

**Sublimation Rate of Energetic Materials in Air: RDX and
PETN**

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Sublimation rate of energetic materials in air:

RDX and PETN

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ABSTRACT

This paper reports measurements in which the sublimation rate in air of RDX and PETN samples was determined. For both explosives the initial samples were prepared by deposition from a solution. For RDX we obtained a continuous thin film while the PETN samples were constituted of small, well separated, single crystals. The sublimation process was monitored using a quartz crystal microbalance (QCM). It is demonstrated that a quantitative description of the sublimation rates can be obtained using molecular diffusion equations in the surrounding air. A quantitative description is limited by the large discrepancy of the reported vapor pressure of these explosives in the literature. An additional obstacle in the accuracy of these predictions is the limited data related to vapor-in-air diffusion coefficients. The results reported here allow us to determine the most relevant vapor pressure source reported in the literature and the most probable diffusion coefficient values.

1. Introduction

Pentaerythritol tetranitrate (PETN) and 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX) are two of the most widely used explosives among the common military energetic materials. These two explosives have been also used by various terrorist groups in different occasions. Both explosives exhibit very low vapor pressure, hence, their detection is limited mainly to detection of solid samples. As a result, law enforcement authorities need improved sampling procedures to collect trace amounts of these explosives that are required for analysis by the analytical tools used. Thus, the main goal of sample collection using swabs of passenger belongings and luggage in airports is to detect minute residues of energetic materials. Trace amounts of material are expected to remain on belongings of people that were involved in preparation or transport of explosives. However, these small particles of energetic materials are expected to exhibit a finite life time since they are located in an infinite open system. It is important to have an accurate estimate of the lifetime of explosive particles since it determines the possibility to detect them after their deposition.

It is well established and confirmed recently¹ that the sublimation rate of small explosive particles in air is limited by the diffusion process. The diffusion model used to estimate sublimation rate requires knowledge of both the diffusion coefficients of the energetic material's molecules in air and the magnitude of the saturation vapor pressures. Since the vapor pressure of most explosives is quite low their accurate measurement is difficult. Hence, considerable discrepancies are found in the literature²⁻⁸. Moreover, to the best of our knowledge, data of direct measurements of diffusion coefficients in air of the two explosives investigated here are absent in literature. A few measurements of PETN and RDX sublimation rates in atmospheric conditions were reported in the literature.⁹⁻¹² Analysis of the results obtained in these experiments is not clear with respect to several important points. For example, in the case of PETN: (i) some of the data was carried out in the temperature range 110°C-125°C in which considerable thermal decomposition of the sample occurs according to the authors^{11,12} (ii) the lower temperature data obtained^{9,10} reveals large discrepancies (of 300-400 times) between the AFM (Atomic Force Microscope) measurements and the TGA (Thermal Gravimetric Analysis) results for similar samples, (iii) the estimation^{9,10} of diffusion coefficient using TGA sublimation

1 rate measurements yields an extremely small value $8 \cdot 10^{-7} \text{ m}^2/\text{s}$. In the case of RDX^{11, 12},
2 the following discrepancies were observed: (i) extremely large estimations of the vapor-
3 in-air diffusion coefficient, of order of $1 \times 10^{-4} \text{ m}^2/\text{s}$, was required for description of the
4 sublimation rate as a diffusion process. These large diffusion coefficients were
5 interpreted by the authors^{11, 12} as a possible consequence of the influence of surface
6 migration. The experiments related to RDX sublimation were carried out as weight loss
7 measurements of the solid RDX sample through a glass tube of known dimensions. The
8 authors could not estimate the influence of the glass walls on the measured data. In the
9 experiments described below we measured the RDX sublimation rate using a quartz
10 crystal microbalance (QCM) which allows continuous measurements of weight change
11 during the sublimation process into the open space without the need for a sublimation cell
12 with walls.

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The quartz crystal microbalance (QCM) is a suitable system to measure sublimation rates due to its high sensitivity to very small mass changes of order of nanograms. Hence, in the present study we used QCM measurements to investigate the sublimation rate of both Pentaerythritol tetranitrate (PETN) single crystals and 1, 3, 5-Trinitroperhydro-1, 3, 5-triazine (RDX) films directly precipitated from a solution of these explosives. The main goal of the study was to obtain reliable data concerning the sublimation rates of these two explosives together with a suitable model that will allow accurate predictions at various conditions.

2. Experimental details

Materials

Military standard of Pentaerythritol tetranitrate (PETN) and 1, 3, 5-Trinitroperhydro-1, 3, 5-triazine (RDX), 4,6-trinitrotoluene solutions in acetonitrile with concentration of 1 g/L and acetonitrile purity of 99.9% were received from Rafael Ltd.

Equipment

The quartz microbalance used is model QCM100 by Stanford Research Systems, Inc. The AT-cut disk-shaped quartz crystal of 1 inch diameter was covered in the central area (0.5 inch diameter) by a thin gold layer. According to the manufacturer data, the crystal holder withstands temperature up to 85°C. However, the preamplifier attached by a BNC

1 connection to the crystal holder may be exposed only to temperatures up to 40°C. To
2 eliminate this restriction, in all experiments reported here the preamplifier was separated
3 from the crystal holder by a 10 inch long cable. The temperature control was achieved by
4 placing the crystal holder with the sample on the crystal surface in an oven with polished
5 stainless steel walls with ventilation located at the top of the oven. Before placing the
6 sample in the oven it was heated to the desired temperature. The sublimation experiments
7 reported below were carried out at constant temperature with fluctuations less than
8 $\pm 0.2^\circ\text{C}$. The quartz crystal holder was usually placed on the bottom of the oven at a
9 distance of 5-6 cm from one of the walls with the sample facing the wall. The position of
10 the crystal was chosen to be as far as possible from the ventilator. To eliminate the
11 accumulation of explosive vapor in the volume above the sample during the sublimation
12 process, the oven was pumped out continuously using a small membrane pump (pumping
13 rate of 18 L/min). The present experiments differ from those described in Ref. 1 by the
14 addition of a preventive cage around the QCM sample holder to eliminate air flow in the
15 neighborhood of the sample (see Figure 1). This setup was very important especially in
16 the experiments with RDX samples whose characteristic dimension is similar to that of
17 the QCM electrode used as the substrate, radius of 0.25 inch. Samples with such a radius
18 require the absence of air flow at distances of at least 2.5 inch. The cage was made of
19 three layers of fiberglass grid with mesh size of 0.5mm x 0.5mm. The size of the cage
20 was ten times larger than the dimensions of the QCM electrode. We verified, by
21 increasing the number of net layers in the cage, that this precaution insured that the
22 measured sublimation rate is independent of the air flow caused by the ventilation in the
23 oven.
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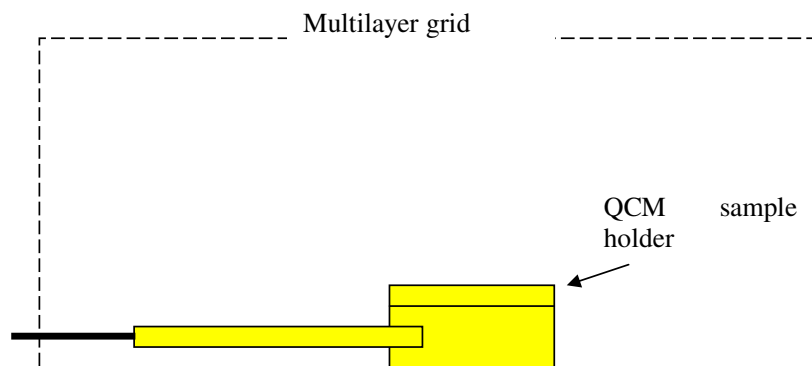


Figure 1. Air flows preventing cage

Sample preparation

PETN

The samples were prepared on the surface of the QCM electrode deposition of 10-20 μl solution. Following solution deposition, the solvent was allowed to evaporate at temperature of 15°C. The resultant PETN layer formed during the precipitation process consisted of a collection of small well separated single crystals.

The crystal holder with the sample was placed in the oven at the desired temperature. The sample reached the desired temperature typically within 2 hours. The data acquisition by a computer was started only after once the target temperature was reached. The sample sublimation process was monitored as fractional mass change as a function of time according to equation

$$\frac{\Delta m}{m_0} = \frac{f - f_i}{f_0 - f_i} \quad (1)$$

where Δm is the sample mass change at time t relative to the initial sample mass m_0 at the beginning of the experiment ($t=0$), while f represent the QCM resonance frequency at time t , f_i is its value at $t=0$ and f_0 represent the fundamental resonance frequency.

RDX

The sample preparation was carried out by deposition of 40 μl solution on the QCM electrode surface. Contrary to the PETN samples, the RDX formed, following solvent evaporation and solute precipitation, an apparently continuous thin film on the QCM surface. The solvent evaporation was carried out at elevated temperature of 60°C. The equilibration time of the RDX sample in the oven was typically about 5 hours, somewhat longer than for PETN probably due to existence of small amount of occluded solvent.

Contrary to PETN, for RDX samples the sublimation process was monitored as mass change in absolute units. This type of measurements is usual for nearly homogeneous samples. As has been shown in Ref. 1, the QCM sublimation measurements are independent of the sample thickness for continuous macroscopic layers. However, there is a necessity to calibrate the QCM readings. The calibration was performed before each experiment once the sample was formed by precipitation at the elevated temperature and cooled down to room temperature.

The QCM sensitivity value was determined by using the formulae

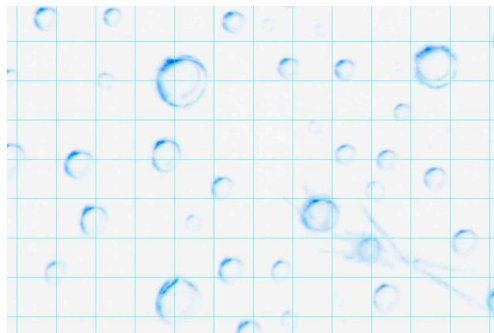
$$G = \frac{\Delta f}{m_0} \quad (2)$$

where G is the QCM sensitivity in $\text{Hz}/\mu\text{g}$, m_0 the dry mass of the sample and Δf the resonance frequency shift relative to fundamental. Usually, the frequency shift during the first 5 hours of the thermal equilibration did not exceed 15-20 % of the full measurement range. This value determines the calibration uncertainty.

3. Results

We shall start the description of the experimental data by an examination of the initial sample morphology of the two explosives examined. Based on enlarged optical microscope images, the PETN and RDX samples exhibit very different morphologies. An optical microscope image of a typical PETN sample morphology is shown in Fig. 2. It is clear that the initial morphology of the PETN layer is composed of well separated transparent micro crystals whose boundaries are easily visible. The diameter of these PETN micro-crystals is in the range of 30-35 micrometers, and their average diameter is

1 31 micron. Similarly, an optical microscope image of the initial RDX sample layer is
2 shown in Figure 3. In this case the initial morphology of the RDX layer corresponds to a
3 nearly continuous film whose diameter is roughly 10 millimeters.
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21 **Figure 2.** Typical optical microscope image of the PETN layer near the central part of
22 QCM electrode. Image taken following precipitation of the PETN from a 1g/l solution.
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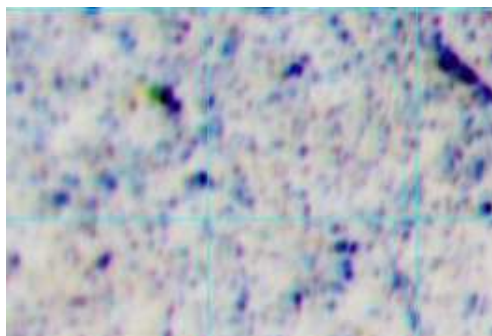


Figure 3. Typical optical microscope image of the RDX layer on the QCM electrode. The layer obtained by precipitation of 40 μg RDX from a solution of 1g/l. The sample seem to be composed of a nearly uniform thin film. The grid size in the picture is 50 microns.

The mass fraction change during the sublimation process of PETN as measured by the QCM is shown in Figure 4 for three different temperatures. The reproducibility of the measurements at any given temperature is very good (each curve corresponds to 2-4 different experiments). This result suggests that the approach used here for sample preparation yield statistically very similar micro-crystal size and shape distributions.

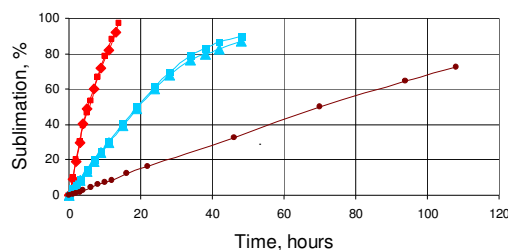
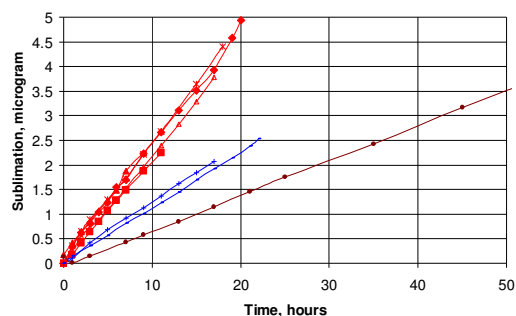


Figure 4. Variation of sample mass fraction of the PETN layers as a function of time. The three groups of lines correspond to different temperatures at which sublimation was monitored: red lines – at 70°C, blue lines - at 60°C and brown line - at 50°C.

1 The initial slopes of the curves presented in Fig. 4 are related to the rate of the
2 sublimation process. The initial rates of changes in the mass fractions at the three
3 different temperature examined are: 10.2%/h at 70°C, 2.66%/h at 60°C and 0.68%/h at
4 50°C. The rates quoted above were obtained from the slopes up to a mass fractional
5 change of 40%. The deviations from linearity of the high temperature curves at large
6 mass fraction sublimation values is related to marked changes in the layer morphology.
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10 Similar measurements of the mass change during the sublimation process of RDX, as
11 recorded by the QCM, are shown in Figure 5 for three different temperatures. The
12 reproducibility of the measurements at any given temperature is also very good,
13 considering the rather long measurement time required. Note that the experiments were
14 terminated after the sublimation of roughly 10% of the initial sample mass.
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33 **Figure 5.** Sample mass change during RDX Sublimation at three different temperatures:
34 red lines - at 70°C, blue – at 65°C and brown line – at 60°C.
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38 The initial slopes of the curves are found to be 0.066 $\mu\text{g}/\text{h}$ at 60°C, 0.119 $\mu\text{g}/\text{h}$ at 65°C,
39 and 0.220 $\mu\text{g}/\text{h}$ at 70°C.
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41 The slope of the various curves is related to the evaporation rate of the sample. The If
42 one assumes an Arrhenius form for the temperature dependence of evaporation rates, the
43 activation energy of the process can be obtained from the slope of the lines shown on the
44 Figures 6 and 7. The value obtained for the activation energy associated with PETN
45 sublimation is 125 kJ/mol comparing to the value of 140 kJ/mol reported in the
46 literature.⁹
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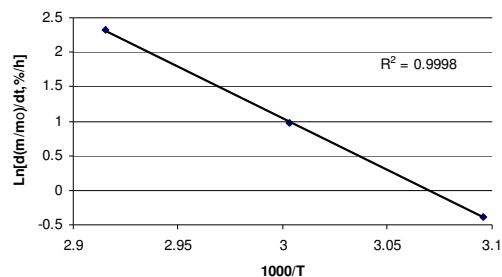


Figure 6. Arrhenius plot of the experimental data for PETN that gives 125 kJ/mol for the activation energy.

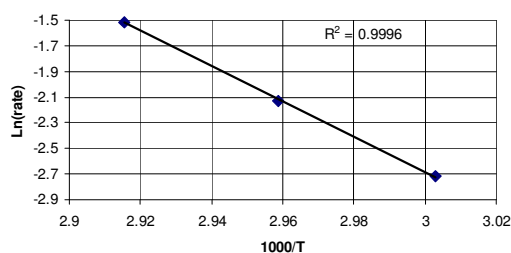


Figure 7. Arrhenius plot of the experimental data for RDX that gives 114 kJ/mol for activation energy.

The respective value for RDX is equal to 114 kJ/mol compared to 131 kJ/mol reported in the literature¹². Inspection of Figs. 6 and 7 shows that the data corresponding to the three temperature values examined here indeed follow an Arrhenius form, namely, the three data points lie on a straight line with high accuracy.

4. Discussion

In the following we shall consider the diffusive motion of the sample's molecules from the sample surface to the surrounding gas phase. It is claimed that the use of the net cage (see Fig. 1) surrounding the sample prevents any influence of the convective or other

1 forced motion that contributes to the measured sublimation rates. Thus, molecular
2 diffusion is basically the only route of explosive molecules to “get away” from the
3 sample surface.
4

5 Let us consider the quasi stationary steady state diffusion process from the sample
6 surface into the open space. The diffusive flow considerably depends on the morphology
7 of the sample. Unfortunately, we have not found in the literature solutions of diffusion
8 equations that describe this process for the case of a sample with arbitrary shape.
9 Analytic expressions were derived for the cases of spherical (or hemispherical)¹³ and
10 disk shaped source terms (i.e. sample shapes).¹⁴
11

12 The diffusive flow from a hemispherical source is expressed as

$$13 \quad dm / dt = 2\pi r_0 DC_{sat}M , \quad (3)$$

14 and from a disk shaped sample as

$$15 \quad dm / dt = 4r_d DC_{sat}M \quad (4)$$

16 where dm/dt is diffusive flow from the source to open space in units of kg/s, r_0 and r_d are
17 radius of the hemisphere and disk respectively, D is the diffusion coefficient of the
18 sample vapor in surrounding medium, C_{sat} represents the concentration of the saturated
19 vapor in the medium and M is the sample molecular mass.
20

21 We shall limit the following discussion to these two sample shapes that fit well our
22 PETN and RDX sample morphologies respectively. It is important to stress that the
23 diffusive flow into the surrounding space is always proportional to the linear dimension
24 of the source object and not to its surface area, as one can see in equations (3 and 4).
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26 In the following each one of the explosives examined will be discussed separately.
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28 *PETN*

29 As can be clearly seen in Figure 2, the precipitated on PETN layer consists of well
30 separated individual micro-crystals whose average diameter is 31 micron. If the shape of
31 each micro-crystal is approximated by a hemisphere the sample can be viewed as a
32 collection of independent hemispherical sources of vapor molecules. If one uses the ideal
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1 gas equation of state for the vapor phase one can transform equation (3) to the following
2 expression
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$$4 \quad -d(m/m_0)/dt = \frac{3DP_{sat}M}{r_0^2 \rho k_B T} \quad (5)$$

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10 where m_0 stands now for initial (at $t=0$) mass of an average sized hemisphere of radius r_0
11 (assumed to be with diameter of 31 microns), P_{sat} represents the saturation vapor pressure
12 of explosive and ρ is the density of the solid sample.
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15 Equation (5) that describes the fractional mass change obtained for a hemispherical
16 particle is used to model the sublimation of PETN samples. Hence, predictions using eq.
17 (5) rely on the availability of saturation vapor pressure and diffusion coefficient for the
18 explosive examined. The vapor pressure data found for PETN in the literature show large
19 discrepancies of order of magnitude.²⁻⁶ The temperature dependence (Clausius-Clyperon
20 plot) of the PETN vapor pressure values reported in the literature are presented in Fig. 8
21 below. The large difference between the various measurements is clearly observed. These
22 vapor pressure data correspond to sublimation heat values in the range from 122 kJ/mol
23 (Crimmins⁶, close to our value of 125 kJ/mol) to a maximal value of 150 kJ/mol
24 (Cundall²).
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36 In addition, as it is pointed out in the introduction, the only, non direct, experimental
37 determination of PETN vapor diffusion coefficient in air we found in the literature¹¹
38 seems to be unusually small ($8 \times 10^{-7} \text{ m}^2/\text{s}$)⁹. A theoretical estimation of PETN diffusion
39 coefficient is about an order of magnitude larger¹⁵, i.e. $D = 5 \cdot 10^{-6} \text{ m}^2/\text{s}$. Therefore, in the
40 following eq. (5) is used, together with the different vapor pressure values reported in the
41 literature²⁻⁶, to evaluate the magnitude of the diffusion coefficient. Thus, the data
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obtained in the sublimation experiments is used to calculate the PETN diffusion coefficient in air by expression

$$D = \frac{[-d(m/m_0)/dt]r_0^2 \rho k_B T}{3P_{sat}M} \quad (6)$$

The calculated values of D for PETN are summarized in Table I. Inspection of the results in Table I shows that the diffusion coefficient values obtained for PETN in air using vapor pressure values of Refs.²⁻⁵ are of order 1×10^{-5} m²/s - 5×10^{-5} m²/s. This estimate seems to be unreasonably large for heavy molecules such as PETN (molecular weight 316). In addition, this value is much larger than the theoretically calculated value which is 5.10^{-6} m²/s. Moreover, for these four vapor pressure data sources the magnitude of D decreases for increasing temperatures in contrary to the usual expectations. The D values obtained using Crimmins⁶ vapor pressure agree very well with the theoretical values and their magnitude increase as a function of temperature.

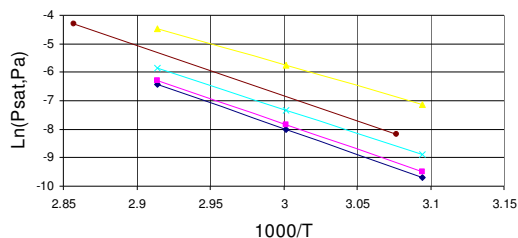


Figure 8. Clausius-Clapeyron plots related to vapor pressure data found in the literature for PETN: blue line - following Cundall et al.², magenta - following Edwards³, light blue - following Dionne et al.⁴, brown - following Burnham et al.⁵, yellow - following Crimmins.⁶

Table I. Diffusion coefficients (in m²/s) of the PETN vapor in air as calculated from the measured evaporation rates using expression (6)

Temperature,	Measured evaporation	Vapor pressure data source
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°C	rate, %/hour	Cundall ²	Edwards ³	Crimmins ⁶	Dionne ⁴	Burnham ⁵
50	0.68	$4.85 \cdot 10^{-5}$	$4.02 \cdot 10^{-5}$	$3.70 \cdot 10^{-6}$	$2.13 \cdot 10^{-5}$	$1.51 \cdot 10^{-5}$
60	2.66	$3.53 \cdot 10^{-5}$	$2.99 \cdot 10^{-5}$	$3.82 \cdot 10^{-6}$	$1.77 \cdot 10^{-5}$	$1.14 \cdot 10^{-5}$
70	10.20	$2.87 \cdot 10^{-5}$	$2.48 \cdot 10^{-5}$	$4.08 \cdot 10^{-6}$	$1.63 \cdot 10^{-5}$	$9.59 \cdot 10^{-6}$

Thus, one can conclude that the vapor pressure data reported by Crimmins⁶ are the best to describe PETN sublimation rate. As described earlier, Burnham et al.⁹ used AFM measurements to evaluate the evaporation rate of PETN samples. The measurements were based on AFM monitoring of the shrinkage rates of PETN micro crystals. The AFM measurement based sublimation rates were compared to results obtained using TGA measurements. These authors found a discrepancy of 300-400 times between the results of the two sublimation rate measurement methods. Unfortunately, the authors⁹ published their results only as reduced quantities. Such presentation of diffusion in the atmosphere is not sufficient without indication of the sample linear dimensions and shape. As a result we cannot compare directly our data with the results reported in Ref. 9. However, we could recalculate the PETN evaporation rates of their AFM measurements⁹ using the particles time dependent shrinkage values presented in the form of graphs in Ref 9. By this procedure we could obtain the original sublimation rate values before their reduction to sample unit area and then compare them with our results. The results of this re-processing of the AFM data are presented in Table II together with results of our recalculation employing eq. (5) and the vapor pressure values reported by Crimmins⁶ together with the corresponding D values in Table I.

Table II. Comparison of the AFM reprocessed sublimation rate of PETN⁹ with those calculated using expression (5) with vapor pressure reported by Crimmins⁶ and the corresponding diffusion coefficient from Table I.

Temperature, °C	Crystal radius, ⁹ nm	Shrinkage rate, ⁹ nm/s	Reprocessed sublimation rate,	Sublimation rate, calculated	Ratio between measured and calculated rate
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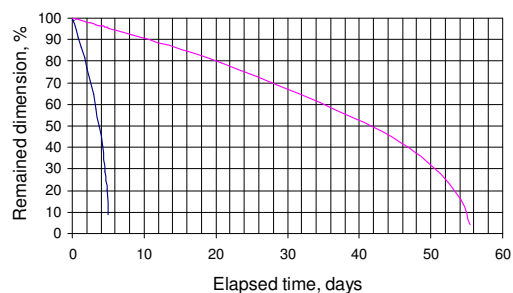
			ng/s	ng/s	values
30	330	0.0394	$4.77 \cdot 10^{-8}$	$3.33 \cdot 10^{-8}$	1.43
35	130	0.1282	$2.41 \cdot 10^{-8}$	$2.95 \cdot 10^{-8}$	0.82
40	320	0.3194	$3.64 \cdot 10^{-7}$	$1.63 \cdot 10^{-7}$	2.23

In Table II one can see that results of the AFM measurements coincide well with the results of our simple diffusion model using vapor pressures and diffusion coefficients values that were fitted to reproduce the data obtained in our QCM measurements. Since QCM measurements are similar by their nature as TGA data, it remains unclear the observed⁹ discrepancy of 300-400 times, between the AFM and TGA rates. Unfortunately we cannot recalculate the TGA results due to the absence of “raw”, untreated, TGA data in the paper.⁹ Once accepted vapor pressure and diffusion coefficient are defined it is possible to follow PETN particles size evolution as a function of time. The equation describing the process for hemispherical particles is¹

$$r_0(t) = \sqrt{r_0^2(t=0) - \frac{2DP_{sat}M}{\rho k_B T} t} \quad (7)$$

where $r_0(t)$ is the time dependent radius of the particle.

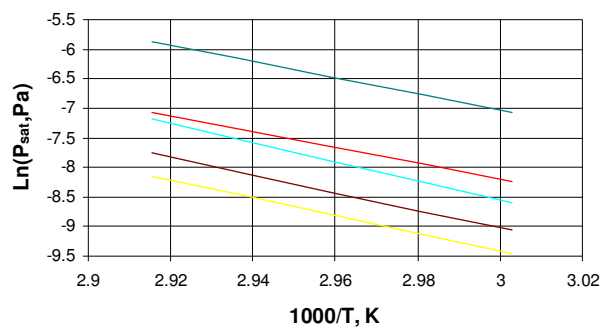
The results presented in Figure 9 were calculated using expression (7) for PETN hemispherical particles of diameters 6 and 20 microns respectively. The particles size variation due to sublimation was carried out at temperature of 30°C. The particle with 6 micron diameter expected to disappear after approximately 5 days while the 20 micron diameter particle will last for about 50 days.



1 **Figure 9.** PETN hemispherical particle size evolution in time at 30 °C: blue line
2 represents particle of 6 micron initial diameter, magenta line is for particle of 20 micron
3 initial diameter
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7 *RDX*

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9 As is clear from observation of the sample morphology shown in Figure 3, RDX
10 precipitated as continuous layer. Hence, its sublimation rate would be described by
11 equation (4). As in the case of PETN, the literature vapor pressure data for RDX is very
12 contradictory.^{2-4,7,8} Figure 9 shows a comparison between the results of various
13 measurements reported in the literature.
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36 **Figure 10.** Clausius-Clapeyron plots of RDX vapor pressure measurements reported in
37 the literature: blue line - after Cundall et al.2, red line - after Edwards3, brown line –
38 after Dionne et al.4, yellow line – after Rosen et al. et al.7 and green line - after Stimac.8
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42 The vapor pressure data presented in Fig. 9 corresponds to the heat of sublimation
43 values in the range 115 kJ/mol ÷ 134 kJ/mol. The lowest sublimation heat corresponds to
44 data of Stimac⁸, 115 kJ/mol, and the largest to Cundall², sublimation heat of 134 kJ/mol.
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47 As for PETN, reliable, i.e. independent of saturated vapor pressure values, diffusion
48 coefficients of the RDX vapors in air were not reported in the literature. The theoretical
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value of the RDX vapors diffusion coefficient, based on molecular theory, is $7.4 \cdot 10^{-6} \text{ m}^2/\text{s}$ at room temperature.¹⁶ If the temperature dependence of the diffusion coefficient of RDX molecules is $T^{1.75}$ as claimed by^{11, 12}, one would expect a theoretical value of $1.05 \cdot 10^{-5} \text{ m}^2/\text{s}$ at 70°C , the highest temperatures used in the present study.

Measurements of RDX sublimation rate have been reported.^{11,12} Exceptionally large diffusion coefficient, $D=1 \cdot 10^{-4} \text{ m}^2/\text{s}$ using the vapor pressure values reported by Dionne⁴ were required^{11,12} to describe the data. However, using vapor pressure data of Stimac⁸ reasonable diffusion coefficient of $D=1.17 \cdot 10^{-5} \text{ m}^2/\text{s}$ at 79°C was suggested. The authors^{11,12} expressed some doubts regarding the vapor pressure values of Stimac⁸ and considered the possible influence of RDX surface migration along the walls of the diffusion cell on the measured results¹⁶. Thus, the best choice of the parameters P_{sat} and D remains uncertain.

In the present investigation wall effects were eliminated. The diffusion coefficient values calculated using expression (4) are shown in Table III for all the available vapor pressure data in the literature.

Table III. Diffusion coefficients (in m^2/s) of the RDX vapor in air as calculated from the measured evaporation rates according to expression (4)

Temperature, °C	Sublimation rate, $\mu\text{g}/\text{h}$	Vapor pressure data source				
		Cundall ²	Edwards ³	Dionne ⁴	Rosen ⁷	Stimac ⁸
60	0.066	$4.77 \cdot 10^{-5}$	$3.32 \cdot 10^{-5}$	$7.63 \cdot 10^{-5}$	$1.12 \cdot 10^{-4}$	$1.04 \cdot 10^{-5}$
65	0.119	$4.26 \cdot 10^{-5}$	$3.34 \cdot 10^{-5}$	$7.20 \cdot 10^{-5}$	$1.06 \cdot 10^{-4}$	$1.03 \cdot 10^{-5}$
70	0.220	$3.98 \cdot 10^{-5}$	$3.51 \cdot 10^{-5}$	$7.11 \cdot 10^{-5}$	$1.05 \cdot 10^{-4}$	$1.07 \cdot 10^{-5}$

Inspection of the data in Table III shows that for all vapor pressures reported in the literature, the best agreement with the theoretical D value is obtained using the vapor pressure by Stimac⁷.

Using these value for the vapor pressure and diffusion coefficient we can estimate the life time of a RDX particle. The variation of particle size was estimated using eq. (7) as for PETN particles described above. The results are shown in Figure 11 for RDX particles

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at 30 °C. This data was obtained using vapor pressure of Ref. 8 and diffusion coefficient of $7.4 \cdot 10^{-6}$ m²/s as recommended¹⁶ for room temperature (and approximately coincide with our data in the Table III). It is clear that the life time of RDX particles is approximately twice than those obtained for PETN.

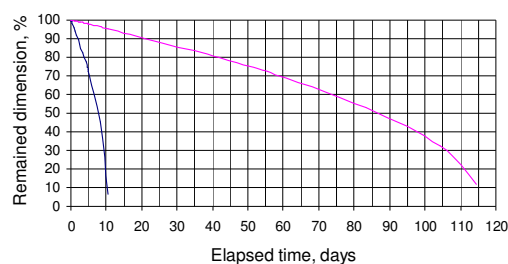


Figure 11. RDX hemispherical particle size evolution in time AT 30 °C: blue line represents particle of 6 micron initial diameter, magenta line is for particle of 20 micron initial diameter

4. Conclusion

We have shown in the present study that sublimation rates of PETN and RDX are well described by the simple expressions based on molecular diffusion. Several vapor pressure sources reported in the literature were examined and we have pointed out those that are the most consistent for both PETN and RDX. The choice of vapor pressure determines in turn the diffusion coefficients that have from the best agreement with those calculated theoretically. Comparison result of the QCM experiments described in this study with data related to AFM measurements reported in the literature of PETN sublimation rate yield good agreement.

The results of the experiments reported here suggest that the life time of small PETN and RDX particles is quite long at room temperature. As expected, the low vapor pressure of these compounds leads to very small sublimation rates. Hence, extrapolation of our data to room temperature for PETN residues suggest life time of about 60 days for a 20 micron diameter particle while for RDX the life time of same size particles becomes about four months. For smaller particles of 6 micron diameter, size that can be carried by air flows in explosive manufacturing and processing places, The lifetimes shorten to approximately 5 and 10 days for PETN and RDX particles. These estimates may undergo marked changes according to the environmental conditions to which the residues are

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1 exposed. For example, UV sun radiation may shorten these estimates dramatically. Such
2 environmental effects on explosives residue life times will be discussed in a future
3 publication.
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15 **References**

- 16
17 1. Gershanik A.P.; Zeiri Y. *J. Phys. Chem. A* **2010**, 114, 12403-12410
- 18
19 2. Cundall, R.B.; Palmer, T.F.; Wood C.E.C. *J. Chem. Soc. Farad. Trans.* **1978**, 74, 1339-
20 1345
- 21
22 3. Edwards, G. *Trans Faraday Soc.* 1950, 46, 423-427
- 23
24 4. B.C. Dionne, D.P. Rounbehehler, E.K. Achter, J.R. Hobbs, D.H. Fine, *J. Energ.*
25 *Mater.* **1986**, 4, 447-472
- 26
27 5. Burnham, A.; Gee, R.; Maiti, A.; Qiu, R.; Rajasekar, P.; Weeks, B.; Zepeda-Ruiz, L.
28 *LLNL Technical Report UCRL TR 216963*, 2005. Experimental results on vapor pressure
29 of PETN documented in this work are from R. Behrens' presentation: "Update on the
30 *Analysis of Thermally and Chemically Stabilized PETN Powders*," *JOWOG Focused*
31 *Exchange Meeting*, May **2003**, Sandia National Lab, Albuquerque, NM.
- 32
33 6. F.T. Crimmins, Report UCRL- 50704, Lawrence Radiation Lab. Ca, **1969**
- 34
35 7. J. M. Rosen, C. Dickinson *J. Chem. Eng Data*, **1969**, 14, 120-124
- 36
37 8. R. Stimac data published in G.A. Eiceman, D. Preston, G. Tiano, J. Rodrigues,
38 J.E. Parmeter, *Talanta* **1997**, 45, 57-74
- 39
40 9. A. K. Burnham, S. R. Qiu, R. Pitchimani, B. L. Weeks, *J. Appl. Phys.*, **2009**, 105,
41 104312
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52
53
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55
56
57
58
59
60
10. R. Pitchimani, A.K. Burnham, B. L. Weeks, *J. Phys. Chem .B Letters*, **2007**,111,9182-9185
 11. J. E. Parmeter, G. A. Eiceman, D. A Preston, G. S. Tiano, *Sandia Report SAND-96-2016C, Conf--960767- 2 1*,**1996**, Sandia National Laboratories, Albuquerque, NM
 12. G.A. Eiceman, D. Preston, G. Tiano, J. Rodrigues, J.E. Parmeter, *Talanta* **1997**, *45*, 57-74 13.
 13. Crank, J. *Mathematics of Diffusion*: Oxford University Press: Oxford, 1975
 - 14.Gray, A.; Mathews, B. B.; MacRobert, T. M. *A Treatise on Bessel Functions and their Applications to Physics*: Macmillan and Co.Ltd: London, UK, 1931
 15. Dortch M.; Furey J.; Meyer R.; Fant S.; Gerald J.; Qasim M.; Fredrickson H.; Honea P.; Bausum H.; Walker K.; Johnson M. *Data Gap Analysis and Database Expansion of Parameters for Munitions Constituents*, US Army Gorps.of Engineers Report ERDC/EL TR-05-16, 2005, 35
 16. McKone T.E.; Layton D.W. *Regulatory Toxicology and Pharmacology*, **1986**, *6*,359-380,

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