

Estimating Ambient Vapor Pressures of Low Volatility Explosives by Rising-Temperature Thermogravimetry

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Abstract

Vapor pressure is a fundamental physical characteristic of chemicals. Some solids have very low vapor pressures. Nevertheless numerous chemical detection instruments aim to detect vapors. Herein we address issues with explosive detection and use thermogravimetric analysis (TGA) to estimate vapor pressures. Benzoic acid, whose vapor pressure is well characterized, was used to calculate instrumental parameters related to sublimation rate. Once calibrated, the rate of mass loss from TGA measurements was used to obtain vapor pressures of the 12 explosives at elevated temperature: explosive salts-guanidine nitrate (GN); urea nitrate (UN); ammonium nitrate (AN); as well as mono-molecular explosives-hexanitrostilbene (HNS); cyclotetramethylene-tetranitramine (HMX), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX), cyclotrimethylenetrinitramine (RDX), pentaerythritol tetranitrate (PETN), 3-nitro-1,2,4-triazol-5-one (NTO), 3-nitro-1,2,4-triazol-5-one (TNAZ), triacetone triperoxide (TATP), and diacetone diperoxide (DADP). Ambient temperature vapor pressures were estimated by extrapolation of Clausius-Clapeyron plots (i.e. $\ln P$ versus $1/T$). With this information potential detection limits can be assessed.

Keywords: vapor pressure, explosive, TGA, guanidine nitrate (GN); urea nitrate (UN); ammonium nitrate (AN); hexanitrostilbene (HNS); cyclotetramethylene-tetranitramine (HMX), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX), cyclotrimethylenetrinitramine (RDX), pentaerythritol tetranitrate (PETN), 3-nitro-1,2,4-triazol-5-one (NTO), 3-nitro-1,2,4-triazol-5-one (TNAZ), triacetone triperoxide (TATP), diacetone diperoxide (DADP).

1 Introduction

Detecting explosives at standoff requires a detection signature produced by vapor or particulates. For most military explosives the vapor pressures are exceedingly low at ambient temperature, making direct determinations difficult or impossible. Commonly used laboratory methods for obtaining ambient vapor pressures include manometry, headspace gas chromatography, mass spectrometry, vacuum diffusion in a Knudsen cell, or boiling point determinations under reduced pressure. These techniques are not sufficiently sensitive for

extremely low vapor pressure solids. Another approach, thermogravimetric analysis (TGA), has been used successfully to study volatilization of relatively non-volatile materials.

Previously we had obtained ambient vapor pressures of 2,4,6-trinitrotoluene (TNT), triacetone triperoxide (TATP), and diacetone diperoxide (DADP)^{1,2} by determination of headspace vapor densities at fixed temperatures using gas chromatography with electron capture detection. Vapor densities of the energetic salts, urea nitrate (UN), guanidine nitrate (GN), and ammonium nitrate (AN) were below detection limits of the headspace method; therefore, an alternative approach, isothermal thermal TGA, was used.³ TATP was also run by this method for comparison and to validate the approach. The isothermal TGA method for determining vapor pressure is well documented and used extensively in pharmaceutical and cosmetic industries.⁴⁻¹¹ The method measures mass loss with time at fixed temperatures, and these are correlated to a vapor pressure calibration standard, often benzoic acid.^{12,13} However, the isothermal TGA method is time consuming. An alternative TGA method measures incremental changes in sample mass with time as the temperature is increased at a programmed rate. This rising-temperature TGA method can be used for extremely low vapor pressure compounds. This technique was used in this study to estimate vapor pressures of low volatility mono-molecular explosives including HMX, RDX, TEX, HNS, TNAZ, NTO, and PETN in addition to the energetic salts GN, AN, and UN. For comparison across methods, the highly volatile peroxide explosives TATP and DADP were also examined (Figure 1).

2 Materials and Methods

Most explosives were obtained from commercial and military sources. TATP, DADP and UN were prepared in our laboratories by previously published methods.¹⁻³ Reagent grade

benzoic acid was purchased from Fisher Scientific. Mass loss determinations were carried out using a TA Q5000 Thermal Gravimetric Analyzer (TGA). During the experiments nitrogen purge gas constantly swept the balance (10 mL/min) and the furnace (25 mL/min). Samples were held in open platinum pans (110 uL, from TA Instruments). Depending on the amount of sample required to cover the entire surface of the pan, 5 to 30 mg of sample was used. Runs were done in duplicate or triplicate or quadruplicate, ramping the samples at 10 degrees/minute from 40°C to 400°C. Since sublimation rates of the solids was necessary, only data before thermal decomposition and/or melting point was used to calculate vapor pressures.

3 Results and Discussion

The basis for the calculation of vapor pressure by TGA is a Langmuir equation:

$$\frac{1}{a} \frac{dm}{dt} = p \alpha \sqrt{\frac{M}{2\pi RT}} \quad (1)$$

The decrease in mass with time (dm/dt) ($\text{kg}\cdot\text{s}^{-1}$) was measured at each temperature increment (i.e. approximately every one degree); a is the area of the platinum TGA pan (m^2); p is pressure in Pascal; M is the molar mass of the analyte ($\text{kg}\cdot\text{mol}^{-1}$); α is an instrumental calibration parameter that is dependent on TGA conditions; T is Kelvin temperature (K); R is the gas constant ($\text{J K}^{-1} \text{mol}^{-1}$). Solving (1) for p gives Equation 2.

$$p = \left\{ \frac{1}{a} \frac{dm}{dt} \sqrt{\frac{T}{M}} \right\} \cdot \left\{ \frac{\sqrt{2\pi RT}}{\alpha} \right\} \quad (2)$$

Where we define

$$v = \frac{1}{a} \frac{dm}{dt} \sqrt{\frac{T}{M}} \quad (3)$$

and

$$k = \frac{\sqrt{2\pi M}}{\alpha} \quad (4)$$

Rearrangement of equation 1 and combining variables, equations 2-4 yields a simplified final expression (equation 5) for calculating vapor pressure.

$$p = kv \quad (5)$$

If the evaporation constant α is known for the instrument, k is known and then the rate of mass loss with temperature rise can be used to calculate vapor pressure at T . Thus, the application of this technique begins with assessing α (actually k) using a material with well-documented vapor pressures at various temperatures. The mass loss with time (dm/dt), calculated each one degree increment, is used to calculate v values. The value of the instrument calibration constant, k , is determined from the slope of a plot of p versus v for a compound for which vapor pressure is well known as a function of temperature.

Benzoic acid, for which the vapor pressure has been measured over a range of temperatures, was used to determine the instrumental constant (k) in equation (5).^{11,12} Four benzoic acid samples (5 to 7 mg) were scanned from 50 to 120°C at a scan rate of 10 degrees per minute and mass loss with time was collected every one degree temperature rise. Plots were constructed using dm/dt data to calculate v every one degree change in temperature. Pressure p (pascals) was calculated from the Antoine equation (6)^{7,14} using A, B, C coefficients from the NIST website (equation 7).¹⁵ With p calculated from equation (7) on the y axis and v calculated from measured dm/dt values on the x axis, a line of slope k was generated. (Figure 2 & Tables 1,2).

$$\text{Log } p = 5 + (A - [B/\{T+C\}]) \quad \text{with } p \text{ in pascal, } T \text{ in Kelvin} \quad (6)$$

$$p = 10^5 \times 10^{4.47834 - (1771.357/(T-127.484))} \quad (7)$$

For the explosive samples the TGA conditions were the same as for the benzoic acid calibration. The explosives were scanned from ambient instrumental temperature ($\sim 40^\circ\text{C}$) to past the melting point; except for guanidine nitrate which was examined above its melting point. With mass loss at temperature (dm/dt), v was calculated for the samples of explosives using equation (3). Table 3 is a tabulation of data used to calculate v for AN which is used with Equation 5 to calculate pressure. In the case of AN, TGA data above and below the melting point was well behaved. Table 4 shows an example of the data collected for GN. Unlike most explosives in this study, the TGA was unable to obtain meaningful data below its melting point. However, TGA data was well behaved above its melting point and was used to obtain a vapor pressure of the liquid GN.

With the pressure (p) values calculated at each temperature increment, the Clapeyron relationship was applied to calculate heat of sublimation, ΔH_{sub} :

$$\ln p = \frac{(\Delta H_{\text{sub}})}{RT} + \text{constant} \quad (8)$$

Figure 3 shows the data collected from four runs of ammonium nitrate. When mass loss was steady, the plot was linear. The lowest temperature, linear portion of the $\ln(p)$ versus $1/T$ plot was used to calculate the slope ($\Delta H_{\text{sub}}/R$). (Figure 3) Deviations from linearity occur with phase changes and thermal decomposition. It should be noted that the rising temperature method of calculating vapor pressure could not be used to determine the vapor pressures of TNT, tetryl, 2,4-dinitrotoluene, ammonium dinitramide, or erythritol tetranitrate because mass loss prior to melting was not significant.

With $(\Delta H_{\text{sub}}/R)$, the vapor pressure could be obtained by extrapolation to the thermodynamic temperature (25°C). The results are summarized in Table 5. This approach assumed that the slope of the line measured at elevated temperatures could be extrapolated to ambient temperature.

The ambient vapor pressures calculated by the rising temperature TGA method are compared to vapor pressures previously obtained by isothermal TGA³ and static headspace GC^{1,2} (Table 6 & Fig. 5). The rising-temperature TGA method estimates vapor pressures approximately an order of magnitude higher than isothermal TGA or headspace GC. Table 7 compares room temperature vapor pressures obtained herein and values published by others. The values estimated by rising temperature TGA usually fall within the wide range bracketed by previous works. This suggests that when estimate of vapor pressure is required one might as well use the quick rising temperature method rather any more elaborate method.

It is instructive to calculate the signature available for detection. Using P/RT to calculate the moles of explosives available in 1 m³ of materials with vapor pressure 10⁻⁷ Pa vs. one with vapor pressure 10⁻¹² Pa, one finds 4 x 10⁻¹¹ mole vs. 4x10⁻¹⁶ of explosive. Considering there are about 41 moles of air in that one cubic meter; that means their explosive signature is 1 ppt vs. 10⁻⁵ ppt which explains why explosives detection instrumentation is unable to detect HMX.

3 Conclusions

We are reporting a relatively simple and rapid method for determining vapor pressures of explosives and other materials. The method has the advantage of requiring only a TGA and no other specialized apparatus. The reported vapor pressures of explosives at 25°C of about 1 Pa

(TATP) to 10^{-12} Pa (HMX) cover a considerable range and are in agreement with published values obtained by others (Table 5, Table 6).

4 Acknowledgements

The authors wish to thank the Department of Homeland Security for funding via Cooperative agreement # 2008-ST-061-ED000 through the University Programs Center of Excellence as well as through the Science & Technology Division.

5 References

1. Oxley, J.C.; Smith, J.L.; Moran, J.; Shinde, K. "Determination of the Vapor Density of Triacetone Triperoxide (TATP) Using A Gas Chromatography Headspace Technique" *Propellants, Explosives, Pyrotechnics*, **2005**, 30.2, 127-130.
2. Oxley, J.C.; Smith, J.L.; Luo, W; Brady, J. "Determining the Vapor Pressure of Diacetone Diperoxide (DADP) and Hexamethylene Triperoxide Diamine (HMTD)," *Propellants Explosives Pyrotechnics*, **2009**, 34(6), 539-543.
3. Oxley, J.C., Smith, J.L., Brady, J., Naik, S. "Determination of Urea Nitrate and Guanidine Nitrate Vapor Pressures by Isothermal Thermogravimetry," *Propellants, Explosives, Pyrotechnics* **2009**, 27,209-216.
4. P. Aggarwal, D. Dollimore, K.S. Alexander, The use of Thermogravimetry to follow the Rate of evaporation of an ingredient used in perfumes, *J. Therm. Anal.* **1997**, 49, 595.
5. B. Cassel, Determining Vapor Pressure by Pressure DSC, *Perkin Elmer Thermal Analysis Newsletter*. **1993**, 49, 2.
6. M. Casserino, D.R. Belvins, R.N. Sanders, An Improved Method for Measuring Vapor Pressure by DSC with Automated Pressure Control, *Thermochim Acta*. **1996**, 284, 145.
7. K. Chatterjee, D. Dollimore, K. S. Alexander, A. Hazra, Estimating Vapor Pressure Curves by Thermogravimetry: A Rapid and Convenient method for Characterization of Pharmaceuticals, *Eur. J. Pharm. Biopharm.* **2002**, 54, 171.
8. S.F. Wright; Dollimore, D.; J.G. Dunn; K. Alexander "Determination of the vapor pressure curves of adipic acid and triethanolamine using thermogravimetric analysis" *Thermochimica Acta* 2004, 421, 25-30
9. J. W. Goodrum, E. M. Siesel, Thermogravimetric Analysis for Boiling Points and Vapor Pressure, *J. Thermal Anal.* **1996**, 44, 1251.
10. H. G. Wiedemann, Applications of Thermogravimetry for Vapor Pressure Determination. *Thermochimica Acta*, **1972**, 3, 355.

11. M. Xie, T.M. Ziemba, M.B. Maurin, Sublimation characterization and Vapor Pressure Estimation of an HIV Nonnucleoside Reverse Transcriptase Inhibitor using Thermogravimetric Analysis, *AAPS Pharm Sci Tech.* **2003**, 4 (2), Article 23.
12. K. Chatterjee, D. Dollimore, K. S. Alexander, A new application for Antoine equation in formulation development, *Int J Pharm.* **2001**, 213, 31.
13. J. P. Elder, Sublimation Measurements of Pharmaceutical Compounds by Isothermal Thermogravimetry, *J. Thermal Anal.* **1997**, 49, 897.
14. V. Majer; V. Svoboda; J. Picks Heats of Vaporization of Fluids, Elsevier Amsterdam, 1989.
15. <http://webbook.nist.gov/>
16. R. B. Cundall, T. F. Palmer, C. E. C. Wood, Vapor Pressure Measurements on some Organic High Explosive, *J. Trans. Faraday Chem Soc.* **1978**, 74, 1339.
17. B. C. Dionne, D. P. Roundbehrer, J. R. Achter, Hobbs, D. H. Fine, Vapor Pressure of Explosives. *J. Energ. Mater.* **1986**, 4, 447.
18. J.D. Brandner, N.M. Junk, J.W. Lawrence, J. Robins, Vapor Pressure of Ammonium Nitrate, *J. Chem. and Eng Data.* **1962**, 7, 227.
19. J. M. Rosen, C. Dickinson, Vapor Pressures and Heats of Sublimation of Some High Melting Organic Explosives, *J. Chem. Eng. Data* **1969**, 14, 121
20. F.T. Crimmins, The Vapor Pressure of Pentaerythritoltetranitrate (PETN) in the Temperature Range of 50 to 98 Degrees Centigrade, *Lawrence Radiation Laboratory, UCRL-50704*, July, **1969**.
21. Taylor, J.W., Crookes, R.J., Vapour Pressure and Enthalpy of Sublimation 1,3,5,7-tetranitro-1,3,5,7-tetra-azacyclo-octane *J. Chem. Soc., Faraday Trans.* **1976**, 72, 723.
22. Minier, L., Behrens, R., Burkey, T., Study of the solid-phase thermal decomposition of NTO using Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry *33rd JANNAF Combustion Subcommittee Meeting 1996*, Monterey, California.
23. Damour, P., Freedman A., Wormhoudt, J., Knudsen Effusion Measurement of Organic Peroxide Vapor Pressures *Propellants, Explosives, Pyrotechnics* **2010**, 35(6), 514-520.

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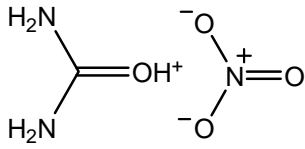
Figure 2: Plot of Antoine Equation of Benzoic Acid

Figure 3: Calculated change in P with temperature (K) for ammonium nitrate (4 runs plotted)

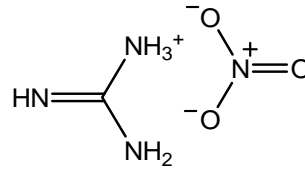
Figure 4a: $\ln p$ (Pa) vs $1/T$ (K) for HNS, HMX, TEX, AN, RDX, TNAZ, TATP, DADP

Figure 4b: $\ln p$ vs T (K⁻¹) for HNS, GN, NTO, AN, UN, TATP, DADP

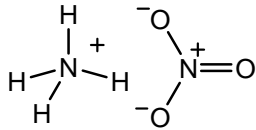
Figure 5: Vapor Pressure at 25°C by rising temperature & isothermal TGA and headspace GC



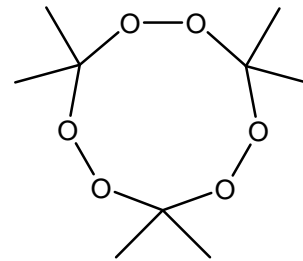
Urea Nitrate (UN)
Melting Point 133°C(dec.)



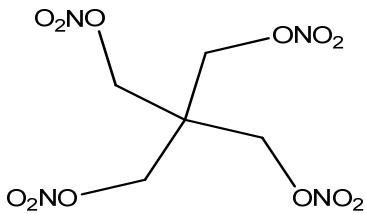
Guanidine Nitrate (GN)
Melting Point 210°C



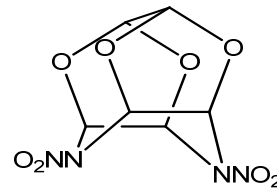
Ammonium Nitrate (AN)
Melting Point 169 °C



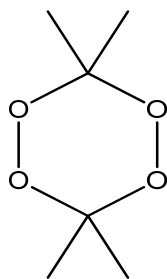
Triacetone Triperoxide (TATP)
Melting Point 95 °C



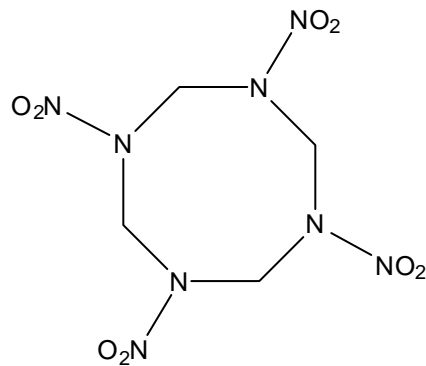
Pentaerythritol tetranitrate (PETN)
Melting point 141°C



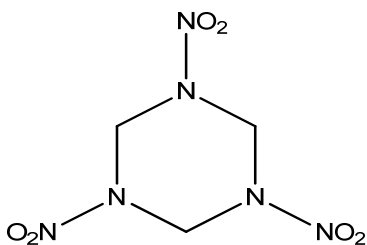
4,10-dinitro-2,6,8,12-tetraoxa-4,10-diaza-tetracyclododecane (TEX)
Melting Point > 250°C (dec.)



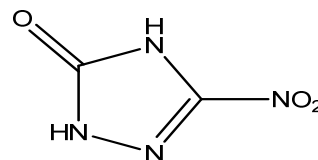
Diacetone Diperoxide
Melting Point 132°C



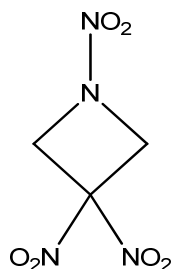
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
Melting point 281°C (dec.)



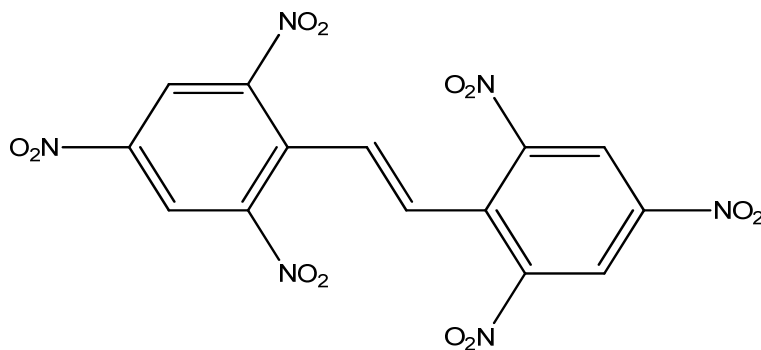
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
Melting Point 205°C (dec.)



5-nitro-1,2,4-triazol-3-one (NTO)
Melting point > 200°C (dec.)



1,3,3-Trinitroazetidine (TNAZ)
Melting point 101°C



2,2',4,4',6,6'-Hexanitrostilbene (HNS)
Melting point 318°C

Figure 1. Structures of Explosives Studied

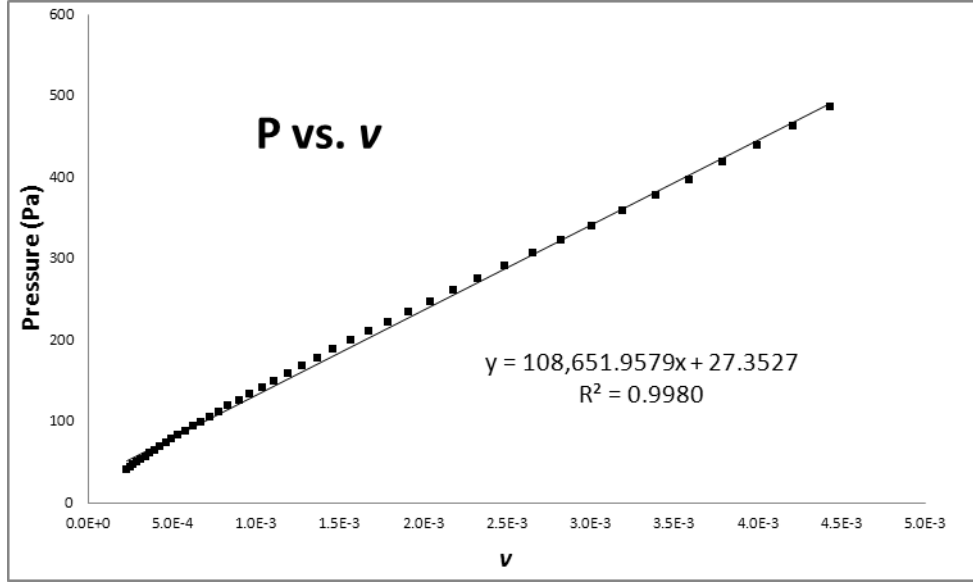


Figure 2: Example of plot benzoic acid standard used to determine instrument parameter k (slope)

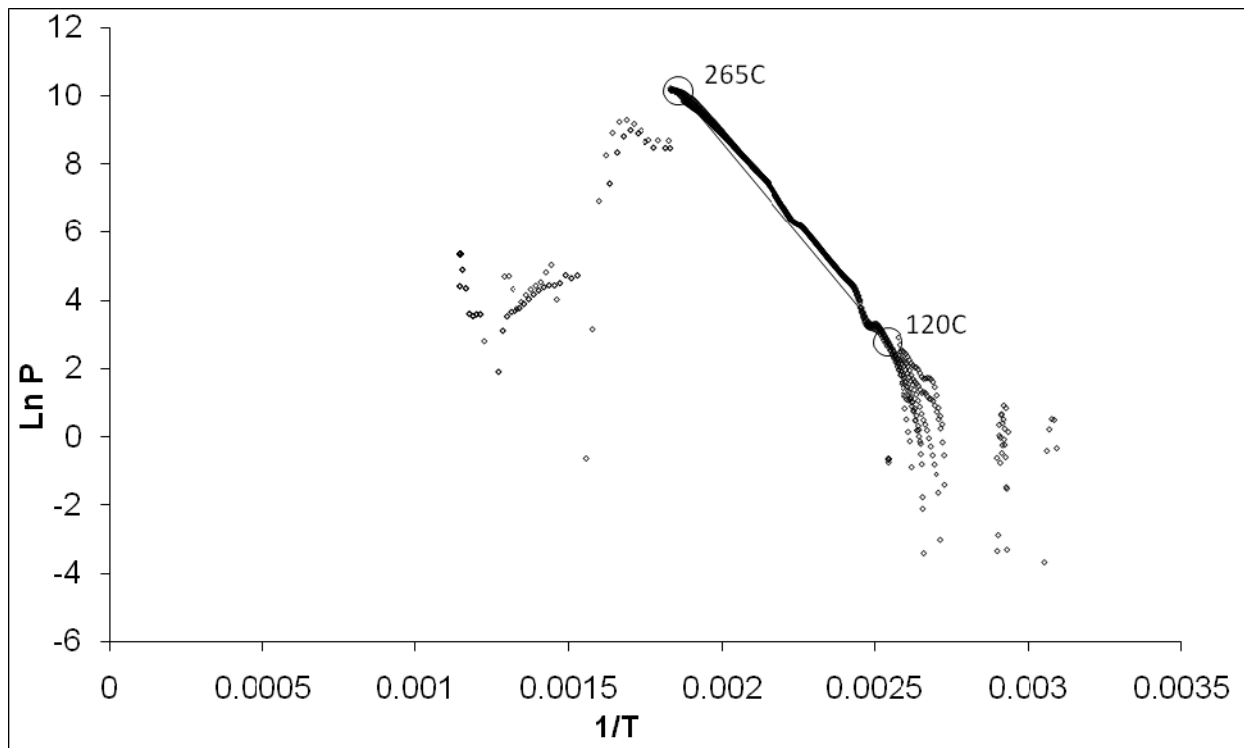


Fig. 3: Calculated change in P with temperature (K) for ammonium nitrate (4 runs plotted).

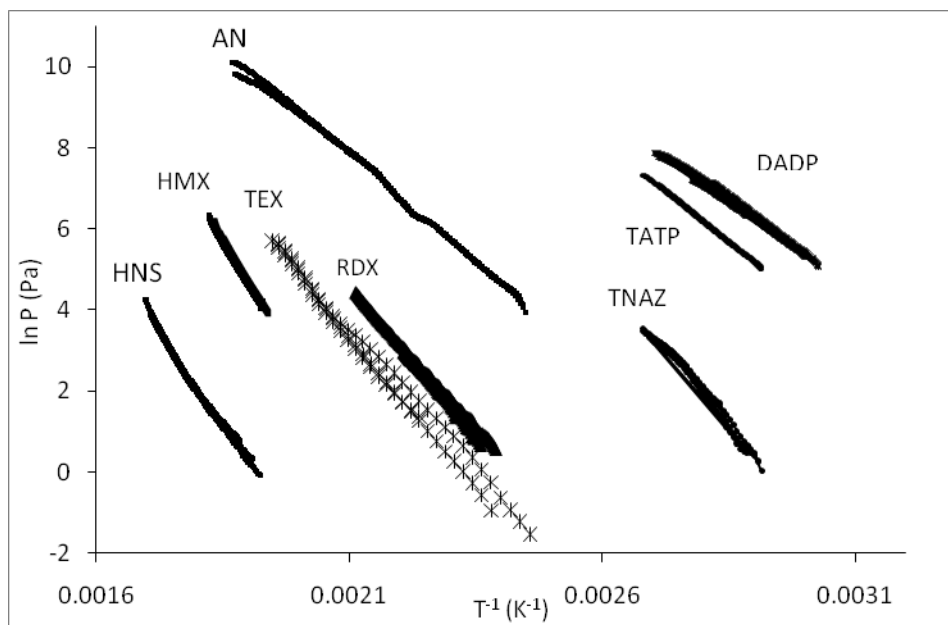


Fig. 4a: $\ln p$ vs T (K^{-1}) for HNS, HMX, TEX, AN, RDX, TNAZ, TATP, DADP

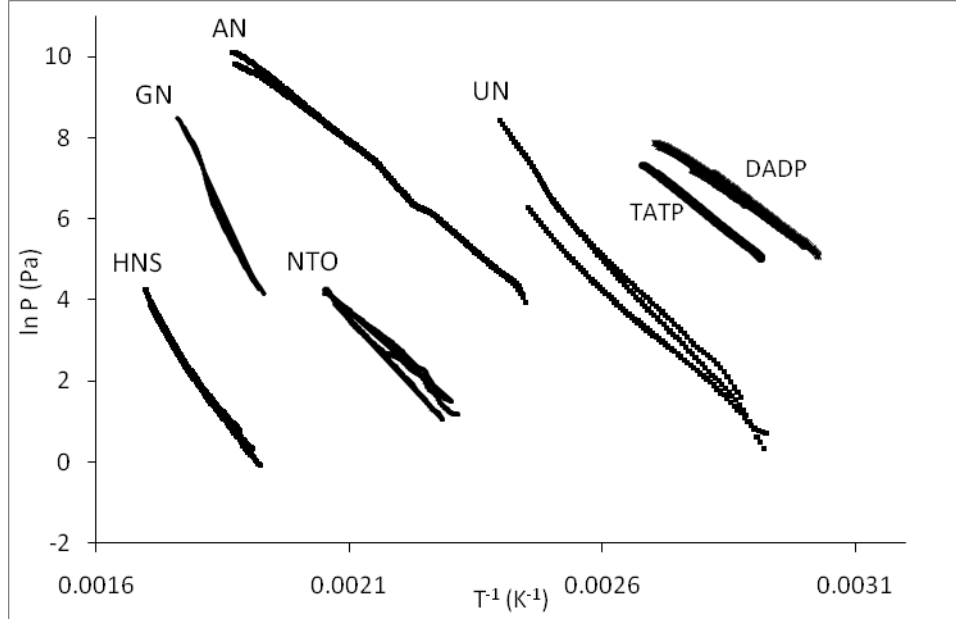


Fig. 4b: $\ln p$ vs T (K^{-1}) for HNS, GN, NTO, AN, UN, TATP, DADP

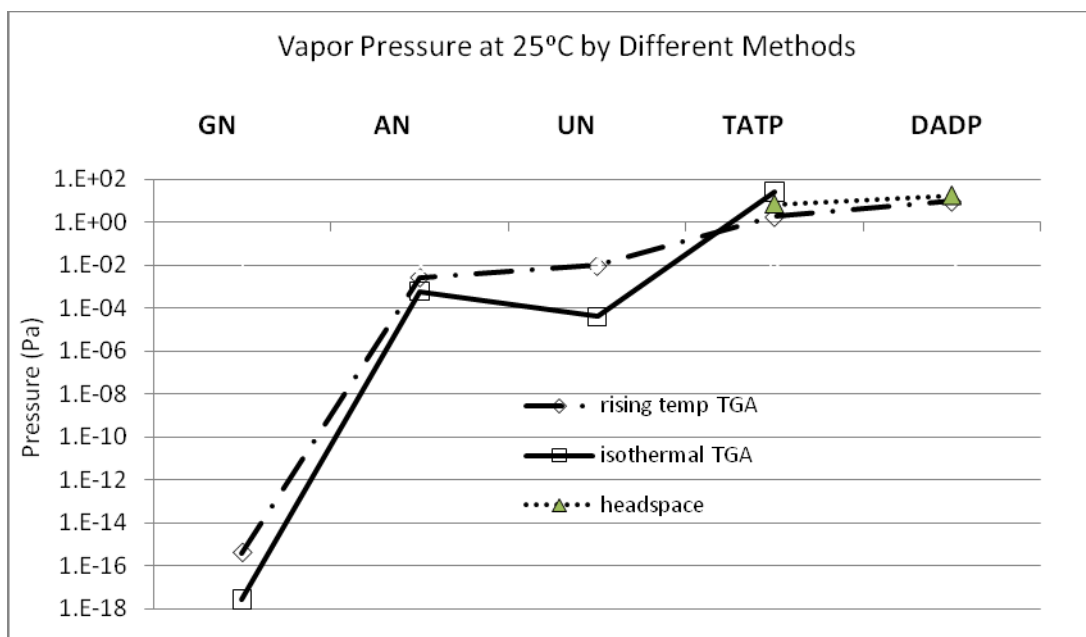


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Table 1: Instrumental constant k as calculated from 4 runs of benzoic acid (example in Fig. 2).

Trial #	slope (k)
1	108652.0
2	102887.4
3	108312.3
4	105209.3
Average	106265.2
Std. Dev.	2733.2
Relative Std. Dev. (%)	2.6

Table 2: Data from TGA run (10°/min) of benzoic acid

Time (min)	Temp (°C)	mass (mg)	dm/dt (mg/s)	Temp (K)	dm/dt (kg/s)	$v = (1/a)(dm/dt)(T/M)^{1/2}$	P (Pa)
22.0042	51.00	5.05995	0.00069	324.15	6.92E-10	0.000014	2.961
25.3292	54.35	5.05785	0.00086	327.50	8.64E-10	0.000018	4.191
30.3292	59.38	5.05259	0.00141	332.53	1.41E-09	0.000030	6.914
35.3292	64.41	5.04344	0.00242	337.56	2.42E-09	0.000051	11.122
40.3292	69.42	5.02796	0.00406	342.57	4.06E-09	0.000087	17.485
45.3292	74.42	5.00215	0.00667	347.57	6.67E-09	0.000143	26.912
50.3292	79.42	4.96032	0.01067	352.57	1.07E-08	0.000231	40.610
55.3292	84.41	4.89407	0.01688	357.56	1.69E-08	0.000368	60.164
60.3292	89.40	4.78973	0.02641	362.55	2.64E-08	0.000580	87.652
65.3292	94.38	4.62762	0.04069	367.53	4.07E-08	0.000899	125.670
70.3292	99.37	4.38016	0.06143	372.52	6.14E-08	0.001367	177.525
75.3292	104.35	4.01004	0.09104	377.50	9.10E-08	0.002039	247.337
80.3292	109.33	3.46393	0.13335	382.48	1.33E-07	0.003006	340.107
85.3292	114.30	2.67704	0.18561	387.45	1.86E-07	0.004212	461.939
90.3292	119.28	1.61321	0.22904	392.43	2.29E-07	0.005230	620.192
92.8292	121.76	0.97884	0.24302	394.91	2.43E-07	0.005567	715.688

Table 3: Representative data from TGA run (10°C/min.) of AN starting below the MP and finishing above the melt.

Time (min)	Temp (°C)	mass (mg)	dm/dt (mg/s)	Temp (K)	dm/dt (kg/s)	$v = (1/a)(dm/dt)(T/M)^{1/2}$	P (Pa)
37.792	136.160	11.8863	6.44E-04	409.31	6.44E-10	5.84E-04	62.100
38.292	141.145	11.8818	9.90E-04	414.30	9.90E-10	9.05E-04	96.118
38.792	146.142	11.8764	1.28E-03	419.29	1.28E-09	1.18E-03	124.902
39.292	151.137	11.8690	1.71E-03	424.29	1.71E-09	1.58E-03	167.665
39.792	156.132	11.8592	2.29E-03	429.28	2.29E-09	2.13E-03	226.420
40.292	161.127	11.8461	3.05E-03	434.28	3.05E-09	2.85E-03	302.945
40.792	166.123	11.8287	4.04E-03	439.27	4.04E-09	3.80E-03	403.286
41.292	171.116	11.8057	5.02E-03	444.27	5.02E-09	4.75E-03	504.880
41.792	176.104	11.7790	5.77E-03	449.25	5.77E-09	5.49E-03	583.290
42.292	181.115	11.7461	8.15E-03	454.27	8.15E-09	7.80E-03	828.653
42.792	186.107	11.6990	1.13E-02	459.26	1.13E-08	1.09E-02	1157.137
43.292	191.103	11.6321	1.58E-02	464.25	1.58E-08	1.52E-02	1620.213
43.792	196.100	11.5420	1.98E-02	469.25	1.98E-08	1.92E-02	2040.574
44.292	201.102	11.4322	2.48E-02	474.25	2.48E-08	2.42E-02	2570.152
44.792	206.099	11.2965	3.01E-02	479.25	3.01E-08	2.96E-02	3142.876
45.292	211.089	11.1308	3.69E-02	484.24	3.69E-08	3.64E-02	3867.229
45.792	216.083	10.9283	4.52E-02	489.23	4.52E-08	4.49E-02	4768.040
46.292	221.081	10.6782	5.50E-02	494.23	5.50E-08	5.49E-02	5832.553
46.375	221.914	10.6313	5.69E-02	495.06	5.69E-08	5.68E-02	6034.559
46.625	224.416	10.4809	6.39E-02	497.57	6.39E-08	6.39E-02	6791.696

Table 4: Partial Data from TGA run (10⁰/min) of Guanidine Nitrate

Time (min)	Temp (°C)	mass (mg)	dm/dt (mg/s)	Temp (K)	dm/dt (kg/s)	$v = (1/a)(dm/dt)(T/M)^{1/2}$	P (Pa)
25.4375	244.513	19.3827	7.19E-04	517.66	7.19E-10	5.97E-04	63.399
25.9375	249.487	19.3785	1.01E-03	522.64	1.01E-09	8.44E-04	89.732
26.4375	254.469	19.3725	1.50E-03	527.62	1.50E-09	1.25E-03	133.000
26.9375	259.449	19.3635	2.29E-03	532.60	2.29E-09	1.93E-03	204.797
27.4375	264.427	19.3494	3.52E-03	537.58	3.52E-09	2.97E-03	315.723
27.9375	269.409	19.3282	5.28E-03	542.56	5.28E-09	4.48E-03	476.366
28.4375	274.390	19.2962	8.20E-03	547.54	8.20E-09	6.99E-03	743.067
28.9375	279.371	19.2438	1.67E-02	552.52	1.67E-08	1.43E-02	1521.070
29.4375	284.353	19.1277	2.79E-02	557.50	2.79E-08	2.40E-02	2548.106
29.9375	289.337	18.9672	3.91E-02	562.49	3.91E-08	3.38E-02	3589.057

Table 5. Heats of sublimation & calculated Vapor Pressures at 25 C extrapolated from temperature range shown

	A	B	R ²	ΔH_{sub}	VP @25°C (Pa)	VP @ 25°C (Torr)	T _{low} (°C)	T _{high} (°C)
UN	39.47	-11185	0.999	93.0	6.94E+00	5.21E-02	69	124
UN	34.52	-11607	0.995	96.5	1.19E-02	8.95E-05	80	134
UN	40.59	-13571	0.992	112.8	7.06E-03	5.29E-05	75	144
UN	42.47	-14354	0.996	119.3	3.34E-03	2.51E-05	69	139
			average	105.4	1.74E+00	1.31E-02		69 - 144
AN	29.27	-10234	0.997	85.1	6.24E-03	4.68E-05	135	260
AN	31.59	-11273	0.996	93.7	1.95E-03	1.46E-05	118	222
AN	31.98	-11454	0.995	95.2	1.57E-03	1.18E-05	115	224
AN	32.44	-11666	0.993	97.0	1.23E-03	9.19E-06	114	262
			average	92.8	2.75E-03	2.06E-05		114 - 262
TNAZ	42.75	-14550	0.992	121.0	2.31E-03	1.73E-05	71	98
TNAZ	43.88	-15011	0.992	124.8	1.51E-03	1.13E-05	70	100
TNAZ	45.57	-15590	0.991	129.6	1.18E-03	8.81E-06	73	97
TNAZ	42.10	-14232	0.994	118.3	3.47E-03	2.60E-05	70	97
TNAZ	46.34	-15722	0.993	130.7	1.63E-03	1.22E-05	70	97
TNAZ	41.86	-14161	0.995	117.7	3.49E-03	2.62E-05	70	97
			average	123.7	2.26E-03	1.70E-05		70 - 97
NTO	26.29	-10728	0.992	89.2	6.09E-05	4.57E-07	161	214
NTO	26.55	-10958	0.990	91.1	3.64E-05	2.73E-07	159	209
NTO	32.15	-13603	0.999	113.1	1.38E-06	1.03E-08	165	214
			average	97.8	3.3E-05	2.47E-07		159 - 215
RDX	31.75	-13042	0.999	108.4	6.04E-06	4.53E-08	146	180
RDX	33.73	-13748	0.974	114.3	4.10E-06	3.07E-08	150	197
RDX	33.81	-13922	0.999	115.7	2.48E-06	1.86E-08	148	200
RDX	37.43	-15572	0.997	129.5	3.66E-07	2.74E-09	151	176
			average	119.8	2.31E-06	2.43E-08		146 - 200
TEX	32.61	-13815	0.997	114.9	1.07E-06	8.04E-09	134	237
TEX	34.97	-15084	0.995	125.4	1.60E-07	1.20E-09	174	247
TEX	35.50	-15294	0.999	127.2	1.34E-07	1.01E-09	147	237
			average	122.5	4.56E-07	3.42E-09		134 - 247
PETN	51.91	-20310	0.999	168.9	8.79E-08	6.59E-10	111	140
PETN	52.63	-20593	0.999	171.2	7.00E-08	5.25E-10	113	140
PETN	52.35	-20519	0.998	170.6	6.77E-08	5.08E-10	115	142
PETN	52.91	-20774	0.995	172.7	5.07E-08	3.80E-10	115	144
			average	171.5	6.28E-08	5.18E-10		111 - 144
HMX	43.51	-20443	0.999	170.0	1.26E-11	9.47E-14	245	270
HMX	43.61	-20529	0.999	170.7	1.05E-11	7.84E-14	245	275
HMX	44.01	-20735	0.999	172.4	7.89E-12	5.92E-14	245	272
HMX	44.32	-20903	0.998	173.8	6.09E-12	4.56E-14	245	275
			average	172.3	8.14E-12	6.95E-14		245 - 275
HNS	33.39	-17382	0.993	144.5	1.47E-11	1.10E-13	257	312
HNS	33.62	-17551	0.993	145.9	1.05E-11	7.88E-14	252	311
HNS	35.23	-18416	0.998	153.1	2.89E-12	2.17E-14	247	312
HNS	35.51	-18549	0.992	154.2	2.45E-12	1.83E-14	251	316
			average	151.1	5.28E-12	5.73E-14		247 - 316
GN	56.61	-27280	0.990	226.8	6.73E-16	5.05E-18	245	290
GN	58.35	-28277	0.990	235.1	1.35E-16	1.01E-18	247	295
			average	231.0	4.04E-16	3.03E-18		245 - 295
DADP	30.32	-8310	0.998	69.1	11.46	0.09	73	90
DADP	30.29	-8395	0.999	69.8	8.30	0.06	75	86
DADP	33.34	-9302	0.999	77.3	8.39	0.06	57	94
DADP	31.92	-8837	0.997	73.5	9.65	0.07	60	97
DADP	32.26	-8955	0.998	74.5	9.13	0.07	60	96
DADP	31.74	-8786	0.997	73.0	9.56	0.07	60	96
			average	72.9	9.41	0.07		57 - 96
TATP	34.37	-10058	0.999	83.6	1.86	0.01	70	96
TATP	34.46	-10098	0.999	84.0	1.78	0.01	70	96
TATP	34.37	-10070	0.999	83.7	1.77	0.01	77	96
			average	83.8	1.80	0.01		70 - 96

Table 6: Comparing vapor pressures at 25°C from this lab

Rising Temperature TGA (this work) Vapor pressure extrapolated to 25°C					Isothermal TGA: Vapor pressure extrapolated to 25°C				Headspace /GC	
	ΔH_{sub} (kJ/mol)	Vapor Pressure (Pa)	# data pts	temperature °C used for extrapolation	ΔH_{sub} (kJ/mol)	Vapor Pressure (Pa)	# data pts	temperature °C used for extrapolation	ΔH_{sub} (kJ/mol)	Vapor Pressure (Pa)
GN	231	4.04E-16	2	245 - 295	279	2.66E-18	12	205 - 220		
AN	93	2.75E-03	4	114 - 262	106	5.98E-04	14	110 - 150		
UN	105	9.51E-03	4	69 - 144	167	3.94E-05	15	80 - 120		
TATP	84	1.8026	3	70-95	91.7	24.8	8	40 - 58	109	6.95
									73	7.85
DADP	73	9.414	6	60-96					82	17.89

Table 7: Comparison of vapor pressures from this work with studies of others

				Vapor Pressure extrapolated to 25°C (this work)			Literature Values for Vapor Pressure		
				MW g/mol	m.p. °C	exotherm max °C	ΔH_{sub} (kJ/mol)	Vapor Pressure (Pa)	temperature (°C) used for extrapolation
GN	122	213	400	231	4.04E-16	245 - 295	279	2.66E-18	3
HNS	450	325	360	151	5.28E-12	247 - 316	172	5.95E-16	19
HMX	296	282	290	172	8.14E-12	245 -275	159	1.04E-11	21
							164	2.81E-12	21
							175	3.85E-13	19
							161	5.87E-16	16
PETN	316	143	212	172	6.28E-08	111 -143	150	7.90E-11	16
							121	1.78E-05	20
							139	1.82E-06	17
TEX	262	250	298	122	4.56E-07	134 - 247			
RDX	222	204	240	120	2.31E-06	146 -200	114	3.15E-07	19
							134	4.06E-09	16
							124	6.08E-07	17
NTO	130	273		98	3.29E-05	159 - 215	120	3.23E-07	22
TNAZ	192	101	245	125	1.67E-03	70 - 100			
AN	80	169	315	93	2.75E-03	114 - 262	68	1.24E-06	17
							106	5.98E-04	3
							179	1.45E-03	18
UN	123	160	170	105	9.51E-03	69 - 144	167	3.94E-05	3
TATP	222	95	220	84	1.80E+00	70-95	109	4.33	1
							86	6.35	23
							73	7.85	2
							92	24.8	3
DADP	148	132	160	73	9.4141	60-96	81	17.9	2
							85	31.3	23