Lawrence Radiation Laboratory
UNIVERSITY OF CALIFORNIA
LIVERMORE

UCRL-50704

**THE VAPOR PRESSURE OF
PENTAERYTHRITOLTETRANITRATE (PETN)
IN THE TEMPERATURE RANGE
OF 50 TO 98 DEGREES CENTIGRADE**

Francis T. Crimmins
Captain, USAF

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Contents

Abstract	1
Theory	1
The Experiment	2
Findings	5
Conclusions	5
References	6
Appendix I. Computer Program for Calculating P_{AVG} (P_M) and P_{EQ} from Knudsen Effusion Data	7
Appendix II. A Typical Vapor-Pressure Determination	9

THE VAPOR PRESSURE OF PENTAERYTHRITOLTETRANITRATE (PETN) IN THE TEMPERATURE RANGE OF 50 TO 98 DEGREES CENTIGRADE

Abstract

The vapor pressure of pentaerythritol-tetranitrate (PETN) has been determined in the temperature range of 50 to 98°C using the effusion technique developed by Knudsen. A least-squares reduction of

the experimental data gave the following equation:

$$\text{Log}_{10} P_{\text{mm}} = 14.44 - 6352/T$$

The enthalpy or latent heat of sublimation calculated from this equation is 29.0 kcal/mole.

Theory

Recent interest in measuring the vapor pressures of various organonitro compounds has led to the development of a technique for determining the equilibrium vapor pressures (P_{EQ}) of these materials at low temperatures (50 to 100°C) and at relatively high vapor pressures (10^{-6} to 10^{-2} mm Hg) using the effusion method developed by Knudsen.¹

The effusion method consists of measuring the weight of material per unit time as it effuses through an orifice of known area at a known temperature into a vacuum. The ideal Knudsen equation² can then be used to calculate the vapor pressure (P_{M}) inside the Knudsen cell.

$$P_{\text{M}}(\text{atm}) = \frac{m}{t} (2\pi RT/M)^{1/2} = \frac{Z(MT)^{1/2}}{44.3 A_o t} \quad (1)$$

where

m = weight loss in g/cm² of
orifice area

A_o = orifice area in cm²

M = mol wt

Z = moles effusing in t sec

T = temperature in °K

In order to relate P_{M} to P_{EQ} , three factors have to be considered: (a) the possible resistance to condensation represented by a condensation coefficient (α) for the surface of the material under consideration; (b) the resistance exerted on the effusing molecules by the body of the cell; and (c) the resistance exerted on the effusing molecules by the orifice.

The condensation or accommodation coefficient (α) is derived by considering that in a steady-state situation the number of molecules that condense on the surface of a material must equal the number of molecules vaporizing from the same surface. But all the molecules condensing on a surface do not always stick. Therefore,

$$\alpha = \frac{\text{No. of striking and sticking molecules}}{\text{No. of striking molecules}}$$

Factors (b) and (c) can be considered as the probability that a given molecule will escape from the cell and the orifice, respectively. Factor (b) can be represented in terms of the cross-sectional area of the cell (A) and the Clausing probability factor³ ($\bar{W}_A$) for the cell. Factor (c) can likewise be represented by the cross-sectional area of the orifice (B) and the Clausing factor (W_B).

Motzfeldt⁴ has derived the following equation relating P_{EQ} to P_M :

$$P_{EQ} = P_M \left[1 + f \left(\frac{1}{\alpha} + \frac{1}{\bar{W}_A} - 2 \right) \right] \quad (2)$$

where

$$f = W_B \left(\frac{r_o}{r_c} \right)$$

r_o = radius of orifice

r_c = radius of cell

Calculations of W_A and W_B for cylindrical geometries have been made by Clausing³ and Whitman.⁵ The influence of factor (c) can be considerably reduced by using a knife-edged orifice. Balson⁶ has developed the following equation to calculate W_B for the conical geometries associated with such knife-edged orifices:

$$W_B = \frac{(1 + \cos \theta) 2}{(1 + \cos \psi) (2 - \cos \psi + \cos \theta)} \quad (3)$$

where

$$\cot \psi = \tan \beta + (L/2r) (1 + \tan^2 \beta)$$

$$\cot \psi = (R^2 + L^2 - r^2)/2rL$$

$$\tan \theta = \frac{1 + (L/r) \tan \beta}{\tan \beta + (L/2r) (\tan^2 \beta - 1)}$$

$$\tan \theta = 2LR/(R^2 - L^2 - r^2)$$

The symbols used in Eq. (3) can best be explained by referring to Fig. 1, which shows an arrangement where the conical outlet of semiangle β , entrance radius r , exit radius R , and length L is enveloped by a circle having a center x . For a complete discussion of the derivation of these equations, see Balson's paper.

An examination of Eq. (2) reveals that as $f \rightarrow 0$, $P_M \rightarrow P_{EQ}$; but $f \rightarrow 0$ as $r_o \rightarrow 0$. Therefore, by plotting P_M versus the orifice area and extrapolating to zero orifice area, P_{EQ} can be obtained independently of α . Once P_{EQ} has thus been obtained, α can be calculated.

Fig. 1. Schematic of the geometric parameters used to derive Eq. (3).

The Experiment

The cell used in this experiment is made of gold-plated stainless steel; it

has a diameter of 0.7 ± 0.001 in. and a height of 0.72 ± 0.003 in. The top of the

cell is threaded to accommodate the cell cover, which is also threaded and which has a thickness (L in Fig. 1) of $0.025^{+0.001}_{-0.004}$ in. The orifice in the cell cover is knife-edged and drilled at an angle of 35° (β in Fig. 1). Four different covers, all interchangeable on the cell, have been made with the orifice diameters listed in Table 1. The Clausing probability factor, W_A , for the cell is 0.5136. W_B has been calculated from Eq. (3) for the four orifice diameters and is listed in Table 1.

Table 1. Cell parameters for four cell covers with different orifice diameters.

d_o (mm)	r_o (in.)	r_{cell} (in.)	W_A	W_B
0.461	0.0091	0.36	0.5136	0.972
0.968	0.0190	0.36	0.5136	0.962
1.993	0.0392	0.36	0.5136	0.965
2.967	0.0584	0.36	0.5136	0.971

A Mettler Thermoanalyzer (MTA) was chosen as the most convenient instrument with which to obtain the weight loss of effusing material as a function of time and temperature. The MTA has an advantage over previous methods of measuring weight loss in that it provides a continuous recording of weight of material versus time and temperature without disturbing the cell or breaking the vacuum. The vacuum system in the MTA is capable of maintaining a vacuum of better than 8×10^{-6} mm Hg in the furnace chamber. The balance has a capacity of 16 g and a sensitivity of 50 μ g. The recorder print-out has a readability of 0.02 mg. The furnace has a maximum temperature fluctuation of $\pm 0.5^\circ\text{C}$.

The pentaerythritoltetranitrate (PETN)

used for this study was prepared by slurring a PETN-acetone solution with activated charcoal, filtering off the charcoal, and precipitating the PETN out of a water-ethanol solution at -23°C . This material was dried at ambient temperature under vacuum for two weeks and then rolled to a uniform particle size. Its melting point was $141.3 \pm 0.2^\circ\text{C}$. Analysis by thin layer chromatography showed the following impurities: tetrapentaerythritoldecannitrate, 0.02-0.04 percent; pentaerythritoltrinitrate, 0.01-0.02 percent; no dipentaerythritolhexanitrate or tripentaerythritooctannitrate.

The equilibrium vapor pressure for PETN as a function of temperature was calculated from Eq. (2) using the computer routine listed in Appendix I. A least-squares calculation was applied to this data, yielding the following equation:

$$\log_{10} P_{\text{mm}} = 14.44 - 6352/T \quad (4)$$

The latent heat or enthalpy of sublimation of PETN was determined from Eq. (4) as:

$$\Delta H_{\text{sub}}^\circ = (-\text{slope}) (2.303) (1.987 \text{ cal/deg-mole})$$

The results of our studies are listed in Table 2 and are shown graphically in Fig. 2.

A typical P_{EQ} determination is followed step by step in Appendix II for the convenience of the reader.

Fig. 2. PETN vapor pressure.

Table 2. PETN vapor pressure.

P_{EQ} (mm Hg)	T(°K)	1/T	D_o (mm)	P_{EQ} (mm Hg)	T(°K)	1/T	D_o (mm)
5.47×10^{-6}	323.46	0.00309	0.968	8.13×10^{-5}	347.85	0.00287	0.968
2.26×10^{-5}	330.88	0.00302	0.968	2.01×10^{-4}	348.59	0.00287	0.461
5.93×10^{-5}	340.14	0.00293	0.968	2.22×10^{-4}	353.72	0.00282	0.968
2.34×10^{-4}	347.58	0.00288	0.461	4.55×10^{-4}	361.48	0.00276	0.968
1.36×10^{-4}	347.72	0.00288	1.993	2.24×10^{-3}	370.09	0.00270	0.968
2.33×10^{-4}	347.72	0.00288	1.993	2.81×10^{-3}	371.45	0.00269	0.968

Findings

For PETN, α [Eq. (2)] was found to be approximately equal to 1.

All weight-loss measurements were taken over a period of at least 24 hr, ignoring the first 2-3 hr weight loss to allow equilibrium to be reached.

Comparison of our data with that previously reported by Edwards⁷ for PETN in the temperature range of 97 to 139°C

shows that our values are slightly higher than his, with the respective slopes converging near 140°C. The least-squares routine used previously was also used to fit his data. The results are shown graphically in Fig. 2. Statistical analysis of the data at the 90 percent confidence level shows that there is a significant difference between the two sets of results.

Conclusions

The vapor pressure of PETN has been determined between the temperatures of 50 and 98°C. The following equation has been found to be the best fit for the resulting data:

$$\log_{10} P_{mm} = 14.44 - 6352/T$$

Using this equation, the enthalpy of sublimation has been calculated to be 29.0 kcal/mole.

References

1. Knudsen, M., "Experimentelle Bestimmung des Druckes gesättigter Quecksilberdämpfe bei 0° und höheren Temperaturen," Ann. Physik 29, 179 (1909).
2. Hollahan, J. R., "Molecular Effusion: Its Newer Features and Applications," J. Chem. Educ. 39, 23 (1962).
3. Clausing, P., "Über die Strömung sehr verdünnter Gase durch Röhren von beliebiger Länge," Ann. Physik 12, 961 (1932).
4. Motzfeldt, K., "Thermal Decomposition of Sodium Carbonate by the Effusion Method," J. Phys. Chem. 59, 139 (1955).
5. Whitman, C. I., "On the Measurement of Vapor Pressures by Effusion," J. Chem. Phys. 20, 161 (1952).
6. Balson, E. W., "Some Aspects of Molecular Effusion," J. Phys. Chem. 65, 1151 (1961).
7. Edwards, G., "Vapour Pressure of Cyclo-Trimethylene-Trinitramine (Cyclonite) and Pentaerythritol-Tetranitrate," Trans Faraday Soc. 49, 152 (1953).

Appendix I

Computer Program for Calculating P_{AVG} (P_M) and P_{EQ} from Knudsen Effusion Data

The following program is written in Fortran IV for use on a CDC 6600 computer in combination with the LRL Octopus teletype system. Included in the program are Knudsen cell geometry factors that are necessary to calculate P_{EQ} from weight-loss data. The following variables are defined in order to assist in understanding the program:

DIAM = the diameter of the orifice hole (mm)
T = temperature of cell (°C)
SEC = time between weight loss readings (hr)
AMOLE = molecular weight of material being investigated
G = weight loss in mg at temperature T during time SEC
RO = radius of the orifice (in.)
RC = radius of the crucible (in.)

```
PROGRAM FRAN2(TAPE 59)
DIMENSION P(25)
DIMENSION GG(25)
DIMENSION SECC(25)
DIMENSION TEMPP(25)
DIMENSION DIAMM(25)
44 K=1
  S=0.
  C=0.
  DO 22 I=1, 25
    P(I)=0.
    GG(I)=0.
    SECC(I)=0.
    TEMPP(I)=0.
    DIAMM(I)=0.
22 CONTINUE
  1 READ(59, 2) G
  2 FORMAT(F20. 7)
  IF(G. EQ. 0. ) GO TO 77
  DIAM=0.968
  T=88.33
  SEC=1.
  AMOLE=316.14
```

```

TEMP=T+273.15
SEC=SEC*60.*60.
WT=G*0.001
F=WB*((RO/RC)**2.)
WB=0.961
RO=0.019
RC=0.36
WA=0.5136
ALPHA=1.
A=((0.7854)*((DIAM*0.1)**2))
Z=WT/AMOLE
GG(K)=G
SECC(K)=SEC
TEMPP(K)=TEMP
DIAMM(K)=DIAM
P(K)=(((Z*((TEMP*AMOLE)**0.5)))/(44.33*A*SEC))*760.
K=K+1
GO TO 1
77 DO 99I=1, 25
  IF(P(I).EQ.0.) GO TO 99
  C=C+1.
  S=P(I)+S
99 CONTINUE
  PAVG=S/C
  PEQ=PAVG*(1.+F*(1./ALPHA +1./WA -2.))
4 WRITE(59,12)PEQ
12 FORMAT(/ /36H EQUILIBRIUM VAPOR PRESSURE IN MM IS, 3X, E20.3
5 WRITE(59,13) PAVG
13 FORMAT(/ /26H AVERAGE PRESSURE IN MM IS, 3X, E20.3)
6 WRITE(59,14)(I, P(I), GG(I), SECC(I), TEMPP(I), DIAMM(I), I=1, 25)
14 FORMAT(/2HP(I2, 2H)=, 1X, E10.4, 2X, 3HWT=, F8.3, 2X, 4HSEC=, F
18.2, 1X, 5HTEMP=, F7.2, 2X, 5HDIAM=, F6.4)
GO TO 44
END

```

Appendix II

A Typical Vapor-Pressure Determination

In this appendix, a typical vapor-pressure determination will be followed step by step.

The conditions for the experiment were as follows:

- (a) Material: PETN (No. 319), rolled to uniform particle size
- (b) Crucible: gold-plated, stainless-steel Knudsen cell
- (c) Orifice diameter in cover: 0.968 mm
- (d) Sample weight: ~1 g
- (e) DTG sensitivity: 5 mg/min
- (f) Recorder Speed: 2 in./hr
- (g) Heating rate to temperature: 2°C/min
- (h) Temperature: 340.14°K

The recorder output from the MTA is shown in Fig. 3. Line 1 on the graph is the pressure output from the ionization gage located just below the sample chamber (pressure values can be read with a template). Line 2 is the temperature output from the sample chamber (25 to 1000°C full scale). Line 3 is the DTG trace. Line 4 is the weight trace (10 mg full scale). Line 5 is another weight trace (100 mg full scale). The numbers on the right side of the chart are the weight readings taken hourly from line 4.

The temperature of the experiment was determined by using a millivolt potentiometer. Weight-loss data for the first four hours of the run was ignored to allow equilibrium to be reached. The data taken from the recorder chart is summarized in Table 3. The P_{AVG} and P_{EQ} data were calculated by the computer program listed in Appendix I using the proper values for the listed variables. The output from this program is shown in Table 4.

Fig. 3. MTA recorder output for a typical PETN vapor-pressure determination.

Table 3. Summary of data from the MTA recorder chart.

Chart reading	Δ wt (mg)	Time (hr)	P_{mm} (mm Hg $\times 10^5$)
7.73		0	
7.63	0.10	1	6.71
7.54	0.09	2	6.04
7.44	0.10	3	6.71
7.35	0.09	4	6.04
7.26	0.09	5	6.04
7.17	0.09	6	6.04
7.09	0.08	7	5.37
7.00	0.09	8	6.04
6.91	0.09	9	6.04
6.83	0.08	10	5.37
6.74	0.09	11	6.04
6.66	0.08	12	5.37
6.58	0.08	13	5.37
6.49	0.09	14	6.04
6.40	0.09	15	6.04
6.32	0.08	16	5.37

Table 4. Computer output for PETN vapor-pressure determination.

.10
.09
.10
.09
.09
.09
.08
.09
.09
.08
.09
.08
.08
.09
.09
.09
.08
0.00

EQUILIBRIUM VAPOR PRESSURE IN MM IS

5.930E-05

AVERAGE PRESSURE IN MM IS

5.915E-05

P(1) = 6.7122E-05	WT= .100	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(2) = 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(3) = 6.7122E-05	WT= .100	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(4) = 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(5) = 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(6) = 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(7) = 5.3697E-05	WT= .080	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(8) = 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(9) = 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(10)= 5.3697E-05	WT= .080	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(11)= 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(12)= 5.3697E-05	WT= .080	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(13)= 5.3697E-05	WT= .080	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(14)= 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(15)= 6.0409E-05	WT= .090	SEC= 3600.00	TEMP= 340.14	DIAM= .9680
P(16)= 5.3697E-05	WT= .080	SEC= 3600.00	TEMP= 340.14	DIAM= .9680

Distribution

LRL Internal Distribution

Michael M. May
D. Seaton
M. Fulk
F. Walker
G. Dorrough/R. Batzel
J. Kury
A. Maimoni
TID Berkeley
TID File 30

External Distribution

D. Ornellas 2
I. G. Gwillim
Atomic Weapons Research Establishment
England

L. Smith
R. Spaulding
Los Alamos Scientific Laboratory
Los Alamos, New Mexico

F. T. Crimmins
AFATL (ATRN)
Elgin AFB, Florida 10

TID-4500 Distribution, UC-4, Chemistry 207

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Printed in USA. Available from the Clearinghouse for Federal
Scientific and Technical Information, National Bureau of Standards,
U. S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65.

GL/lh