient vapor pressures is to take advantage of increased

vapor pressures with elevated temperature. The temperatures and vapor pressures can then be fitted to the Clapeyron equation allowing for extrapolation of vapor pressures at other temperatures. Good linearity for this equation implies that the heat of sublimation is relatively constant over the temperature range. Our laboratory has used this approach to obtain estimates of the ambient vapor pressures of 2,4,6-trinitrotoluene (TNT), triacetone triperoxide (TATP), diacetone diperoxide (DADP), and hexamethylene triperoxide diamine (HMTD) [1, 2]. For these studies detection and quantification of headspace vapors was accomplished using gas chromatography with electron capture detection. Energetic salts, such as urea nitrate (UN) and guanidine nitrate (GN), generate difficult to detect products with such a low volatility that quantification is not possible at ambient temperature. An alternative approach, thermal gravimetric analysis (TGA), was used in this study to obtain sublimation rates at different temperatures, which were correlated to a vapor pressure calibration standard, benzoic acid. The TGA method for determining the vapor pressure is well documented and used extensively for evaluations in the pharmaceutical and cosmetic industries [3–8]. In addition to UN and GN, ambient vapor pressures of ammonium nitrate (AN) and TATP were obtained by the TGA method. The chemical structures of UN, GN, AN, and TATP are given in Figure 1. Comparisons with ambient vapor pressures of AN and TATP, obtained by other methods from the literature, were used to validate the TGA method.

## 2 Experimental Part

UN (98% purity) was purchased from TCI America. GN (reagent grade) was obtained from Fluka Chemika. Reagent grades of benzoic acid and AN were acquired from Fisher Scientific. The reference material, TATP, was synthesized in our laboratory [1]. Mass loss determinations

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**Figure 1.** Structures of UN, GN, AN, and TATP.

were carried out using a TA Instruments Model SDT 2690 thermal gravimetric analyzer (TGA). A constant nitrogen gas purge (80 mL min<sup>-1</sup>) was used during the experiments. Samples were analyzed in open aluminum pans purchased from TA Instruments. AN, UN, and GN samples were kept under vacuum to avoid moisture until used for TGA analysis. The TATP remained at -10 °C until use.

The TGA furnace was heated to a desired temperature and maintained for 10 min with nitrogen purge to flush the furnace space. An empty sample pan was tared in the temperature equilibrated furnace prior to the addition of the sample. The pan was quickly removed and the sample added (3–10 mg depending on the sample) and promptly returned to the furnace to avoid significant temperature change. Runs were done in duplicate or triplicate at the specified temperatures.

The Antoine equation was used to relate vapor pressure to mass loss per time (i.e. µg min<sup>-1</sup>) [9–11]. Benzoic acid, with verified vapor pressures via TGA and other methods,

was used as reference material to calibrate the TGA for vapor pressure determinations of the other samples by isothermal thermogravimetry.

### 3 Results and Discussion

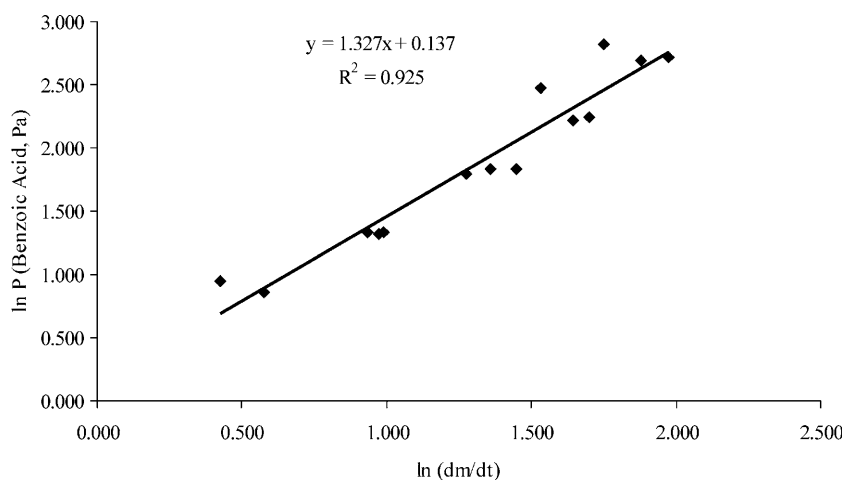
Benzoic acid, whose vapor pressure at different temperatures is well documented [9, 10], is used extensively for such calibrations. The TGA instrument expresses sublimation rate as change in weight percent with time (in minutes). Table 1 includes the instrument calibration data for benzoic acid. Vapor pressures of benzoic acid at the specified temperatures were obtained using the Antoine coefficients in the NIST (<http://webbook.nist.gov>). Figure 2 is a plot of natural logarithm of benzoic acid vapor pressures versus natural logarithm of the sublimation rate in µg min<sup>-1</sup>. The slope and intercept of Figure 2 yields the two pseudo Antoine constants (A and B) for the experimental conditions used in this study according to the Eq. (1):

$$\ln P = A \ln \left( \frac{dm}{dt} \right) + B \quad (1)$$

where  $dm/dt$  is the experimentally determined sublimation rate in µg min<sup>-1</sup> and  $P$  is the vapor pressure. Based on these results the Antoine constants are  $A = 1.327$  and  $B = 0.137$ , as obtained in Figure 2 and shown in Eq. (2).

$$\ln P = 1.327 \ln \left( \frac{dm}{dt} \right) + 0.137 \quad (2)$$

Vapor pressures of AN, UN, GN, and TATP were obtained using Antoine constants determined from the above and experimentally determined sublimation rates, at specified temperatures. Figures 3 and 4 are representative thermographs of UN and GN percent mass loss with time. The sublimation rates and calculated vapor pressures, at specified temperatures, from Eq. (2), are given in Tables 2–



**Figure 2.** Plot of Antoine equation of benzoic acid to determine the Antoine constants A (slope) and B (intercept).

**Table 1.** Sublimation rates for benzoic acid used in Figure 2. Temperatures are averages of  $n$  measurements reported by the TGA during the isothermal experiments. Standard deviations in temperature measurements are also reported.

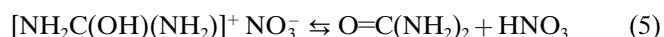
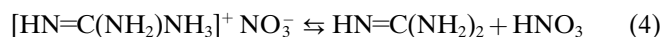
$n =$	$T$ (K)	Std. Dev.	$P$ (Pa)	$dm/dt$ ( $\mu\text{g min}^{-1}$ )	$\ln(dm/dt)$	$\ln(P)$
1020	322.1	0.17	2.376	1.779	0.576	0.865
1440	322.9	0.70	2.588	1.527	0.423	0.951
720	326.4	0.16	3.731	2.649	0.974	1.317
616	326.5	0.08	3.793	2.548	0.935	1.333
780	326.5	0.07	3.795	2.692	0.99	1.334
720	331.1	0.12	5.989	3.587	1.277	1.790
720	331.5	0.07	6.225	3.899	1.361	1.829
720	331.5	0.16	6.235	4.258	1.449	1.830
600	335.5	0.17	9.197	5.181	1.645	2.219
600	335.8	0.26	9.432	5.470	1.699	2.244
600	338.3	0.20	11.862	4.620	1.530	2.473
600	340.6	1.28	14.715	6.564	1.882	2.689
600	340.9	0.23	15.095	7.197	1.974	2.714
706	342.2	0.26	16.856	5.755	1.750	2.825

5. Using these vapor pressures, at specified temperatures, it is possible to use the Clapeyron equation to construct graphs of the dependence of vapor pressure on temperature [1, 2, 12]. These plots are shown for AN, UN, GN, and TATP in Figure 5.

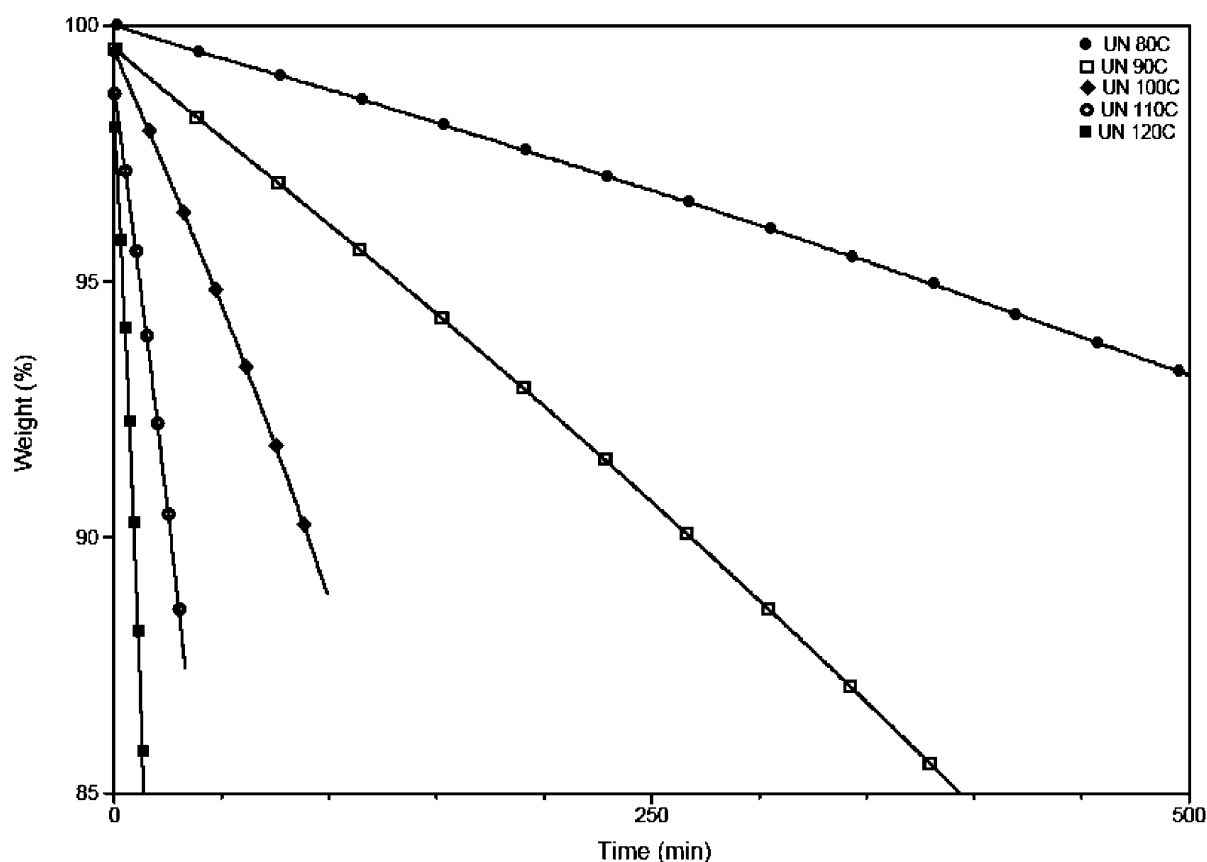
AN and TATP, whose vapor pressures have been determined by other methods, were selected for this study to confirm the validity of the TGA method. The TGA method provides vapor pressure but gives no indication of the composition of the vapor. Like UN and GN, AN is also an energetic salt with a significant vapor pressure at elevated temperature. AN vaporizes by dissociation above its melting point according to Eq. (3) [13].



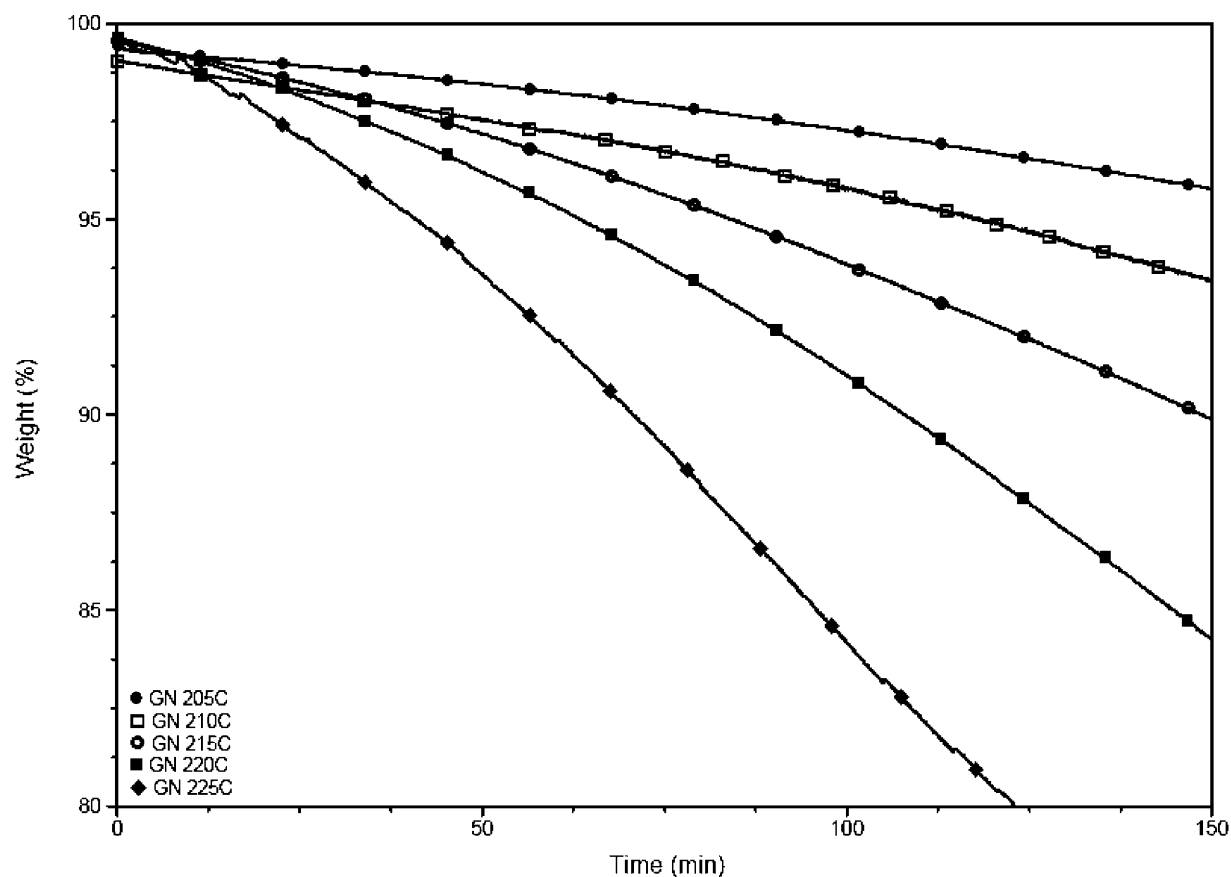
By analogy a similar dissociation mechanism for vaporizations of GN and UN (Eqs. (4 and 5), respectively) are suggested.



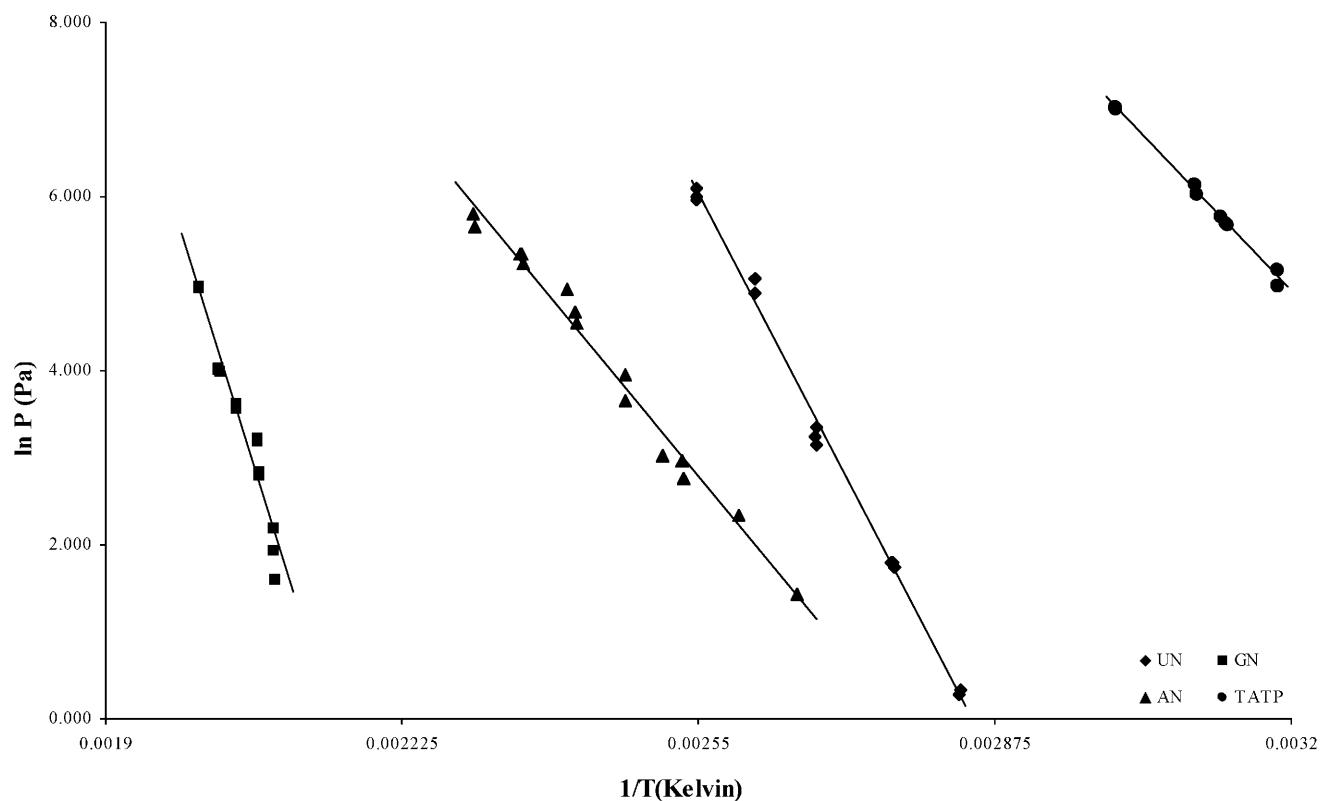
These mechanisms are highly speculative, especially for the ambient conditions. Urea decomposes at its melting point ( $132^\circ\text{C}$ ) and guanidine has a very low melting point ( $50^\circ\text{C}$ ). Other mechanisms and further decompositions are possible. Lack of neutral guanidine or urea in the vapor does not necessarily limit vapor detection to alert for UN or GN. In bulk detection of the explosive TNT, it has a very low



**Figure 3.** Thermograph of percent mass loss of UN with time (sublimation rate). The sublimation rates for UN are tabulated at the specified temperatures in Table 2.



**Figure 4.** Thermograph of percent mass loss of GN with time (sublimation rate). The sublimation rates for GN are tabulated at the specified temperatures in Table 3.



**Figure 5.** Clapeyron equations for UN, GN, AN, and TATP.

**Table 2.** Sublimation rates at specified temperatures for UN (see Figure 3). Temperatures are averages of  $n$  measurements reported by the TGA during the isothermal experiments. Standard deviations in temperature measurements are also reported.

$n$	$T$ (K)	Std. Dev.	$dm/dt$ ( $\mu\text{g min}^{-1}$ )	$\ln(P)$	$P$ (Pa)	$P$ (Torr)
780	352.4	0.07	1.164	0.338	1.403	0.011
1080	352.6	0.07	1.107	0.272	1.312	0.01
1090	352.7	0.12	1.114	0.28	1.323	0.01
540	362.0	0.09	3.486	1.793	6.009	0.045
660	361.7	0.05	3.361	1.745	5.725	0.043
703	362.0	0.12	3.497	1.798	6.036	0.045
100	373.1	0.29	11.219	3.344	28.338	0.213
201	373.4	0.14	10.39	3.242	25.594	0.192
201	373.3	0.26	9.741	3.157	23.495	0.176
70	382.9	0.16	35.917	4.888	132.696	0.995
70	382.8	0.31	40.903	5.061	157.673	1.183
68	382.8	0.16	40.492	5.047	155.577	1.167
35	392.4	0.29	89.125	6.094	443.138	3.324
35	392.4	0.26	80.351	5.956	386.207	2.897
35	392.5	0.25	82.984	5.999	403.092	3.023

**Table 3.** Sublimation rates at specified temperatures for GN (see Figure 4). Temperatures are averages of  $n$  measurements reported by the TGA during the isothermal experiments. Standard deviations in temperature measurements are also reported.

$n$	$T$ (K)	Std. Dev.	$dm/dt$ ( $\mu\text{g min}^{-1}$ )	$\ln(P)$	$P$ (Pa)	$P$ (Torr)
3804	479.6	0.18	2.982	1.586	4.886	0.037
3800	479.5	0.04	3.854	1.926	6.865	0.051
3800	479.8	0.10	4.697	2.189	8.926	0.067
3819	483.3	0.09	7.374	2.787	16.238	0.122
3790	483.3	0.09	7.674	2.84	17.122	0.128
3798	483.9	0.13	9.994	3.191	24.309	0.182
3799	483.9	0.14	10.184	3.216	24.923	0.187
3800	489.3	0.10	13.141	3.554	34.953	0.262
3800	489.1	0.09	13.802	3.619	37.305	0.28
3799	493.7	0.05	18.238	3.989	53.992	0.405
3800	494.1	0.20	18.337	3.996	54.384	0.408
3799	494.2	0.09	18.68	4.021	55.736	0.418
3800	499.2	0.05	37.446	4.943	140.24	1.052
3798	499.1	0.08	38.065	4.965	143.324	1.075

vapor pressure and if confined is highly immobile. Contaminating dinitrotoluene (DNT) has much higher vapor pressure, is highly mobile, relatively easy to detect, and alerts of the probable presence of TNT. Likewise, other vapor products traceable to UN or GN could be used in detection. This study provides evidence for the existence of a vapor associated with these compounds albeit the specific composition of the vapor is not known.

The Clapeyron equations, illustrated in Figure 5, describe temperature dependence of the vapor pressures for the four energetic materials studied. They are as follows:

$$\text{For UN} \quad \ln P(\text{Pa}) = 57.377 - 20131/T \quad (6)$$

$$\text{For GN} \quad \ln P(\text{Pa}) = 72.189 - 33589/T \quad (7)$$

$$\text{For AN} \quad \ln P(\text{Pa}) = 35.141 - 12690/T \quad (8)$$

**Table 4.** Sublimation rates at specified temperatures for AN. Temperatures are averages of  $n$  measurements reported by the TGA during the isothermal experiments. Standard deviations in temperature measurements are also reported.

$n$	$T$ (K)	Std. Dev.	$dm/dt$ ( $\mu\text{g min}^{-1}$ )	$\ln(P)$	$P$ (Pa)	$P$ (Torr)
3800	376.1	0.13	2.659	1.434	4.196	0.031
3801	385.3	0.08	5.26	2.339	10.373	0.078
3797	394.7	0.12	7.254	2.766	15.89	0.119
3794	398.2	3.08	8.414	2.962	19.345	0.145
3794	395.0	0.20	8.763	3.016	20.418	0.153
3797	404.9	0.09	14.119	3.649	38.447	0.288
3797	404.9	0.10	17.582	3.940	51.434	0.386
3797	413.8	0.06	27.551	4.536	93.336	0.700
3797	414.1	0.11	30.304	4.663	105.908	0.794
3818	415.5	0.54	36.975	4.927	137.907	1.034
3799	424.5	0.03	46.267	5.224	185.679	1.393
3799	424.7	0.17	50.195	5.332	206.878	1.552
3799	424.0	0.05	50.537	5.341	208.751	1.566
3799	434.1	0.22	63.698	5.648	283.787	2.129
3799	433.8	0.09	71.059	5.793	328.103	2.461

**Table 5.** Sublimation rates at specified temperatures for TATP. Temperatures are averages of  $n$  measurements reported by the TGA during the isothermal experiments. Standard deviations in temperature measurements are also reported.

$n$	$T$ (K)	Std. Dev.	$dm/dt$ ( $\mu\text{g min}^{-1}$ )	$\ln(P)$	$P$ (Pa)	$P$ (Torr)
60	313.9	0.05	38.167	4.969	143.837	1.079
60	314.0	0.04	43.825	5.152	172.789	1.296
94	319.5	0.07	64.83	5.672	290.498	2.179
60	319.6	0.04	65.371	5.683	293.723	2.203
30	320.1	0.07	69.524	5.764	318.733	2.391
45	322.9	0.06	84.521	6.024	413.027	3.098
45	323.0	0.22	91.02	6.122	455.683	3.418
30	332.4	0.23	179.955	7.026	1125.73	8.444
30	332.5	0.11	176.727	7.002	1099.01	8.243

$$\text{For TATP} \quad \ln P(\text{Pa}) = 40.194 - 11026/T \quad (9)$$

Given that the slopes of the above Clapeyron equations are enthalpies of sublimation ( $\Delta_{\text{sub}}H$ ) divided by the gas constant ( $R$ ), it is possible to calculate  $\Delta_{\text{sub}}H$ . Enthalpies of sublimation and vapor pressures extrapolated to 25 °C from the corresponding Clapeyron equation are given in Table 6. The vapor pressure of TATP, extrapolated to 25 °C from its Clapeyron equations (Eq. (9)), was determined to be 24.8 Pa (0.186 Torr) for TATP. We have previously determined the vapor pressure of TATP at 25 °C using a gas chromatography/head space method to be 6.95 Pa (0.0521 Torr) [1]. Using the TGA method vapor pressures of TATP are within the range of that reported in the literature. Brandner et al. have reported vapor pressures of solid AN in the temperature range of 76–165 °C [14]. Using their experimentally determined Clapeyron equation, the extrapolated vapor pressure of AN at 25 °C would be  $1.48 \times 10^{-3}$  Pa ( $11.1 \times 10^{-6}$  Torr). They used a method of transpiration involving the collection specifically of ammonia and nitric acid (see Eq. (1)) by flowing dry air or nitrogen over

**Table 6.** Enthalpies of sublimation and vapor pressure at 25 °C for UN, GN, and AN.

	$\Delta_{\text{sub}}H$ (kJ mol <sup>-1</sup> )	Vapor Pressure at 25 °C	
		Vapor Pressure (Pa)	Vapor Pressure (Torr)
Urea Nitrate	167	$3.94 \times 10^{-5}$	$2.96 \times 10^{-7}$
Guanidine Nitrate	279	$2.66 \times 10^{-18}$	$1.99 \times 10^{-20}$
Ammonium Nitrate	106	$5.98 \times 10^{-4}$	$4.49 \times 10^{-6}$
TATP (this work)	91.7	24.8	0.186

10–20 g of AN. The current study, using TGA, reports a lower vapor pressure of  $5.98 \times 10^{-4}$  Pa ( $4.49 \times 10^{-6}$  Torr) when calculated from our Clapeyron equation [Eq. (8)].

In conclusion enthalpies of sublimation and vapor pressures extrapolated to 25 °C from the corresponding Clapeyron equations for the three energetic salts (UN, AN, GN) and TATP are given in Table 6. In previous studies we have extensively used quantification of headspace vapors by gas chromatography for solid explosives, such as TNT, with relatively low vapor pressures [1, 2, 13]. This has the advantage of identifying the vapor composition by chromatography. Due to exceedingly low vapor pressures we had been unable to use this approach for energetic salts such as AN, UN, and GN. The TGA method used in this study can be used for solids with extremely low vapor pressures where gas chromatography is not practical. It was limited in that it provided no information on the composition of the vapor.

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