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VAPOR PRESSURES AND HEATS OF SUBLIMATION OF SOME HIGH MELTING ORGANIC EXPLOSIVES

By
Jerome M. Rosen
Charles Dickinson

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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ABSTRACT: The Langmuir method was used to determine the vapor pressures and heats of sublimation of several high melting organic explosives. The temperatures at which each compound would have a vapor pressure of 10^{-7} torr are: (1) cyclotrimethylenetrinitramine (RDX), 48.0°C; (2) cyclotetramethylenetetranitramine, beta polymorph, (β-HMX), 121.9°C; (3) 2,4,6-trinitroaniline (TNA), 44.0°C; (4) 1,3-diamino-2,4,6-trinitrobenzene, form I polymorph, (DATB-I), 79.8°C; (5) 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 131.4°C; (6) 2,2',4,4',6,6'-hexanitrostilbene (HNS), 170.6°C. Within a series those compounds which form the strongest intermolecular hydrogen-bonds have the highest heats of sublimation.

Carl Boyars, Chief
Advanced Chemistry Division
CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

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Explosives have been used to perform a variety of functions in space and military systems. Information contained in this report makes it possible for design engineers to select the appropriate explosive for each device and mission. The very low vapor pressure of HNS has contributed to its selection for many applications in the Apollo program. This work was done under Task Numbers ORD-332-001/092-1/UF17-354-301, Explosives Characterization and MAT 03L 000/ZR 011 01 01, Explosives Chemistry.

E. F. SCHREITER
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

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INTRODUCTION

Measurements of the vapor pressure of high energy compounds are of both theoretical and practical importance. From the practical viewpoint, one is able to compute a rate of recession of a free surface of an explosive heated in a hard vacuum (equivalent to outer space), as a function of temperature. This type of information is of value to the design engineer concerned with space applications of explosive devices, particularly those involving long exposure times at elevated temperatures. If there is a potential problem arising from losses of material in an explosive device by sublimation, the engineer is able to estimate the magnitude of the problem by calculating recession rates.

The vapor pressure and heat of sublimation data are of theoretical importance in computing bond energies. For bond energy estimates, the heat of formation of the vapor is required. This is the sum of the heat of formation of the solid and the heat of sublimation. Because the heat of sublimation has been difficult to determine and thus generally not available, it has been estimated by many investigators. The direct determination of the heat of sublimation removes a source of uncertainty in calculating bond energies.

EXPERIMENTAL

The Langmuir method was used for the determination of vapor pressures from measurements of the rates of sublimation at constant temperature[9,4]. Vapor pressures were computed from the observed weight loss of the sample heated in a vacuum. The expression used was:

$$P(\text{torr}) = 17.14 \times G \times (T/M)^{\frac{1}{2}},$$ where

G is the weight loss in $\text{gm/cm}^2\text{/sec}$,
T is the absolute temperature
M is the molecular weight.

In the calculations a condensation coefficient of 1 is assumed. This, we feel, is justified by the good agreement between the results obtained from the Langmuir and Knudsen method results for RDX.

Samples were heated at a constant temperature in a glass vacuum apparatus, Figure 1. After centering the sample holder in the jacketed section, the section was sealed and the system evacuated to at least 5×10^{-7} torr. Two types of sample holders were used, Figure 2. One consisted of a metal plate with machined, circular depressions. The other type was constructed by cutting a glass sample vial about 8 mm from the closed end. The sample was heated by passing the vapors of a refluxing liquid through the jacket of the sample section. Two 500 ml round-bottomed flasks heated by electric mantles and located near the ends of the jacketed region were used for the reflux liquid, and the vapors were condensed by a single water-cooled condenser located as indicated. The jacketed section was insulated with eight layers of aluminum foil.

Constant temperatures were provided by a series of liquids, Table 1, maintained at the reflux point. The boiling points of the liquids were determined in the usual manner. However, the temperature at the sample is lower than the boiling point of the refluxing liquid. For example, in the case of water this difference was 2.1°C. A temperature correction then, was applied for all the liquids used.

Temperatures inside the vacuum apparatus at the sample position were determined for five of the liquids at reflux. This was done by sealing a chromel-alumel thermocouple inside the apparatus. From the measurements of these five liquids a temperature correction curve, Figure 3, was constructed from the differences between the temperature inside the vacuum apparatus and the temperature of the refluxing liquid. Temperature corrections for all liquids were taken from this curve.

We feel that the uncertainty in the temperature represents the largest source of experimental error. This uncertainty is estimated to be about 0.2°C to 0.3°C at the temperatures below 150°C for heating periods less than 72 hours. At higher temperatures and

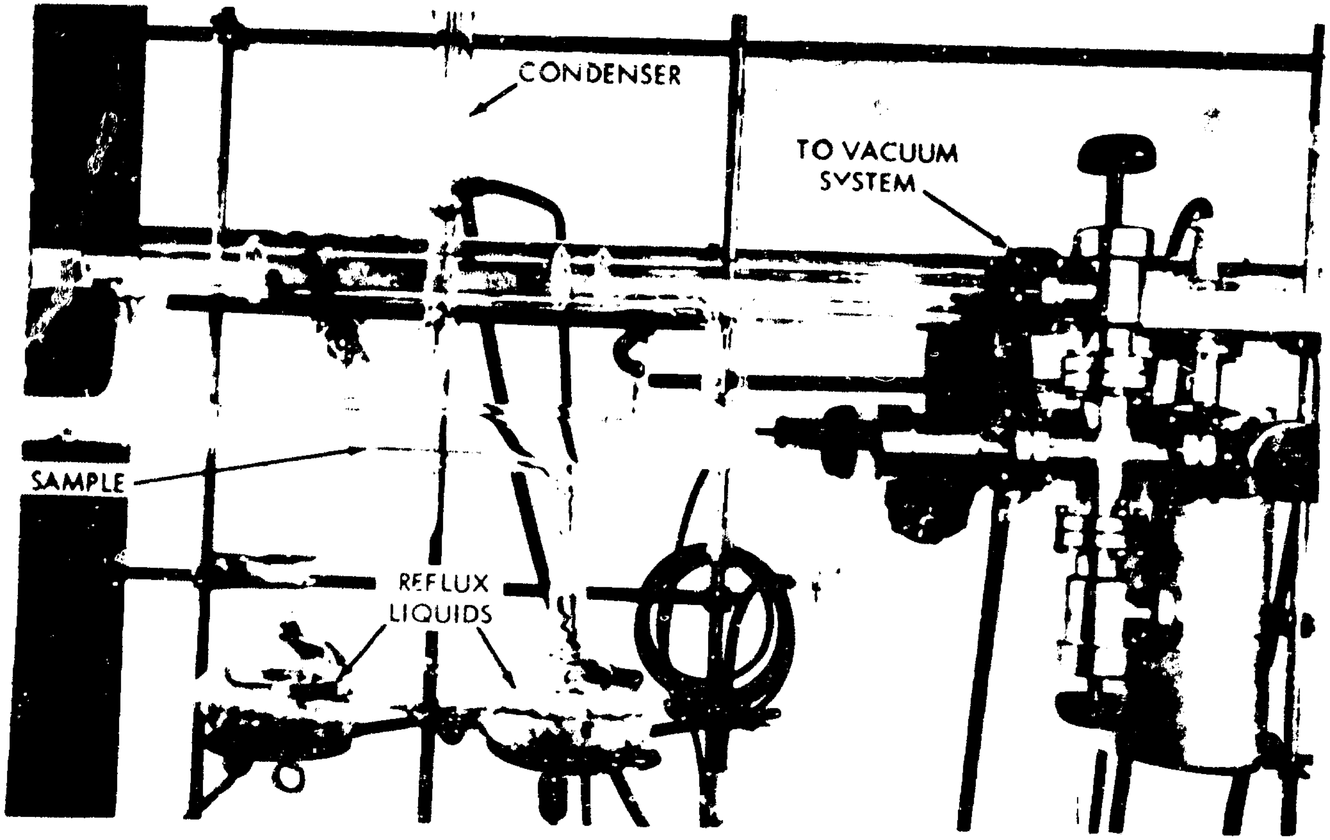

FIG. 1
VAPOR PRESSURE APPARATUS

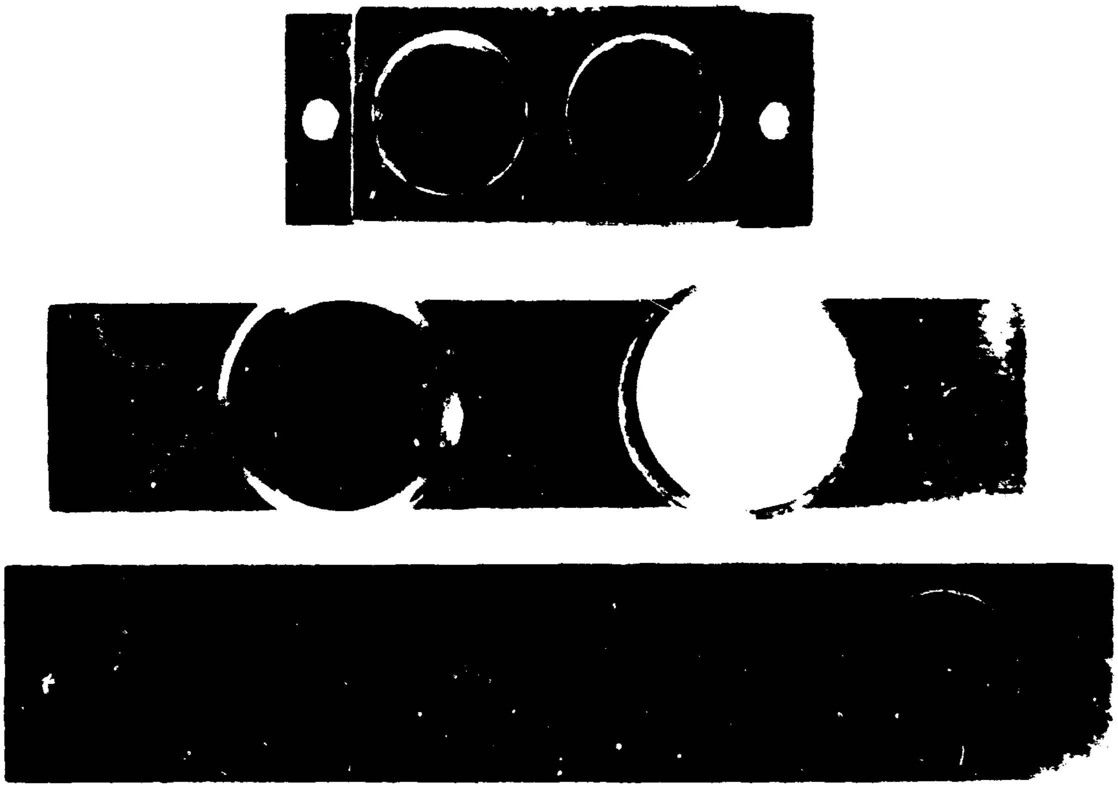

FIG. 2 SAMPLE HOLDERS

TABLE 1. Temperature of Reflux Liquids.

Liquid	Boiling Temperature*	Temperature in Vacuum Apparatus
Methyl acetate	57.4°C	55.7°C
Methanol	64.4	62.6**
Benzene	80.1	78.2
n-Propanol-water azeotrope	87.3	85.3**
Water	99.8	97.7**
Toluene	110.3	108.1
n-Butanol	117.8	115.6
Chlorobenzene	131.8	129.3
m-Xylene	138.8	136.2
Anisole	152.7	150.0
Mesitylene	164.4	161.4**
Phenetole	169.4	166.3
o-Dichlorobenzene	180.5	177.3
Benzonitrile	189.3	185.8
Nitrobenzene	210.3	206.3**

* At 755 torr atmospheric pressure

** Temperatures determined by thermocouple measurements with external pressure of 755 torr

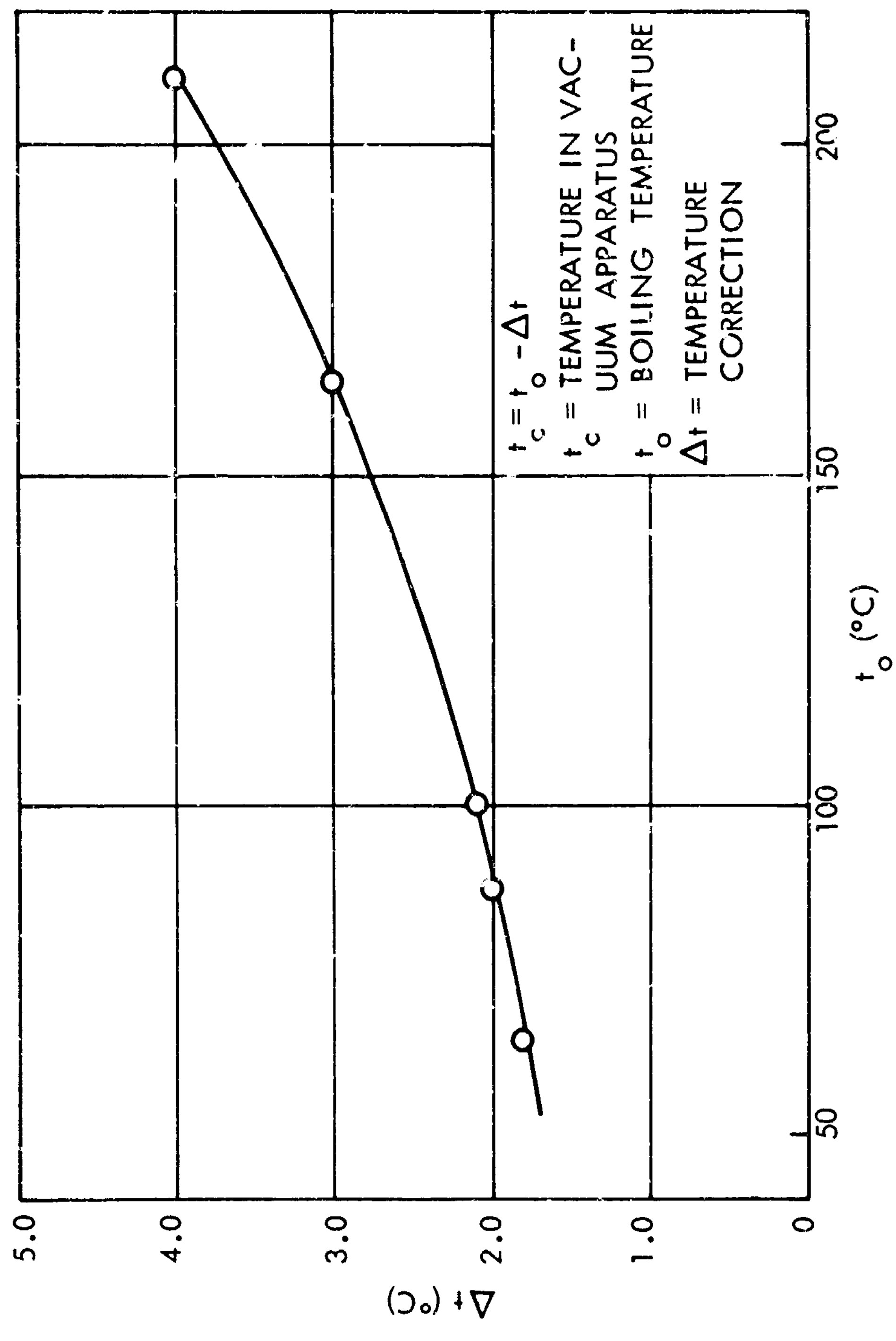

FIG. 3 TEMPERATURE CORRECTION CURVE

longer times the estimated error is slightly greater, perhaps 0.5°C. Barometric pressure fluctuations affect the boiling points of the heating liquids and this is likely to be a source of some error during the longer runs.

About 40 to 50 minutes are required for the sample to reach its maximum temperature after beginning to heat the reflux liquid. This time interval was determined by following the temperature increase at the sample position as a function of time. To determine time intervals for the experimental runs a time of 40 minutes after the initiation of heating was used as time zero in every case. At the completion of the heating period the jacketed section was cooled with an air gun for about 15 minutes, after first removing a part of the aluminum foil insulation. The error in the measurement of the heating interval is probably about 0.2 hour.

The vacuum system consists of an eight liter per second Varian Vac Ion pump and a Varian titanium sublimation pump connected to a stainless steel manifold. The manifold is a cross fitting with four stainless steel, high vacuum valves in the arms of the cross. One valve isolates the pumps from the system, a second valve isolates a fore pump. The remaining two valves connect two glass, jacketed units to the vacuum system through glass to metal seals. All glass parts are made of 1.5 inch I.D. borosilicate glass. Each unit may be operated independently.

All of the samples were carefully purified by repeated recrystallization and thoroughly dried to remove residual solvent. In general, these materials represent the highest quality available for study. The purity of the samples was tested by at least one of the following techniques in each case: thin layer chromatography, melting point, or gas chromatography. The compounds in this work have all been studied at temperatures far higher than any used in the determination of vapor pressures. At these elevated temperatures no decomposition was detected as determined by gas evolution techniques[11] and thin layer chromatography[7].

HMX has four well characterized polymorphs. β-HMX is stable up to 102°C, although it does not undergo a solid-solid transition until well above 150°C. Thus, all of the measurements on β-HMX except the one at 97.6°C are in the temperature range where this crystal modification of HMX is unstable. It was necessary to heat β-HMX for forty days at 97.6°C to obtain a measurable loss in weight. At the completion of this run, the apparatus was rinsed with acetone. All of the sublimed material was collected and identified as β-HMX by refractive index measurements, indicating no decomposition had occurred. Upon completion of the run at the highest temperature, 129.3°C, the sample was examined by X-Ray diffraction and found to still be the β polymorph.

DATB has two well characterized polymorphs, the I→II transition occurring at 217°C. In contrast to HMX, DATB easily undergoes this transition even in the solid phase, which may be explained by the rather higher vapor pressure of DATB. However, the highest temperature used for DATB-I in these vapor pressure measurements (108°C) is over 100° lower than the transition point. At these relatively low temperatures no detectable amount of I→II conversion has ever been found.

RESULTS AND DISCUSSION

The vapor pressures of the compounds at the temperatures of the experiments are reported in Table 2, along with a summary of the experimental data. The least squares fits of the vapor pressures to the equation:

$$\log_{10}P = B/(4.576 \times T^{\circ}K) + A$$

are given in Figures 4 through 9. The line constants A and B, B representing the heat of sublimation, are also given in Table 2.

The vapor pressure of RDX is in good agreement with the data obtained by the National Bureau of Standards (NBS) using a Knudsen cell[10]. The NBS sample, supplied by this laboratory, was a part of the same sample used in this work. Vapor pressure measurements on RDX by Edwards using a Knudsen cell are somewhat higher, although his data at 131°C and 138°C would appear to be in reasonable agreement with the other data[5].

TABLE 2. Results and Data

COMPOUND/TEMP(°C)	VAPOR PRESSURE (x10^7 torr)	WEIGHT LOSS (gm x 10^3)	TIME (seconds)	AREA (cm^2)	LINE CONSTANTS	
					A	B
RDX					14.18	-31,110
55.7	3.50	9.63	424,080	1.355		
55.7	3.24	5.05	424,080	0.766		
55.7	3.42	5.06	424,080	0.728		
62.6	8.21	7.63	144,900	1.351		
62.6	7.14	11.54	144,900	2.35		
62.6	8.63	15.02	144,900	2.53		
78.2	69.3	45.09	177,300	0.791		
78.2	78.7	20.79	72,000	0.791		
85.3	155	53.90	57,600	1.317		
97.7	735	108.48	24,120	1.355		
97.7	667	55.72	24,120	0.766		
97.7	702	55.68	24,120	0.728		
TNA						
55.7	5.48	4.82	235,080	0.770	12.10	-27,710
55.7	5.37	4.62	235,080	0.753		
55.7	4.80	10.60	322,200	1.410		
55.7	4.92	19.50	322,200	2.53		
62.6	10.80	13.25	331,200	0.770		
62.6	11.10	13.84	331,200	0.783		
78.2	68.0	18.86	76,680	0.770		
78.2	65.6	18.11	76,680	0.766		
78.2	68.3	18.54	76,680	0.753		
85.3	163	125.20	65,160	2.53		
97.6	628	52.60	23,760	0.770		
97.6	625	53.19	23,760	0.783		

TABLE 2. Continued

DATB-I					13.73	-33,470
62.6	0.081	3.3	303,200	6.33		
78.2	0.879	12.4	459,360	6.33		
85.3	2.36	4.9	68,400	6.33		
85.3	2.25	5.9	86,400	6.33		
85.3	2.09	5.1	80,280	6.33		
97.6	9.80	15.3	52,200	6.33		
97.6	9.12	15.9	58,320	6.33		
108.1	34.0	31.0	30,960	6.33		
					16.18	-41,890
β-HMX						
97.6	0.0324	3.7	3,456,000	6.33		
108.2	0.164	4.6	860,400	6.33		
115.6	0.390	1.97	424,080	2.34		
115.6	0.385	1.98	424,080	2.38		
115.6	0.419	2.09	424,080	2.31		
129.3	2.83	4.92	145,800	2.38		
129.3	2.87	4.83	145,800	2.31		
					14.73	-40,210
TATB						
129.3	0.733	4.06	845,280	1.403		
129.3	0.746	4.10	845,280	1.392		
136.2	1.83	6.36	315,000	2.38		
136.2	1.93	6.50	315,000	2.31		
150.0	10.3	11.02	172,800	1.355		
150.0	9.42	10.41	172,800	1.403		
150.0	9.73	10.67	172,800	1.392		
161.4	32.2	29.28	86,400	2.34		
161.4	32.3	29.00	86,400	2.31		
166.4	45.8	42.09	86,400	2.38		
177.3	167.0	49.16	28,440	2.34		

TABLE 2. Continued

						14.19	-43,010
HNS							
	161.4	0.396	4.10	688,680	2.53		
	166.4	0.592	12.8	578,880	6.33		
	177.3	2.15	22.9	288,000	6.33		
	185.8	4.97	12.25	168,480	2.53		
	206.5	39.4	36.55	64,800	2.53		

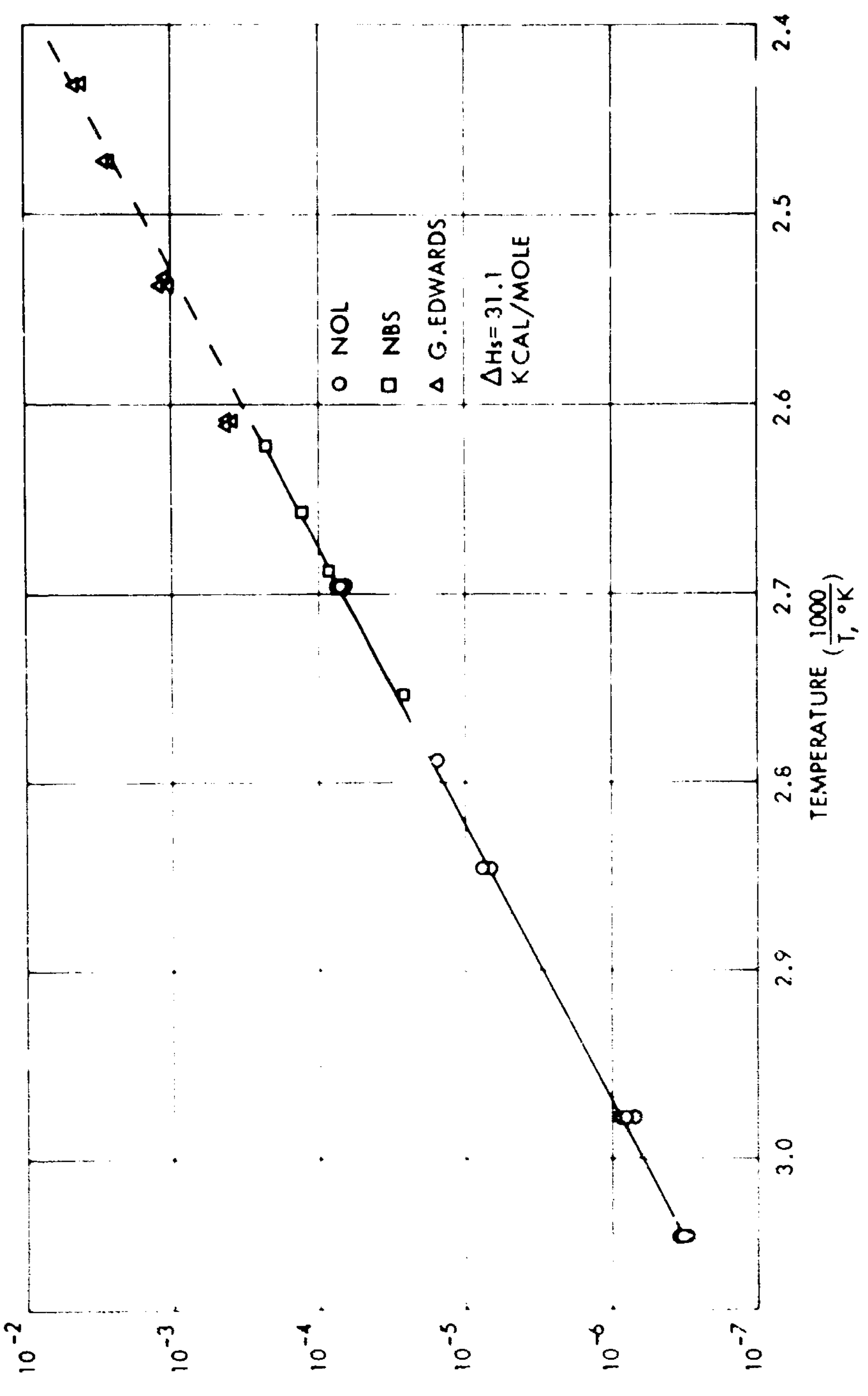

FIG. 4 VAPOR PRESSURE OF RDX

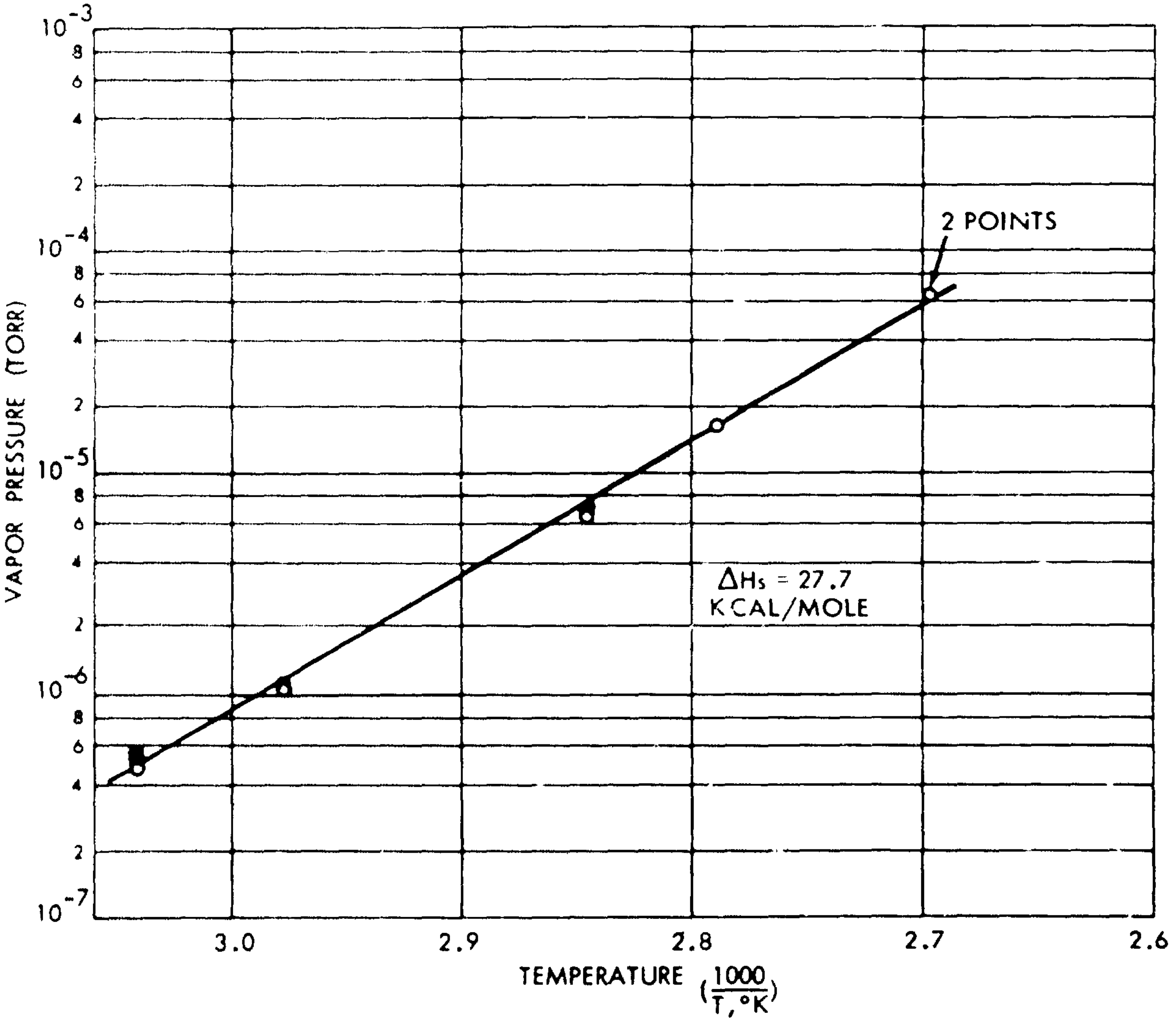

FIG. 5 VAPOR PRESSURE OF TNA

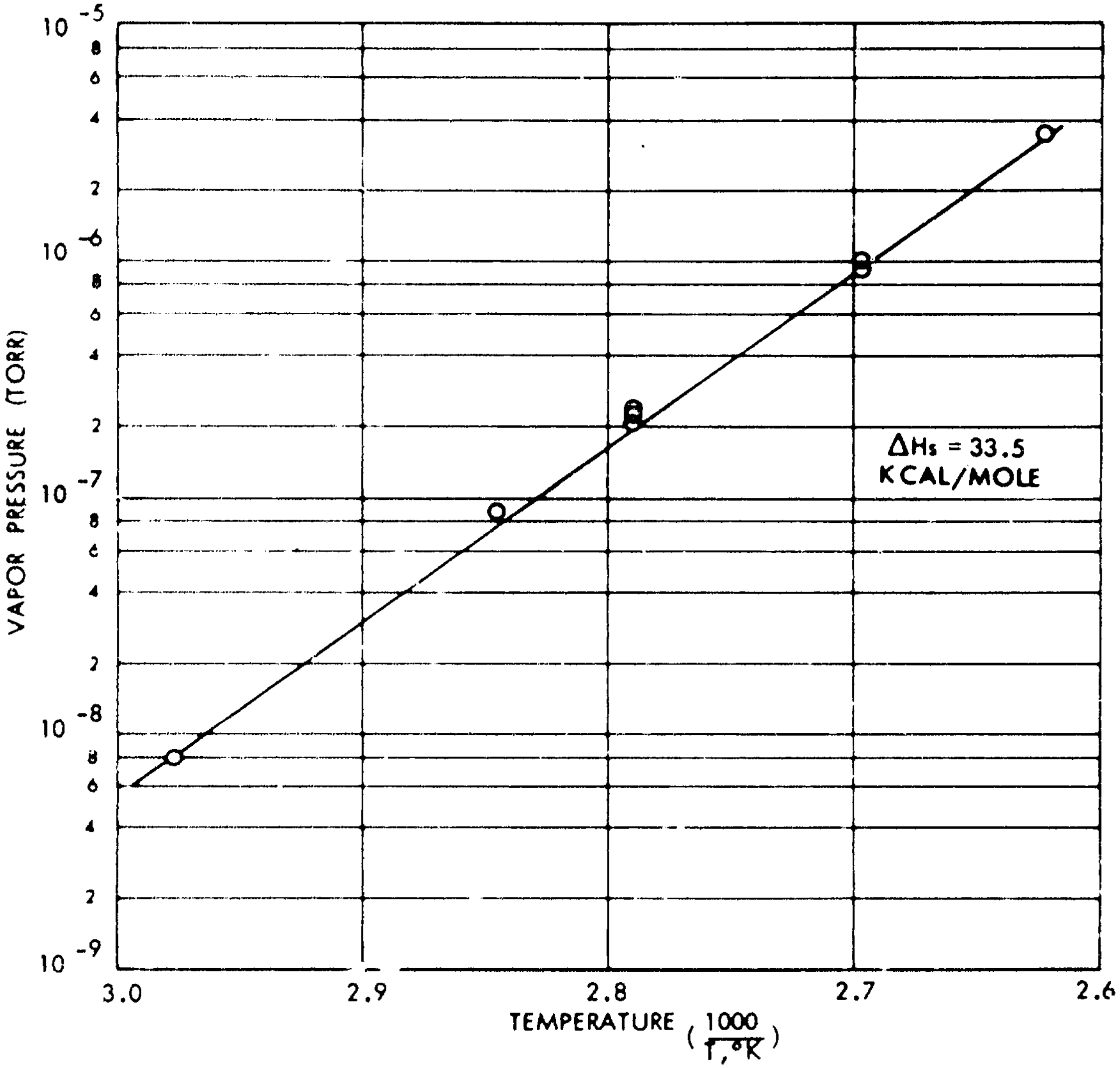

FIG. 6 VAPOR PRESSURE OF DATB-I

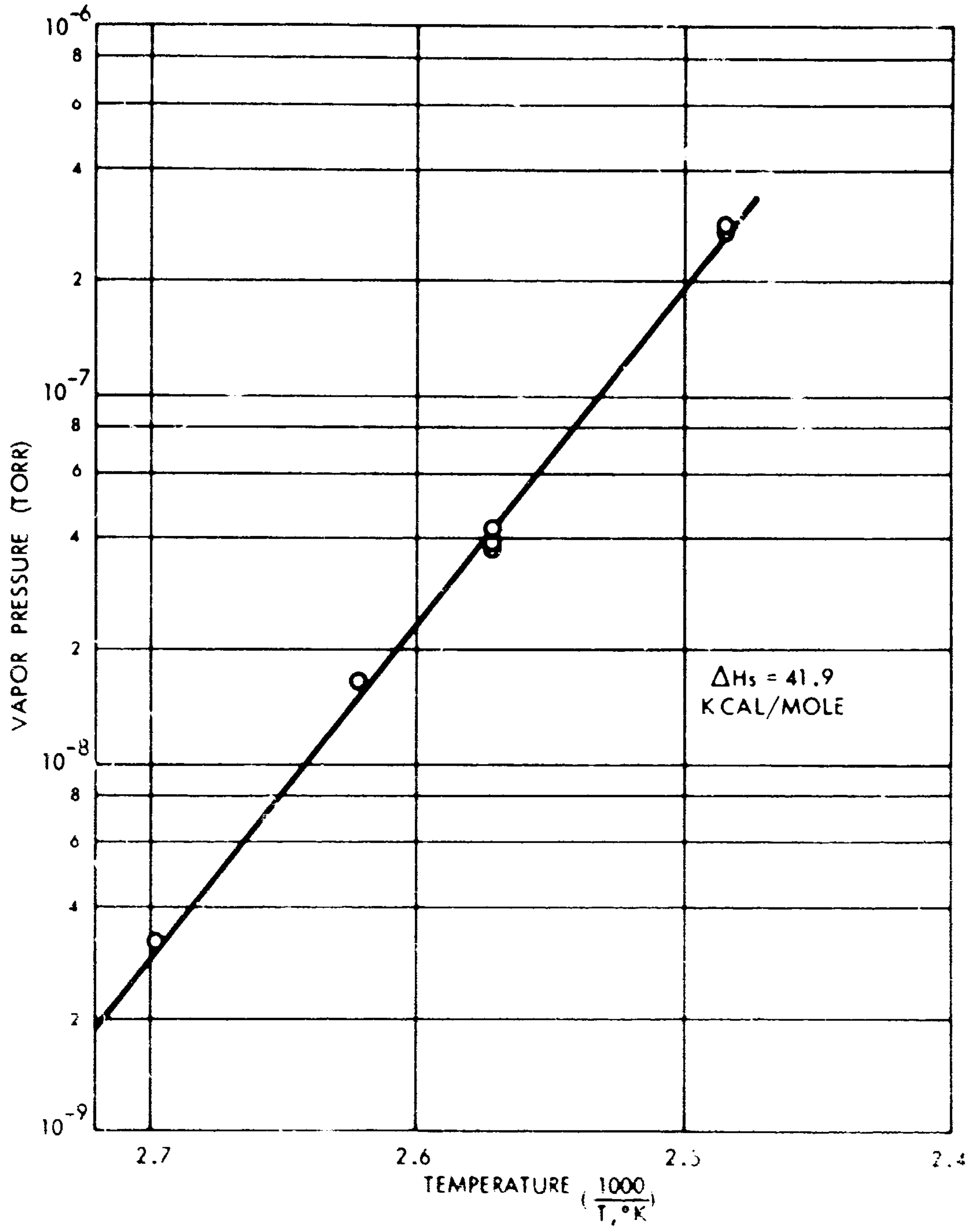

FIG. 7 VAPOR PRESSURE OF β-HMX

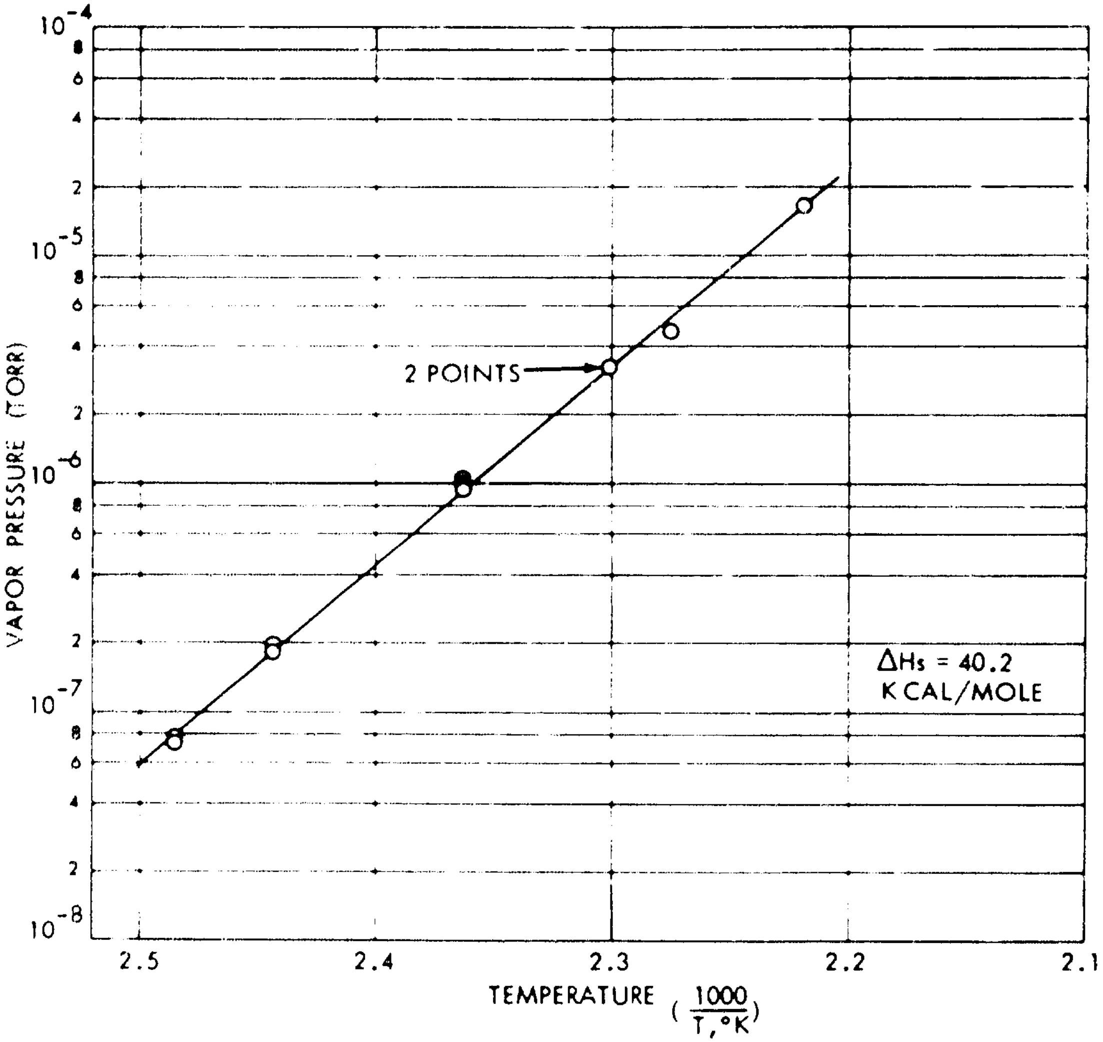

FIG. 8 VAPOR PRESSURE OF TATB

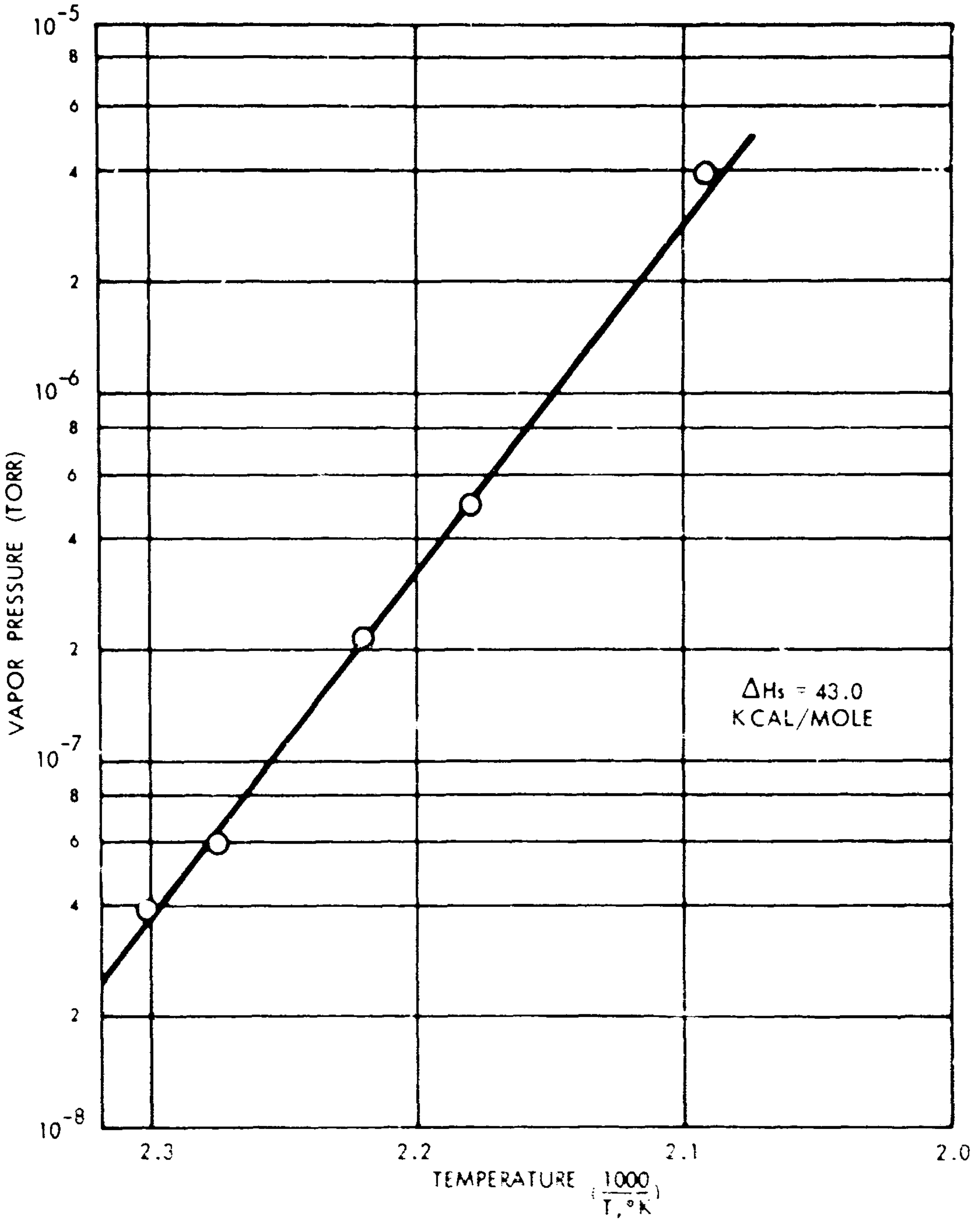

FIG. 9 VAPOR PRESSURE OF HNS

Ignoring any effects caused by not correcting to a standard temperature, several interesting observations may be made on the heats of sublimation and the properties of the compounds. Thus the difference between the molar heats of sublimation of RDX and β-HMX, 10.78 kcal/mole, apparently is largely a function of molecular weight. This is indicated by the specific heats of sublimation, 140.0 and 141.4 cal/gm, respectively, and agrees with the known structures of β-HMX[1] and RDX[6] which indicate no marked difference in intermolecular forces.

On the other hand, the trend in the molar heats of sublimation in the series of trinitro-aromatic amines persists even when the specific heats are considered, Table 3. This trend agrees, at least in a qualitative sense, with what we know about the structures of these solids based on published crystal structure determinations. The structures of DATB-I[8] and TATB[2] are quite different. The former is hydrogen bonded into chains with two intermolecular hydrogen bonds per molecule within a chain and only weak interactions between the chains. TATB, however, is hydrogen bonded into a layered structure with six strong intermolecular hydrogen bonds per molecule. Although the structure of TNA has not been reported, the structures of other nitro anilines such as p-nitroaniline[12] and 2,3,4,6-tetranitroaniline[3] have been determined and these compounds exhibit hydrogen bonding schemes similar to one another and weaker than that found either in DATB-I or TATB, based on the intermolecular separation between amino and nitro functional groups. If the structure of TNA is comparable to these compounds, at least with respect to intermolecular hydrogen bonding, then the intermolecular forces due to this cause in TNA should be smaller than in DATB-I which in turn should have smaller forces than TATB. Thus ignoring other factors which affect the heats of sublimation (polarity, dispersion, temperature, etc.), it can be seen that within this series of polynitroaromatic amines the trends in intermolecular hydrogen bonding and heats of sublimation parallel one another in a qualitative sense. A more exact discussion would require inclusion of the factors ignored here as well as some method for estimating the strengths of hydrogen bonding systems that is more meaningful than internuclear separation.

TABLE 3. Heats of Sublimation

Compound	Molar Heat* of Sublimation	Specific Heat of Sublimation	Molecular Weight	Mid-point of Temperature Range
RDX	31.11 kcal	140.0 cal/gm	222.2	76.70°C
β-HMX	41.89	141.4	296.2	113.45
TNA	27.71	121.5	228.1	76.65
DATB-I	33.47	137.6	243.2	85.35
TATB	40.21	155.7	258.2	153.30
HNS	43.01	95.5	450.3	183.85

* For intercomparison these should be corrected to the same temperature. Unfortunately, no data exists concerning the heat capacities of these compounds as solids and gases and the authors feel no correction is better than a poorly founded one.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Vapor Pressure						
High Melting						
Organic Explosives						
Heat of Sublimation						
RDX						
β-HMX						
TNA						
DATB-I						
TATB						
HNS						