

THERMAL PROPERTIES

L. C. Myers

DEVELOPMENT DIVISION

APRIL - JUNE 1975
SANL NO. 363-004

For
Lawrence Livermore Laboratory
Livermore, California

MASTER



Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 647
AMARILLO, TEXAS 79177
806-335-1581

operated for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
under
U. S. GOVERNMENT Contract DA-11-173-AMC-487(A)

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.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor their employees, nor any of their contractors, subcontractors, or 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.

THERMAL PROPERTIES

L. C. Myers

DEVELOPMENT DIVISION

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or 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.

April - June 1975
SANL No. 363-004

ABSTRACT

Chemical reactivity test data are reported which indicate a correlation between the volume of gas evolved by PBX 9404 and (1) the sample holder, (2) the order in which the samples are run and/or the position the samples are conditioned in the oil bath. Runs were also made on samples that were immersed 63.5 and 76.2 mm into the bath.

Thermal decomposition data are given for PETN which show its reaction mechanism to be dependent on temperature and/or the extent of the reaction. Activation energies of 6000 and 980 joule/mole (22 and 4 kcal/mole) were calculated from the data.

DISCUSSION

INVESTIGATION OF THE VARIABLES IN THE CHEMICAL REACTIVITY TEST DATA

The investigation into the source of the variations in the chemical reactivity test has continued this quarter. Previously, it has been shown that (1) a one degree change in the temperature would cause a 9% change in the volume of gas evolved from PBX 9404, (2) small variation in the weight of the PBX 9404 would have caused only very small variations in the total gas evolved, and (3) a change in the immersion depth from 50.8 to 76.2 mm depth of the sample holder in the oil bath would cause a significant variation in total gas evolved.

If chemical reactivity samples of PBX 9404 are conditioned in an oven (complete immersion), the samples evolved about the same amount of gas as a sample immersed 76.2 mm in the oil bath. Therefore, a preliminary test was made this quarter to compare data from samples immersed 63.5 mm to those immersed 76.2 mm. These data are given in Table I, but only two samples immersed 63.5 mm were run and these had such a large variation in the total gas evolved (0.352 to 380 ml) that no conclusion can be made. It will be necessary to make additional runs next quarter.

Another series of tests was run using the same sample holders, but varying the order in which they were run. Run No. 1 was the first run of the day and the sample was located in the front of the oil bath. Run No. 2 was the second and it was located in the oil bath just behind No. 1. Table II lists the data from the same sample holders in the order of increasing total gas volumes minus the nitrogen^a. With only one exception (sample holder No. 16 Run No. 4) the gas volume increases with run number indicating a possible correlation between the sample holder, run number and/or position in the oil bath with the volume of gas evolved from the sample.

^aNitrogen was excluded from the total gas evolved to reduce the variations caused by small air leaks.

Table I. Chemical Reactivity Test Data
for PBX 9404

(Gas Volumes in ml at STP)

(0.250 g Conditioned at 120 C for 22 hrs)

<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>
76.2 mm Immersion Depth					
0.017	0.032	0.195	0.115	0.014	0.372
0.015	0.031	0.194	0.116	0.015	0.371
0.015	0.033	0.207	0.122	0.015	0.387
0.019	0.034	0.200	0.118	0.015	0.387
63.5 mm Immersion Depth					
0.014	0.030	0.188	0.107	0.013	0.352
0.010	0.031	0.200	0.123	0.015	0.380

Table II. Chemical Reactivity Test Data for PBX 9404

(Gas Volume in ml at STP)

(0.250 g Conditioned at 120 C for 22 Hours)

Sample Holder No.	Run Order No.	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>	<u>Total -N₂</u>	<u>Mean of Total -N₂</u>	<u>σ</u>
13	1	0.024	0.035	0.190	0.118	0.015	0.381	0.357		
13	1	0.022	0.032	0.192	0.121	0.015	0.382	0.360	0.366	0.009
13	6	0.019	0.034	0.200	0.120	0.015	0.387	0.368		
13	6	0.039	0.037	0.201	0.124	0.015	0.415	0.378		
14	2	0.019	0.032	0.189	0.122	0.015	0.377	0.358		
14	2	0.055	0.032	0.190	0.135	0.016	0.429	0.374	0.371	0.011
14	5	0.017	0.034	0.203	0.127	0.016	0.397	0.380		
15	3	0.011	0.030	0.191	0.125	0.016	0.372	0.361		
15	3	0.011	0.033	0.191	0.124	0.016	0.376	0.365	0.368	0.009
15	4	0.013	0.033	0.200	0.132	0.017	0.400	0.387		
16	4	0.024	0.030	0.184	0.116	0.015	0.368	0.344		
16	3	0.023	0.034	0.188	0.114	0.015	0.374	0.351	0.352	0.009
16	4	0.019	0.035	0.193	0.119	0.016	0.381	0.362		
17	2	0.017	0.032	0.194	0.112	0.014	0.369	0.352		
17	5	0.025	0.031	0.187	0.114	0.015	0.377	0.352	0.358	0.010
17	5	0.017	0.035	0.199	0.120	0.015	0.387	0.370		
18	1	0.017	0.032	0.195	0.115	0.014	0.372	0.355		
18	1	0.019	0.032	0.193	0.118	0.015	0.376	0.357	0.364	0.009
18	6	0.015	0.037	0.200	0.118	0.015	0.385	0.370		
18	6	0.018	0.034	0.200	0.124	0.016	0.392	0.374		
Mean							0.385	0.364		
Std. Dev.							0.015	0.011		

A-4

All of the runs given in Table II were made over a seven day period and the mean and standard deviation for the total volume of gas and the total volume of gas minus the nitrogen are 0.385 ± 0.015 and 0.364 ± 0.011 , respectively.

If the data from sample holders 13 and 18 are compared, then the run order number is the more significant variable. As can be seen in Table III, the mean and standard deviation for the total gas evolved minus the nitrogen from Run No. 1 and No. 6 are 0.357 ± 0.002 and 0.373 ± 0.004 ml, respectively, indicating that the run number and/or position has a greater effect on the variation in the gas evolved than the particular sample holder.

Three possible sources of variation are:

1. Variations in the instrumentation during the day such as the condition of the column or the sensitivity of the detector, etc.
2. Variation in the temperature of the oil bath with time, or a temperature gradient in the oil bath.
3. Difference in the sample holders.

Some preliminary runs were made on a third series of tests which will be completed next quarter. In this test series, the position of the sample in the oil bath and the run number were changed from that used in the series described previously. These data are given in Table IV for two sets of runs made 21 days apart^b. The variation between run No. 1 and No. 6 has been eliminated; the reason for the variation remains unknown.

The tests to date indicate that a better temperature controlled oil bath would help to reduce the variations in the chemical reactivity test data.

THERMAL DECOMPOSITION OF PETN

Last quarter a limited amount of data were reported indicating that the thermal decomposition mechanism of PETN is dependent on temperature and/or the extent of the reaction. Additional data collected this quarter continue to indicate this dependency.

^b During the second set of runs, the laboratory air conditioning was not working and the temperature varied from a low of 24 C to 32 C during the day and this may have caused the second set of runs to have a larger volume of gas evolved.

Table III. Chemical Reactivity Test Data for PBX 9404

(Gas Volumes in ml at STP)
 (0.250 g Conditioned at 120 C for 22 Hours)

Sample Holder No.	Run Order No.	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>	<u>Total -N₂</u>	Mean of Total -N ₂	<u>σ</u>
13	1	0.022	0.032	0.192	0.121	0.015	0.382	0.360		
13	1	0.024	0.035	0.190	0.118	0.015	0.381	0.357	0.357	0.002
18	1	0.019	0.032	0.193	0.118	0.015	0.376	0.357		
18	1	0.017	0.032	0.195	0.115	0.014	0.372	0.355		
18	6	0.018	0.034	0.200	0.124	0.016	0.392	0.374		
13	6	0.039	0.037	0.201	0.124	0.015	0.415	0.378	0.373	0.004
18	6	0.015	0.037	0.200	0.118	0.015	0.385	0.370		
13	6	0.019	0.034	0.200	0.120	0.015	0.387	0.368		

A-6

Table IV. Chemical Reactivity Test Data for PBX 9404

(Gas Volume in ml at STP)

(0.250 g Samples Conditioned at 120 C for 22 Hours)

<u>Run No.</u>	<u>Date</u>	<u>Position in Bath</u>	<u>N</u>	<u>CO</u>	<u>NO</u>	<u>CO</u>	<u>N₂O</u>	<u>Total</u>
1	06/17/75	Back	0.019	0.033	0.196	0.121	0.015	0.384
6	06/17/75	Front	0.010	0.032	0.199	0.122	0.015	0.378
1	07/08/75	Back	0.016	0.036	0.209	0.131	0.016	0.408
6	07/08/75	Front	0.014	0.035	0.209	0.132	0.016	0.406

The reaction rate can be represented by,

$$dC/dt = Ae^{-E/RT}C^n \quad (1)$$

where C is the extent of the reaction at time t and temperature T, A is the pre-exponential factor, E is the activation energy and n is the degree of the reaction. Equation (1) reduces to

$$\int dC/C^n = (Ae^{E/RT})t + \text{constant} \quad (2)$$

If the extent of the reaction is constant, then $\int dC/C^n = f(C) = \text{constant}$ and equation (2) can be simplified to

$$\ln t = E/R (1/T) + \text{constant}.$$

The activation energy can be determined from the slope of the plot of the log of time as a function of 1/T for given extents of reaction.

The data collected to date are given in Table V, and Figs. 1 and 2 are plots of the total volume of gas evolved as a function of time. From these graphs the time for given extents of reaction were determined. Fig. 3 is a graph of the log time as a function of 1/T for given extents of reaction. The data produce a family of curves, rather than straight lines, indicating that the apparent activation energy is changing with temperature. The activation energy, calculated from two different parts of the curve A and B, were 6000 and 980 joule/mole (22 and 4 kcal/mole), respectively.

In addition to the dependency of the reaction mechanism on time and/or temperature, other data have previously been presented which indicate that the rate of decomposition is also particle size dependent.

The major interest in the thermal decomposition of PETN is below 100 C, and since the sample holders used are subject to leak over long periods of time, all glass sample holders with break seals are being acquired for the low temperature, long time runs.

FUTURE WORK, COMMENTS, CONCLUSIONS

Previously the investigation into the variations in the chemical reactivity test data have shown that small variations in the temperature of the oil bath used to condition the samplers and the depth the samples are immersed into the oil bath were the major sources of variation in the volume of gas evolved from PBX 9404.

Tests made this quarter show a correlation between the volume of gas evolved, the sample holder, and the order in which the samples are run and/or their position in the oil bath. Additional tests are planned to determine the degree of variation each of the above parameters produce.

Table V. Chemical Reactivity Test Data for PETN

(Gas Volume in ml Corrected to STP)

(0.250 g Samples)

Time at Temperature (hrs)	Temperature (C)	N ₂	CO	NO	CO ₂	N ₂ O	Total	Fractional Decomposition Total 200 ml × 10 ⁻²
22	120	0.046	0.014	0.028	0.046	0.004	0.138	0.069
46	120	0.179	0.130	0.177	0.294	0.031	0.811	0.406
55	120	0.252	0.205	0.273	0.458	0.049	1.237	0.619
70	120	0.674	0.605	0.614	1.188	0.145	3.226	1.613
88	120	1.088	1.083	1.059	2.325	0.339	5.894	2.947
94	120	1.445	1.296	0.944	2.639	0.386	6.710	3.305
78	115	0.032	0.006	0.009	0.025	0.005	0.077	0.039
166	115	0.105	0.039	0.057	0.131	0.022	0.354	0.177
242	115	0.322 ^a	0.198	0.189	0.734	0.099	1.542	0.771
243	115	0.223	0.134	0.159	0.504	0.072	1.092	0.546
118	100	0.001			0.001	0.001	0.003	0.002
673	100	0.006	0.003	0.038	0.012	0.010	0.069	0.035
768	100	0.006	0.004	0.042	0.014	0.008	0.074	0.037
936	100	0.007	0.005	0.026	0.015	0.010	0.063	0.032
1150	100	0.022	0.006	0.070	0.027	0.015	0.140	0.070
1342	100	0.014	0.008	0.053	0.027	0.023	0.125	0.063
1656	100	0.143	0.011	0.072	0.056	0.020	0.307	0.154

^aAir leak

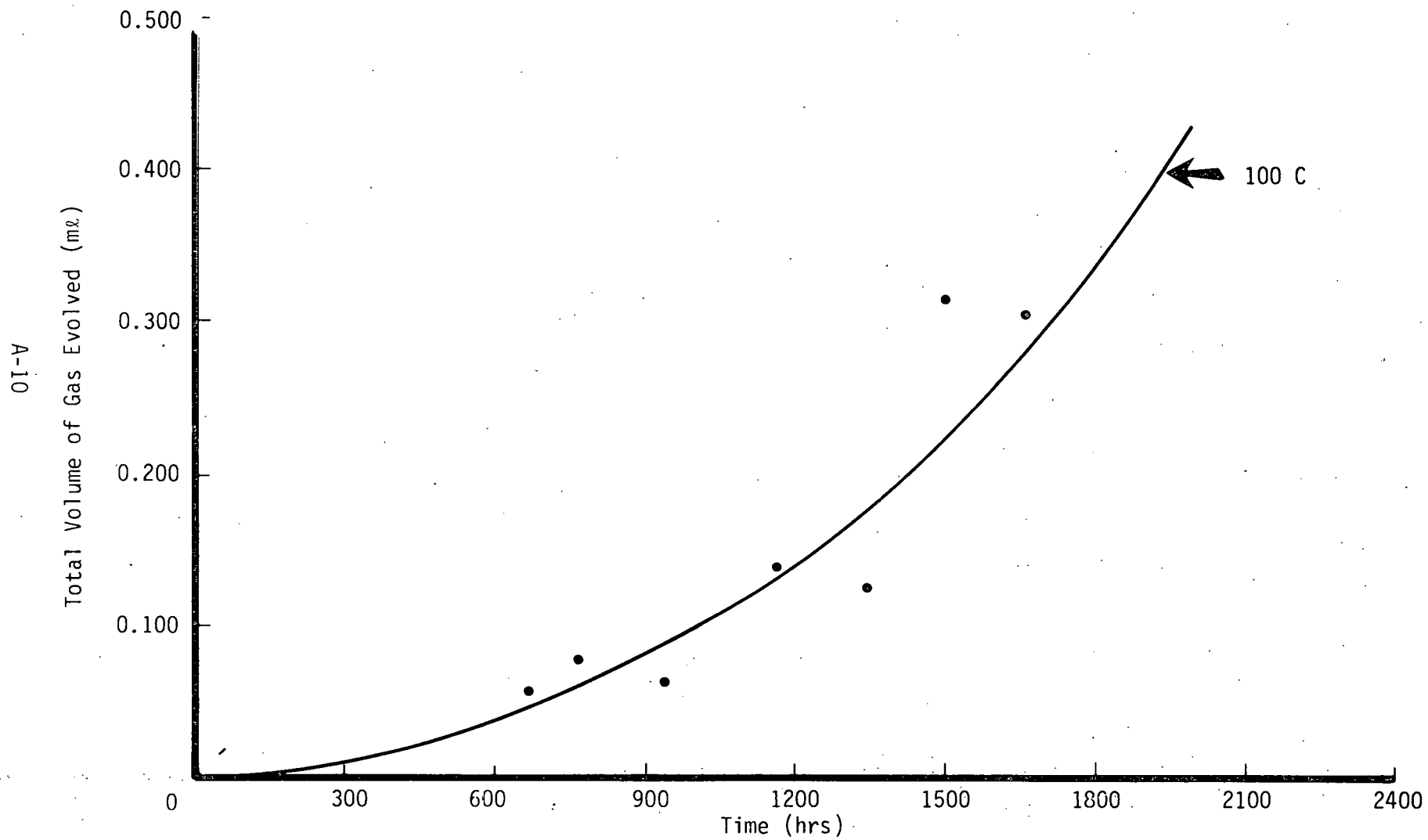


Fig. 1. Total Gas Evolved from PETN as a Function of Time

A-11

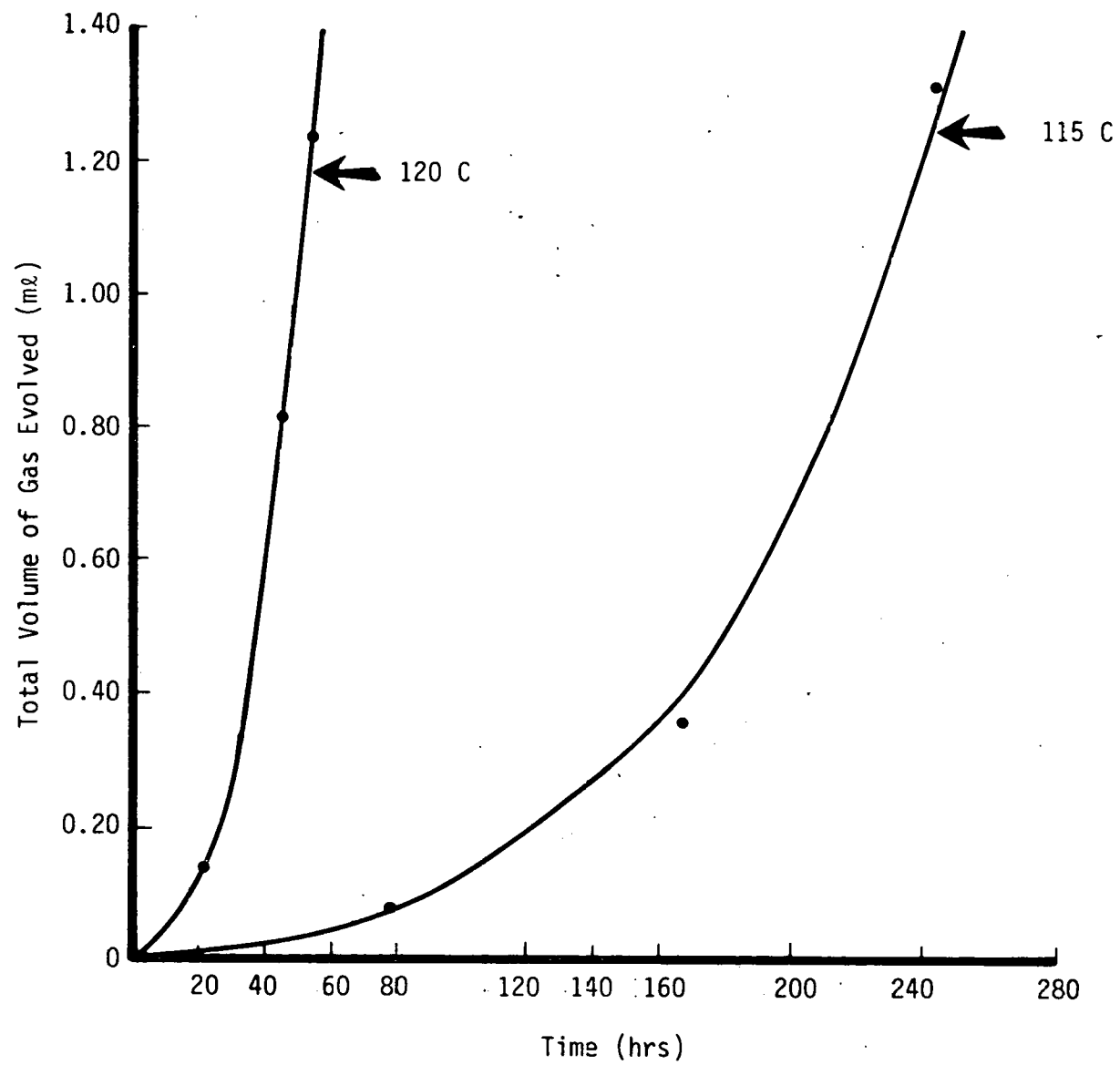


Fig. 2. Total Gas Evolved from PETN as a Function of Time

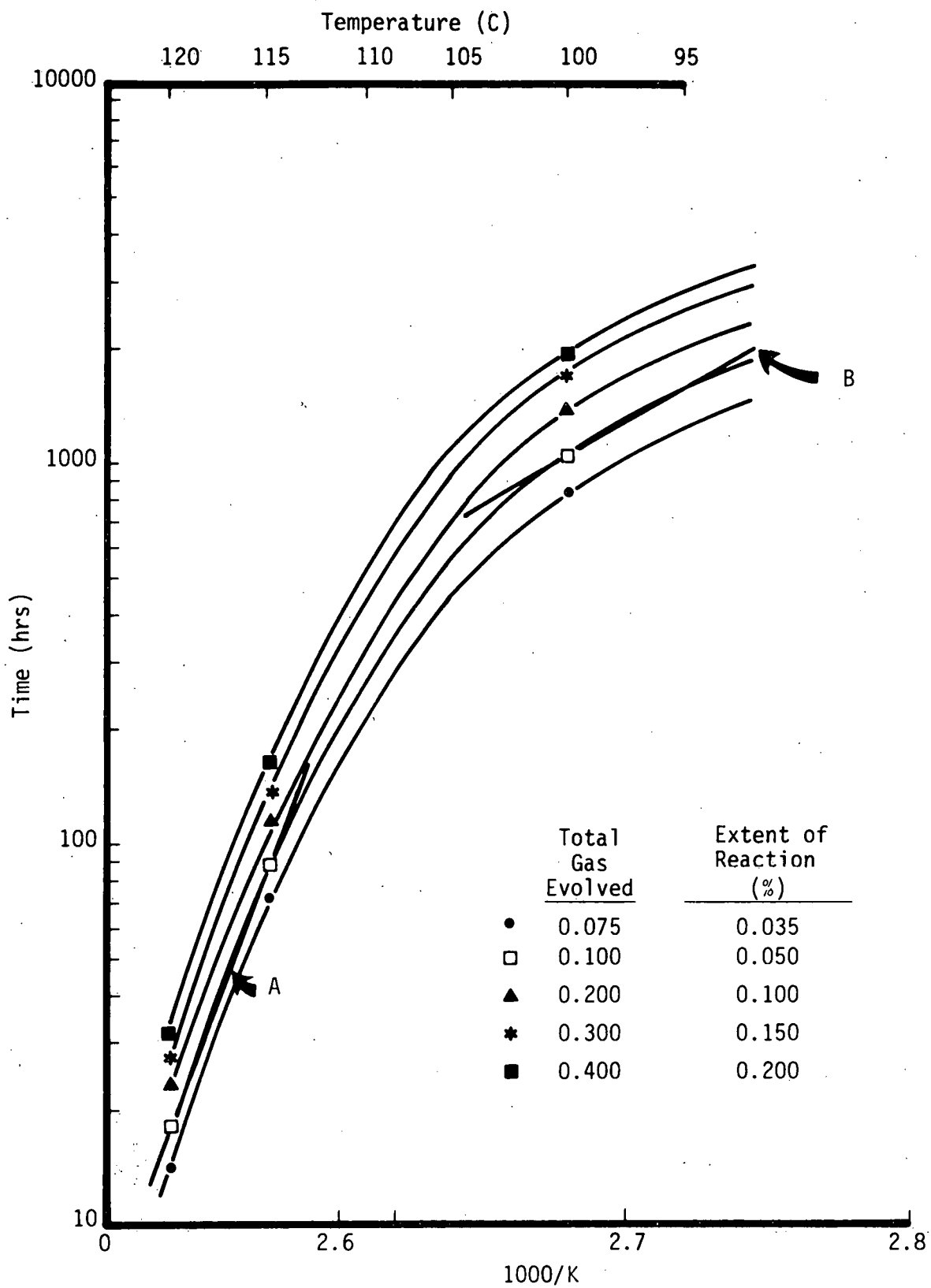


Fig. 3. Log of Time as a Function of the Reciprocal of the Absolute Temperature for Various Extent of Reaction of PETN

The investigation into the thermal decomposition of PETN was continued this quarter, and the data continue to indicate that the reaction mechanism is temperature and/or extent of reaction dependent.

Because of the leaks encountered with the chemical reactivity test's sample holders, it will be necessary to use another type of sample holder to investigate the decomposition below 100 C. Therefore, glass sample holders with break seals will be used to obtain data at 100 C and below.