

THE THERMAL ANALYSIS OF LIQUID AND SOLID PROPELLANTS

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ABSTRACT

Kinetic constants from differential scanning calorimetry data using heat evolution and variable heating rate methods were obtained for the thermal decomposition of a liquid monopropellant; good agreement was found between the observed and predicted half-life for the first order decomposition reaction. The rate of volatilization of nitroglycerin in a crosslinked double base propellant was investigated by isothermal and dynamic thermogravimetry and was found to be first order. The effect of sample size, atmospheric environment, aging and crosslink density of the propellant on the volatilization rate was determined. It was observed that the rate increased as (1) the sample was changed from a cylindrical plug to a powdered form, (2) the atmosphere around the sample was changed from nitrogen to helium to vacuum, (3) as the thermal stability of the sample decreased, and (4) the relative crosslink density was changed from a higher to a lower value. A kinetic compensation effect was found for cylindrical plugs but not for powdered samples.

INTRODUCTION

Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) techniques have been applied towards the characterization of propellants and explosives (ref. 1). In the present study the kinetics of decomposition of a liquid monopropellant was followed by DSC. The data were analyzed by four methods and three of them were in good agreement. The thermal stability of original and aged crosslinked double base propellant (CDB) was determined by an isothermal TG study of the volatilization of the plasticizer (nitroglycerin, NG). The effects of sample size, atmospheric environment, and relative crosslink density on the volatilization of NG in a CDB propellant were investigated.

EXPERIMENTAL

Instrumentation

A DuPont 990 Thermal Analyzer with 990 DSC and TG modules was used.

Liquid Monopropellant

The sample mass was 1 to 3 mg. The heating rate was 5°C/min with a time base of 2 min/in. Unsealed gold pans were used i.e. sample pans with covers. The DSC runs were carried out in a nitrogen atmosphere using a flow rate of 100 ml/min. The DSC module was isothermally heated to about 135°C, the sample pan was placed in its position and the run started. In addition a variable heating rate study was carried out at 1 to 20°C/min.

Crosslinked Double Base Propellants

Five samples were investigated. They were labelled CDB-1, aged CDB-1 (aged 6 months at 120°F and 81.2% relative humidity), CDB-2, aged CDB-2 (aged 18 months at 120°F and 20% relative humidity) and CDB-3. The CDB-1 samples were ground into powder form using a Wiley Mill. The mass of the powdered samples used in the TG runs was 15 ± 2 mg. The CDB-2 and CDB-3 samples were cylindrical plugs and were about 0.12 in. by 0.12 in. and weighed 60 ± 5 mg. The CDB-1 and CDB-2 samples were similar in composition and had approximately nine times more nitrocellulose content than CDB-3 and therefore had a higher relative crosslink density because of the higher concentration of hydroxyl groups available for crosslinking. Scale expansion was used to follow the volatilization of NG. The TG data was expressed as fraction volatilized (α) and varied from 0 to 1 for NG. The NG volatilizes in a temperature range where the rest of the propellant is thermally stable. The atmospheric environment was varied from nitrogen to helium using a flow rate of 100 ml/min. When vacuum was used, it was 29 inches. The TG furnace was equilibrated at the desired temperature before the sample and quartz furnace tube were inserted into the furnace. Time base runs were varied from 10 to 1 min/in. Dynamic TG runs were carried out at heating rates of 0.5, 1 and 2°C/min.

DISCUSSION

Kinetic Methods

The kinetic data generated by DSC were analyzed by four methods. They were as follows, (1) Urichek (ref. 2) method where:

$$\Delta \log \left(\frac{\Delta H / \Delta t}{A-a} \right) / \Delta \left(\frac{1}{T} \right)$$

is plotted to obtain $E/2.3R$. In this equation $\Delta H / \Delta t$ is the rate of heat flow, $(A-a)$ is the area of the unreacted portion of the curve, and E is the activation energy; (2) Rogers and Morris (ref. 3) method where $\Delta (\log D)$ versus $\Delta (1/T)$ is

plotted to obtain $E/2.3R$. In this case (D) is the vertical displacement from the baseline to the DSC curve; (3) the third method (ref. 4) is where the reaction rate doubles in the temperature interval (ΔT); the differential form of the Arrhenius equation becomes $E = 1.38 T^2/\Delta T$; thus by measuring the temperature interval of ΔT during which the curve displacement from the baseline doubles, an estimate of the activation energy may be made; and (4) the variable heating rate method developed by Flynn and Wall (ref. 5) and Ozawa (ref. 6). The basic equation is $\Delta \log \beta/\Delta (1/T) \approx 0.457 E/R$ where β is the programmed heating rate ($^{\circ}\text{C}/\text{sec}$) and T is the temperature at a constant degree of conversion which in the DSC run is the reaction peak maximum. Thus as the heating rate is increased the reaction peak shifts to higher temperature and therefore an estimate of the activation energy may be made. The pre-exponential factor (A) is conveniently obtained in the first order form by Rogers and Smith (ref. 7) using the equation $A = (\beta E/RT_{\text{max}}^2) \exp (E/RT)$. All the parameters are known so no additional measurements need to be made. Methods 1 to 3 assume a first or zero order reaction while method 4 is independent of the order of the reaction.

The kinetic data generated by isothermal TG were analyzed by three methods. They are as follows, (1) Manche-Carroll (ref. 8) method where $\log (\Delta\alpha/\Delta t)/\Delta(1/T)$ is plotted to obtain $E/2.3R$, α is the fraction reacted and $\Delta\alpha/\Delta t$ is the rate at fixed values of α . The Arrhenius frequency factor is obtained from the equation $\log A = E/2.3RT - \log (\Delta\alpha/\Delta t)$; (2) a first order plot of $\log (1-\alpha)$ versus time to obtain the rate constant ($k/2.3$) followed by a plot of $\Delta \log k/\Delta(1/T)$ to obtain $E/2.3 R$; and (3) Kishore (ref. 9) method where $\Delta \log t_{0.5}/\Delta(1/T)$ is plotted to obtain $E/2.3R$, $t_{0.5}$ is the time when the fraction reacted, $\alpha = 0.5$. In addition the Avrami-Erofeev equation $(-\ln(1-\alpha))^{0.5}$ and the contracting area equation $1-(1-\alpha)^{0.5}$ were tried but found not to be applicable. Values of α in the range of 0.3 to 0.7 were used in the calculation of kinetic constants.

Dynamic TG runs were carried out at heating rates of 0.5, 1 and $2^{\circ}\text{C}/\text{min}$. Doyle (ref. 10) developed a relationship between isothermal and dynamic TG runs. By plotting $\Delta(\log t)_{150}$ versus $\Delta(1/T)_{\text{DYN}}$ for fixed values of α , a slope of $0.457 E/R$ was obtained. Flynn and Wall (ref. 5) and Ozawa (ref. 6) methods originally developed for dynamic TG were used also. As before $\Delta(\log \beta)/\Delta(1/T) = 0.457 E/R$ is plotted for fixed values of α .

Liquid Monopropellant

The liquid monopropellant studied was a liquid nitrate ester which contained a few percent of a desensitizing agent and a stabilizer. Figure 1 shows the DSC curve for the sample. Kinetic data were obtained along points 1 to 8 for the Urichcek and Rogers and Morris methods. It should be noted that two baselines were drawn. A slanted line which followed the DSC curve and a dashed horizontal baseline whereby the decay and acceleratory portions of the DSC curve

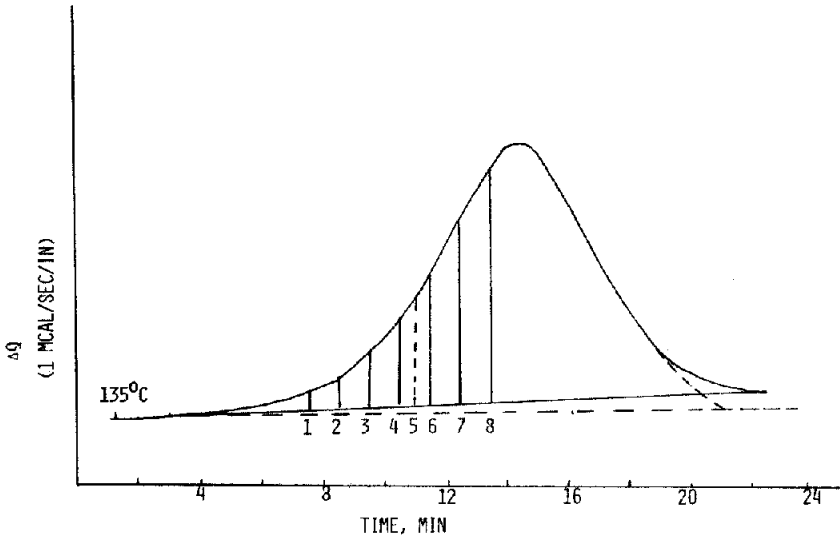


FIGURE 1: DSC CURVE FOR LIQUID MONOPROPELLANT

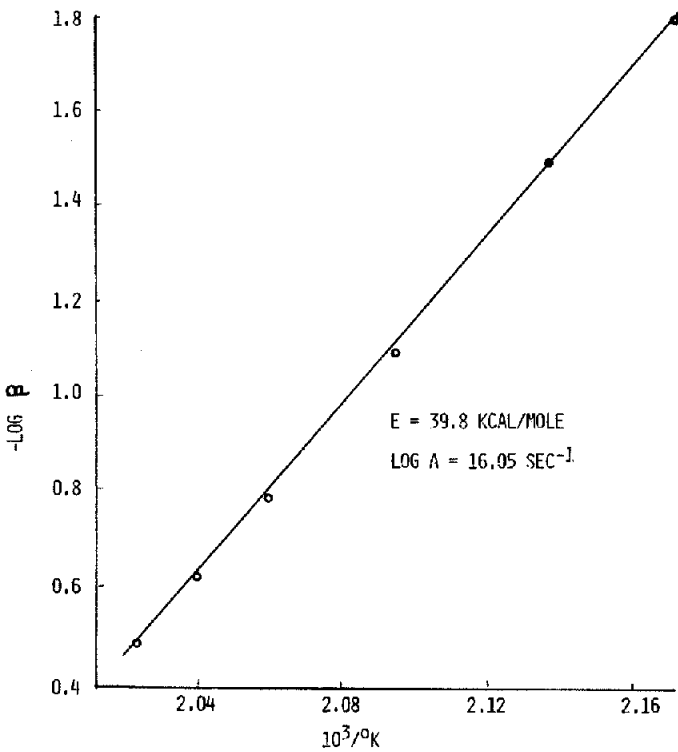


FIGURE 2: VARIABLE HEATING RATE VERSUS RECIPROCAL OF THE ABSOLUTE TEMPERATURE (OZAWA PLOT) FOR A LIQUID MONOPROPELLANT

were fitted to the same baseline level. Straight line kinetic plots are shown in Figures 2 and 3. There is good agreement in the values obtained for the activation energy (Table I) by the different methods except for Uricheck's. In the latter case if the band shape is made more symmetric by extending it to the dashed baseline then good agreement is obtained with this method also. This observation points out the value in using more than one method for calculating the activation energy. Still an independent check on the activation energy would be desirable. Duswalt (ref. 4) proposed an isothermal test for predicting the half-life for the reaction at some convenient temperature using the kinetic values in question. This suggestion was followed. Kinetic values obtained from the variable heating rate method of Flynn and Wall (ref. 5) and Ozawa (ref. 6) were used. The half-life for a first order reaction is $0.693/k$. At 180°C the half-life was calculated to be 15.6 minutes. The sample was then heated for this time in the DSC cell, the sample and cell cooled to room temperature and then programmed through the reaction peak at $5^{\circ}\text{C}/\text{min}$. The heat of reaction for decomposition was measured and found to be 65 cal/gram. The original value found at a heating rate of $5^{\circ}\text{C}/\text{min}$ was 135 cal/gram. The percent change was $66/135 = 49\%$ which is in excellent agreement with the theoretical value of 50%. This also proved that the decomposition of this liquid monopropellant was first order

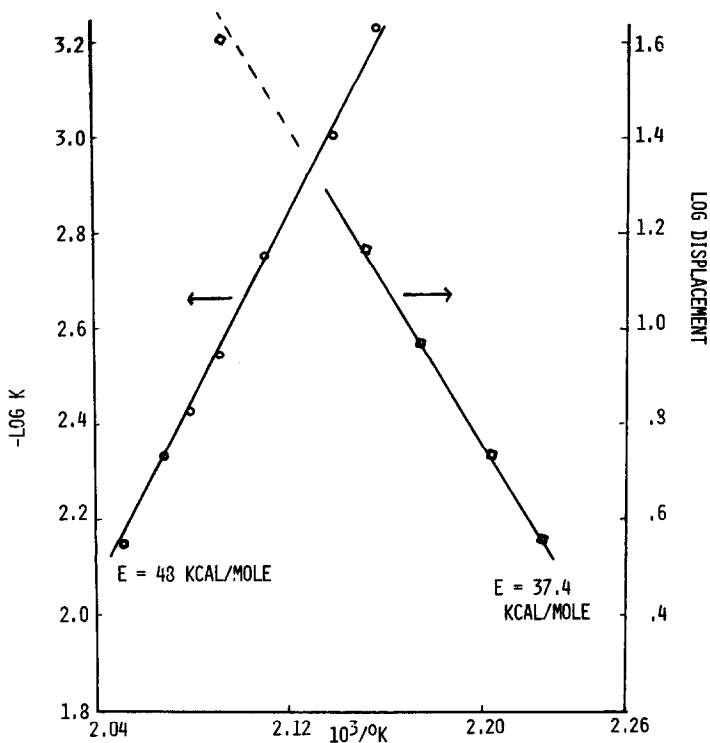


FIGURE 3: PLOT OF LOG K (URICHEK) AND LOG DISPLACEMENT (ROGERS AND MORRIS) VERSUS RECIPROCAL OF THE ABSOLUTE TEMPERATURE FOR A LIQUID MONOPROPELLANT

TABLE I
KINETIC DATA FOR LIQUID MONOPROPELLANT

1. ACTIVATION ENERGY BY DIFFERENT METHODS

URICHEK	ROGERS AND MORRIS	DOUBLE REACTION RATE	VARIABLE HEATING RATE
<u>E, KCAL/MOLE</u>			
48.1 (40.4)*	37.4 (35.9)*	39.1 (37.7)*	39.8

*VALUES FOUND USING DASHED BASELINE

2. VARIABLE HEATING DATA

β , °C/MIN	1	2	5	10	15	20
T _{MAX} , °C	187.5	197.5	204.5	212.5	216	222

3. HEAT EVOLUTION DATA

CURVE FRACTION	HEIGHT BLOCKS	AREA*, IN ²	TEMP., °C
1	3.6	0.24	176.5
2	5.6	0.42	181
3	9.3	0.74	186.5
4	14.5	1.31	191.5
5	18.5	1.83	194.5
6	22.2	2.26	196.5
7	31.4	3.63	201.5
8	39.5	5.41	206.5

*TOTAL AREA OF CURVE IS 13.63 IN²

Crosslinked Double Base Propellants

Effect of atmosphere on volatilization of NG. A typical isothermal TG curve for the volatilization of NG in a CDB propellant is shown in figure 4. The curves are redrawn with emphasis on the time required to reach an α value of 0.8; the actual figures are curved below and above α values of 0.2 and 0.8 respectively and linear as shown in between. The effect of the atmosphere on the volatilization rate of NG in a CDB propellant is shown in figure 5; the rate decreases in the order vacuum > helium > nitrogen. The observation in helium and nitrogen indicate that the rate of volatilization of NG is proportional to the thermal conductivity of the atmosphere. Helium has a thermal conductivity approximately six times greater than that of nitrogen. In addition helium has a smaller molecular volume than nitrogen and may therefore more readily diffuse through and displace the layer of volatilization gases than lie above the surface of the sample and thereby increase the volatilization rate. It may be because of its smaller size penetrate deeper into the surface of the sample and facilitate the displacement of volatile plasticizer. Caldwell (ref. 11) et al. observed the same type of atmospheric effect on the thermal decomposition of calcium carbonate.

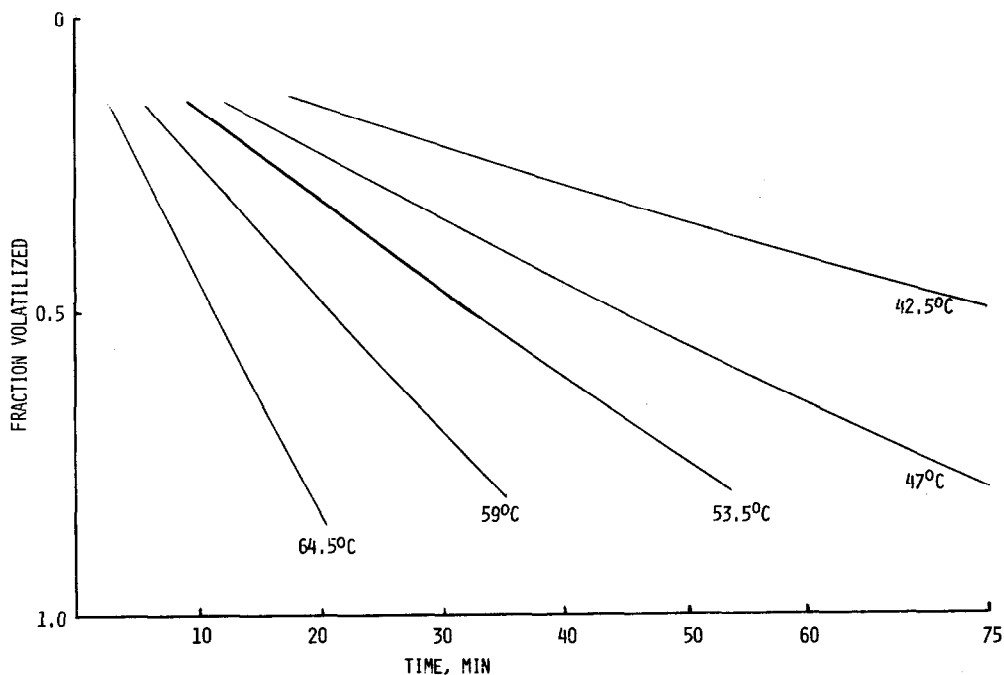


FIGURE 4: ISOTHERMAL TG CURVES IN VACUUM FOR NITROGLYCERIN IN CROSSLINKED DOUBLE BASE PROPELLANTS (CDB-1, POWDER FORM)

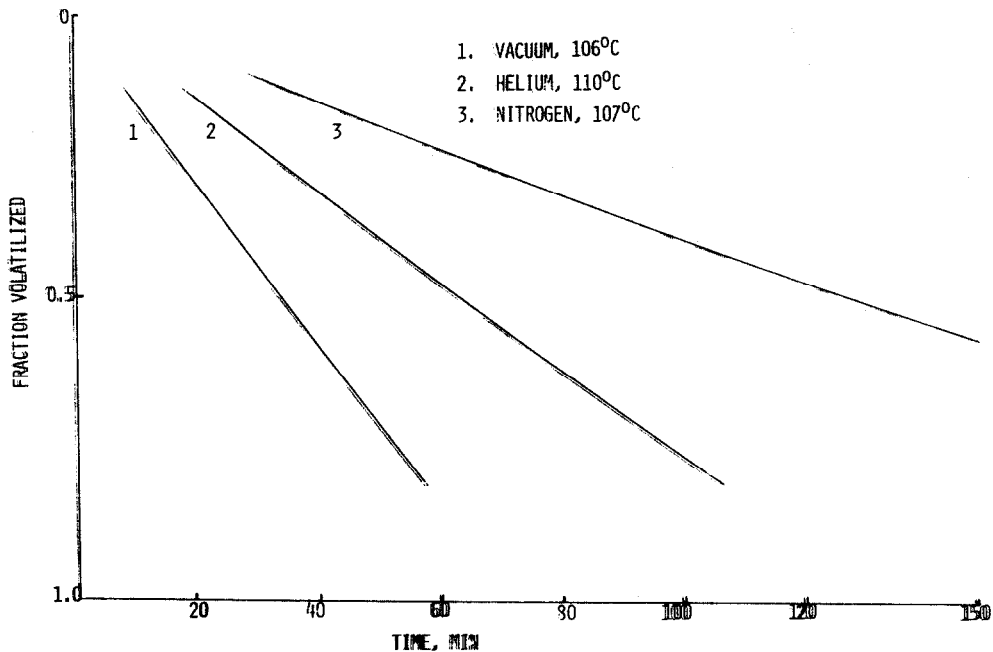


FIGURE 5: ISOTHERMAL TG CURVES FOR NITROGLYCERIN IN CROSSLINKED DOUBLE BASE PROPELLANTS (CDB-3) IN VACUUM, HELIUM, AND NITROGEN

Effect of sample geometry on volatilization of NG. The effect of sample size of the CDB propellant i.e. powder (15 mg) or cylindrical plug (60 mg) on the volatilization rate of NG is shown in figure 6. The volatilization rate of NG is faster in a CDB powder than in a cylindrical plug because of the greater surface area in the powder and consequently the volatilization of NG is facilitated.

Effect of aging on volatilization of NG. The effect of aging on the volatilization rate is seen in figure 6. Aged CDB-1 is more thermally degraded than the original because it was aged in a high relative humidity environment and consequently it has a higher volatilization rate of NG. Conversely aged CDB-2 has a lower volatilization rate of NG than the original and this may be due to the fact that CDB-2 was aged in a low relative humidity environment and consequently may have undergone postcure and thus is more thermally stable.

Effect of crosslink density on volatilization of NG. CDB-3 has a higher volatilization rate of NG than CDB-2. Both are cylindrical plug samples. The latter has a higher relative crosslink density than the former because its nitrocellulose content is nine times greater and thus has extra hydroxyl groups available for crosslinking, consequently it has a lower volatilization rate of NG.

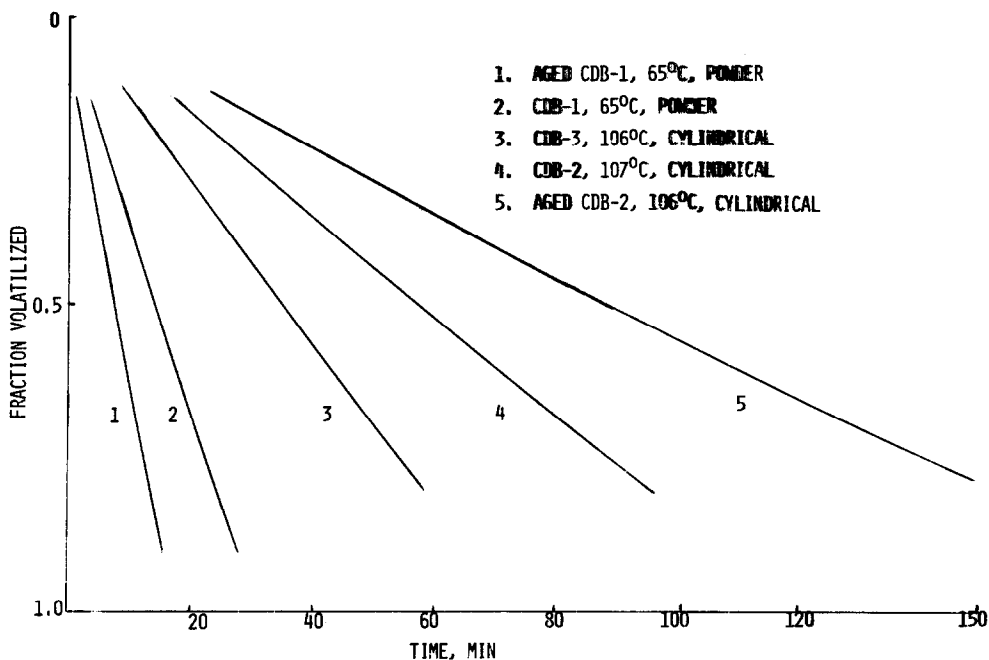


FIGURE 6: ISOTHERMAL TG CURVES IN VACUUM FOR NITROGLYCERIN IN CROSSLINKED DOUBLE BASE; PROPELLANTS IN THE FORM OF POWDERS AND CYLINDRICAL PIECES

SUMMARY OF EFFECTS ON VOLATILIZATION OF NG

It appears that the rate of volatilization of the plasticizer NG in CDB propellants depends upon the physical state of the propellant. That is, if the sample has more crosslinks either through post cure or by having extra hydroxyl groups available for crosslinking then there is a greater physical entrapment of the plasticizer and hence it is more difficult for the plasticizer to migrate and reach the surface of the propellant and volatilize upon being heated. Conversely if crosslink bonds are broken by hydrolysis as happens in aging a sample at a high relative humidity then it is easier for the plasticizer to migrate to the surface and volatilize. Finally, the larger the surface area of the sample then the more plasticizer there is on the surface and consequently it will volatilize at a faster rate since the slow step in the volatilization process would be the diffusion of the plasticizer from the interior to the surface of the propellant.

Dynamic Thermogravimetry

Dynamic TG curves for the volatilization of NG in CDB propellants are shown in figures 7 and 8. In the former the effect of the heating rate is shown i.e. an increase in the heating rate causes the TG curves to shift to higher temperature

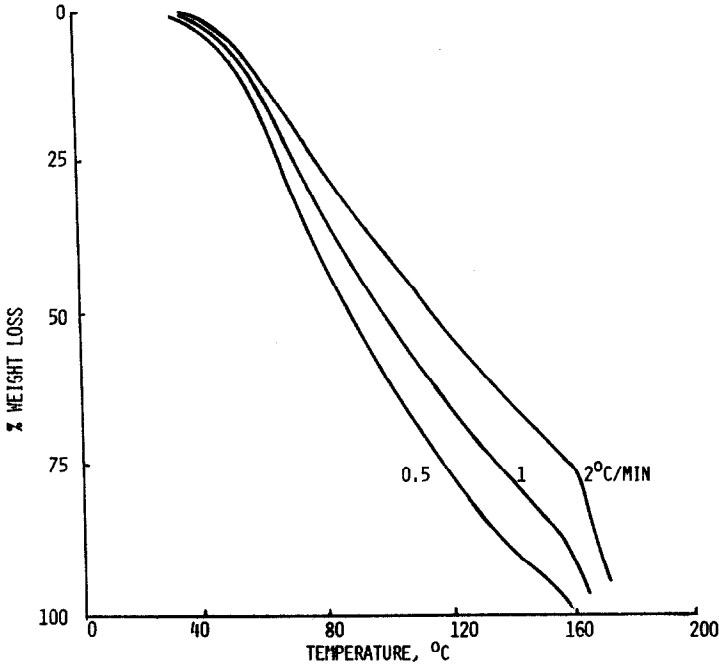


FIGURE 7: DYNAMIC TG CURVES FOR NITROGLYCERIN IN CROSSLINKED DOUBLE BASE PROPELLANT (CDB-2) IN VACUUM AT DIFFERENT HEATING RATES

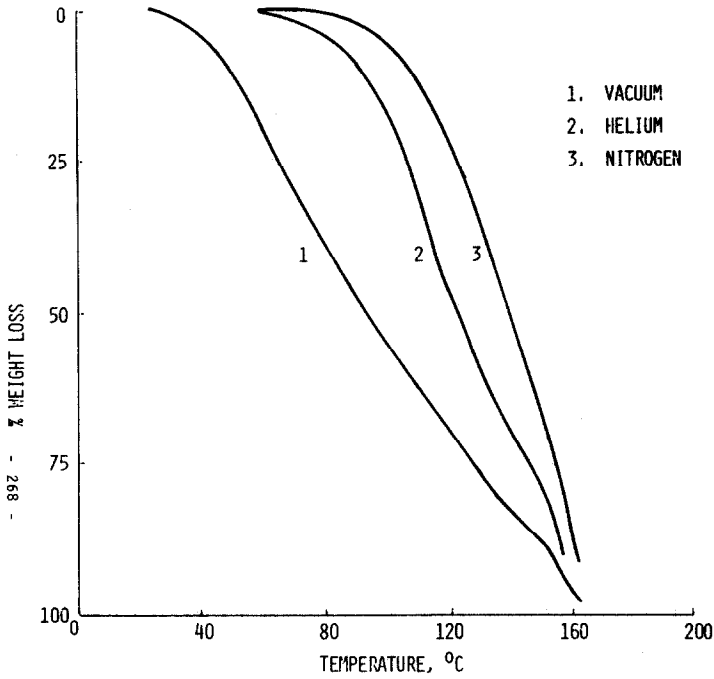


FIGURE 8: DYNAMIC TG CURVES FOR NITROGLYCERIN IN CROSSLINKED DOUBLE BASE PROPELLANTS (AGED CDB-2) IN VACUUM, HELIUM, AND NITROGEN AT 0.5°C/MIN

and in the latter figure the effect of the atmospheric environment is shown i.e. the fraction volatilized of NG comes at a lower temperature in the series vacuum < helium < nitrogen. It is apparent in figure 8 that the three curves are converging near 160°C. This indicates that the NG has volatilized by this temperature and that the atmospheric environment does not appear to have an effect on the initial stage of the decomposition of the propellant but only has an effect on the volatilization of the plasticizer. By inspection the dynamic TG curves do not appear to be as useful as the isothermal TG curves in following the volatilization rate of NG in CDB propellants.

Reduced Time

A reduced time plot i.e. $t_R = t/t_{0.5}$ where $t_{0.5}$ is the time when $\alpha = 0.5$ is shown in Figure 9. The utility of this plot is that if the curves at different isothermal temperatures superimpose under an α versus t_R plot then the order of the

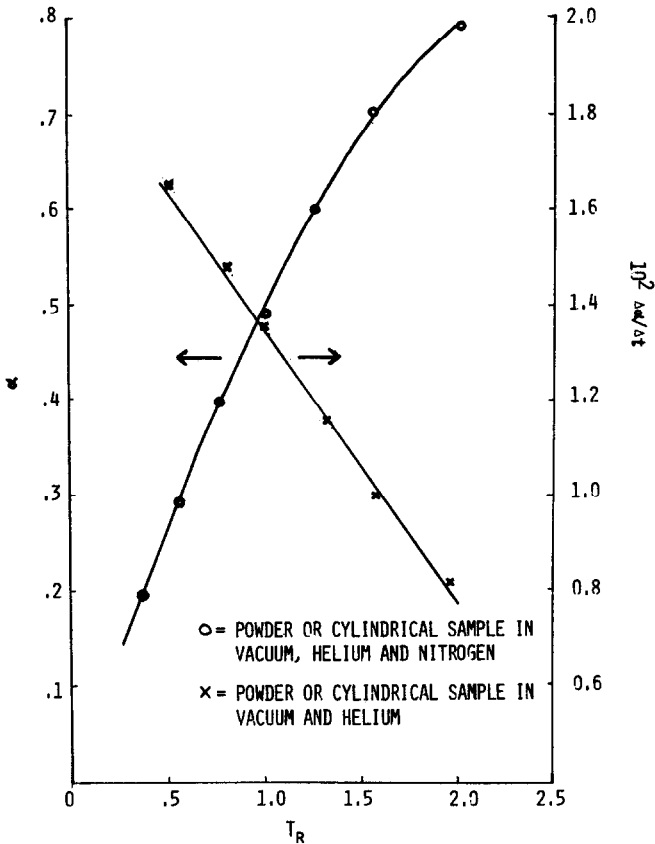


FIGURE 9: REDUCED TIME PLOT FOR VOLATILIZATION OF NITROGLYCERIN IN A CROSSLINKED DOUBLE BASE PROPELLANT (CDB-1 POWDER, CDB-3 CYLINDRICAL)

reaction at different temperatures is constant i.e. the kinetic behavior remains the same. It is seen in figure 9 that the points fall on the same line whether a powder or cylindrical sample is used and regardless of the atmospheric environment. Garn (ref. 12) suggested plotting $\ln d\alpha/dt$ vs $t\alpha$ and showed theoretical plots for different model processes. This type of plot is shown also in figure 9 and it resembles Garn's plot for a phase boundary control process. The plot in nitrogen is not shown but it is also a straight line with a slope only one-fifth that in vacuum or helium.

Kinetics of Volatilization of NG

Typical straight-line kinetic plots for the volatilization of NG in CDB propellants are shown in figures 10 to 12 using Manche-Carroll, Kishore and Arrhenius plots. The kinetic reaction appears to be first order. An isothermal versus dynamic TG plot (Doyle) is shown in figure 13. Figure 14 shows curved lines for an Avrami-Erofeev or contracting area plots and thus these expressions are not applicable in the α value range of 0.3 to 0.7.

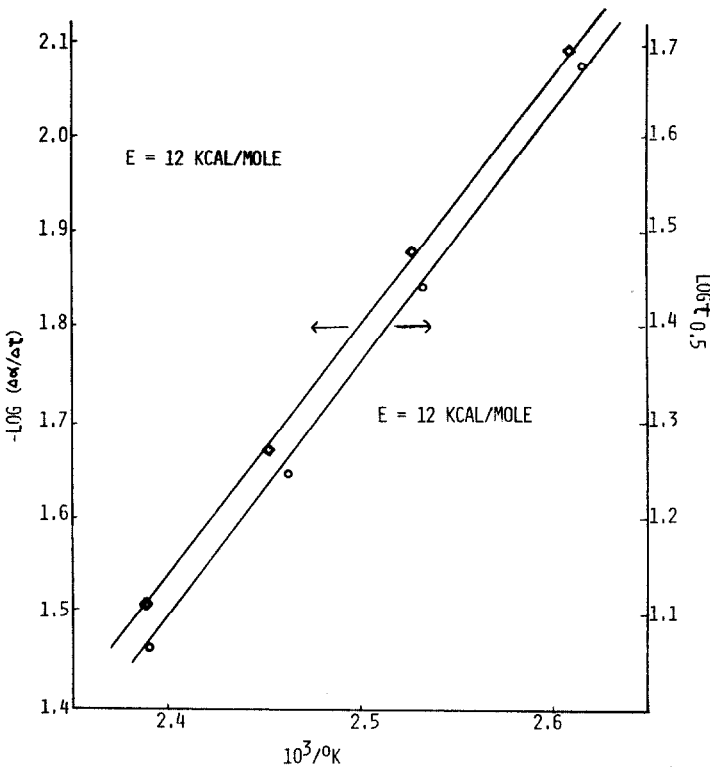


FIGURE 10: PLOT OF $\text{LOG } (d\alpha/dt)$ (MANCHE-CARROLL) AND $\text{LOG } t^{0.5}$ (KISHORE) VERSUS RECIPROCAL OF THE ABSOLUTE TEMPERATURE FOR VOLATILIZATION IN HELIUM OF NITROGLYCERIN IN A CROSSLINKED DOUBLE BASE PROPELLANT (CDB-3, CYLINDRICAL)

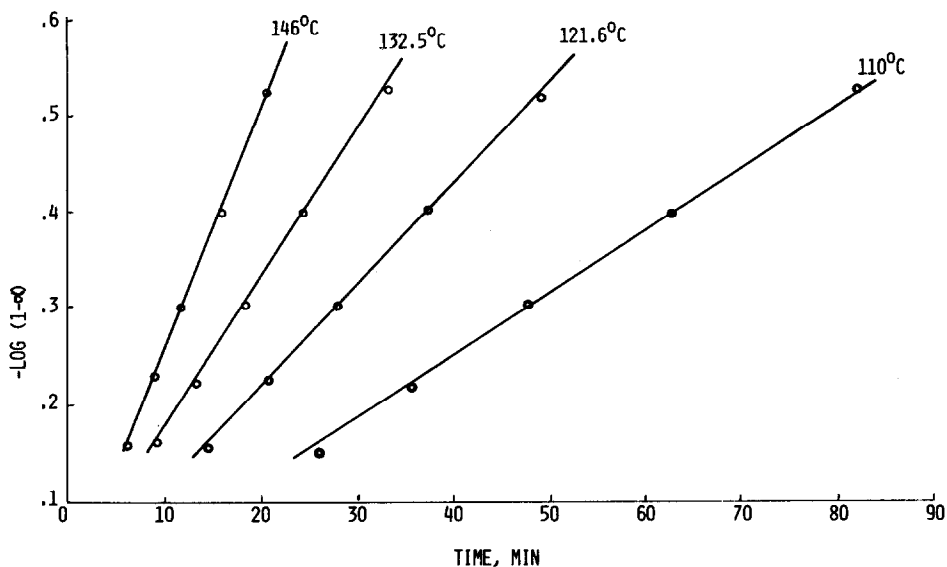


FIGURE 11: PLOT OF $\text{LOG}(1-\alpha)$ (FIRST ORDER) VERSUS TIME FOR VOLATILIZATION IN HELIUM OF NITROGLYCERIN IN A CROSSLINKED DOUBLE BASE PROPELLANT (CDB-3, CYLINDRICAL)

Activation energies for the volatilization of NG from cylindrical plugs of CDB propellant are given in Table II. Good agreement was obtained for the activation energies using the isothermal TG methods of Manche-Carroll, Kishore, and the first order Arrhenius equation. Higher values were found using the dynamic TG methods of Doyle or Ozawa. Zsako (ref. 13) observed a similar disagreement in activation energies obtained by isothermal and dynamic TG and ascribed it to the influence of the heating rate. The activation energy values are in the order vacuum < helium < nitrogen and CDB-3 < CDB-2 < aged CDB-2. The rate constants and half-life for the volatilization reaction were calculated for 40°C and are given in Table II. The half-life ratio for helium to nitrogen parallels the thermal conductivity ratio (5.9 at 0°C) for helium to nitrogen. For cylindrical plug samples it appears that the activation energy and the rate of volatilization for NG were influenced by the atmospheric environment and the relative crosslink density of the sample. As the crosslink density increased due to postcure or extra hydroxyl groups available for crosslinking, the rate of volatilization decreased and the activation energy increased.

Activation energies for the volatilization of NG from powdered CDB propellants are given in Table III. The values are the same in the different atmospheric environments and whether the sample is aged or original did not make any

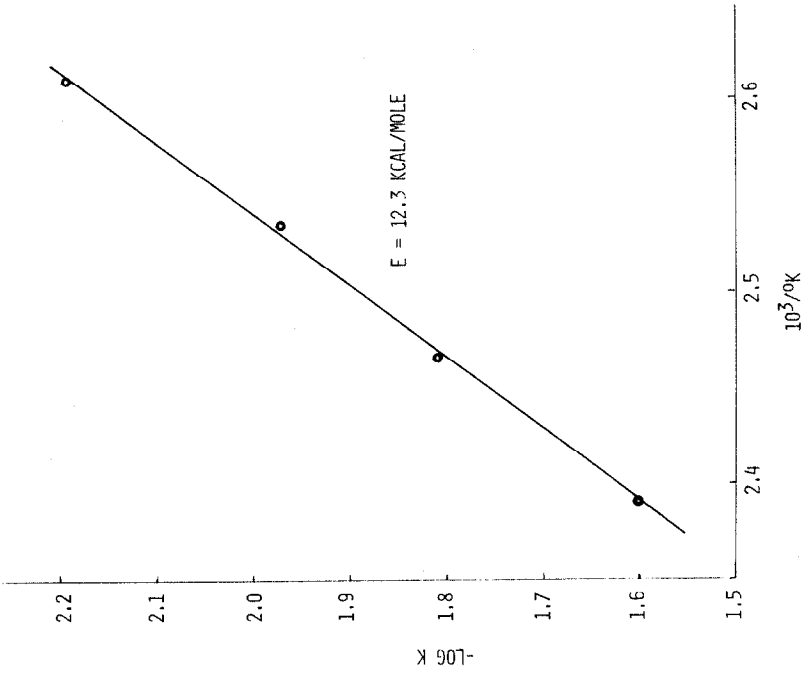


FIGURE 12: ARRHENIUS PLOT FOR VOLATILIZATION IN HELIUM OF NITROGLYCERIN IN A CROSSLINKED DOUBLE BASE PROPELLANT (CDB-3, CYLINDRICAL)

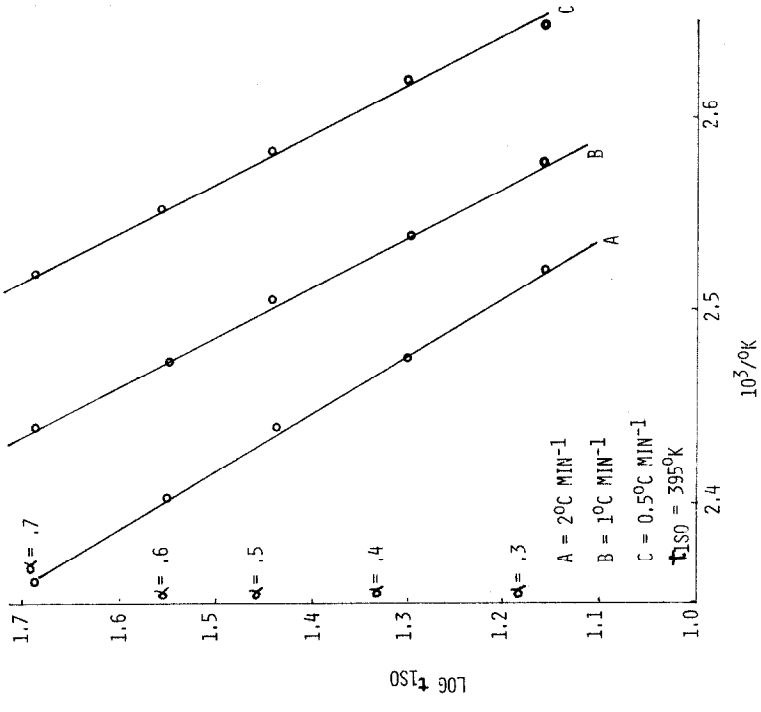


FIGURE 13: CORRELATION BETWEEN ISOTHERMAL AND DYNAMIC HEATING AT THE SAME VOLATILIZATION FRACTION (DOYLE'S METHOD) IN HELIUM OF NITROGLYCERIN IN A CROSSLINKED DOUBLE BASE PROPELLANT (CDB-3, CYLINDRICAL)

difference. However the rate constants for the volatilization of NG were different. Thus it appears that the surface area of the sample influenced the determination of the activation energy for the volatilization of NG in powdered samples while the rate constants were influenced by the atmospheric environment and relative crosslink density of the sample. A powdered CDB propellant aged in a high humidity environment undergoes hydrolytic degradation owing to the

TABLE II

KINETIC CONSTANTS FOR THE VOLATILIZATION OF NITROGLYCERIN IN A
CROSSLINKED DOUBLE BASE PROPELLANT (CYLINDRICAL)

SAMPLE	CONDITION	E(1) KCAL/MOLE	LOG A MIN ⁻¹	K(2)	T _{0.5} ⁽³⁾ DAYS
CDB-2	VACUUM	8.5	2.97	1.09×10^{-3}	0.4
	HELIUM	13.0	5.16	1.22×10^{-4}	3.9
	NITROGEN	16.7	6.97	2.05×10^{-5}	23.5
AGED CDB-2	VACUUM	9.8	3.22	2.40×10^{-4}	2.0
	HELIUM	15.4	6.43	4.78×10^{-5}	10.1
	NITROGEN	19.2	8.34	8.66×10^{-6}	55.6
CDB-3	VACUUM	6.9	2.23	2.58×10^{-3}	0.2
	HELIUM	12.2	4.86	2.20×10^{-4}	2.2
	NITROGEN	13.8	5.39	5.72×10^{-5}	8.4
CDB-3	HELIUM	12 ⁽⁴⁾			
	HELIUM	12 ⁽⁵⁾			
	HELIUM	18 ⁽⁶⁾			
	HELIUM	18 ⁽⁷⁾			

(1) ACTIVATION ENERGY OBTAINED FROM LOG ($\Delta\alpha/\Delta t$) DATA (MANCHE-CARROLL METHOD)

(2) RATE CONSTANT IN MIN⁻¹ AT 40°C

(3) HALF-LIFE IN DAYS AT 40°C FOR FIRST ORDER REACTION

(4) VALUE FROM FIRST ORDER PLOT

(5) VALUE FROM KISHORE PLOT

(6) VALUE FROM OZAWA PLOT

(7) VALUE FROM DOYLE PLOT

TABLE III

**KINETIC CONSTANTS FOR THE VOLATILIZATION OF NITROGLYCERIN IN A CROSSLINKED
DOUBLE BASE PROPELLANT (POWDER)**

SAMPLE	CONDITION	E ⁽¹⁾ KCAL/MOLE	LOG A MIN ⁻¹	K ⁽²⁾	$\tau_{0.5}$ ⁽³⁾ DAYS
CDB-1	VACUUM	18	10.26	4.95×10^{-3}	0.1
	HELIUM	18	8.78	1.64×10^{-4}	2.9
	NITROGEN	18	8.21	4.40×10^{-5}	10.9
AGED CDB-1	VACUUM	18	10.37	6.38×10^{-3}	0.07
	HELIUM	18	8.88	2.06×10^{-4}	2.3
	NITROGEN	18	8.35	6.02×10^{-5}	8.0
CDB-1	HELIUM	18 ⁽⁴⁾			
	HELIUM	18 ⁽⁵⁾			

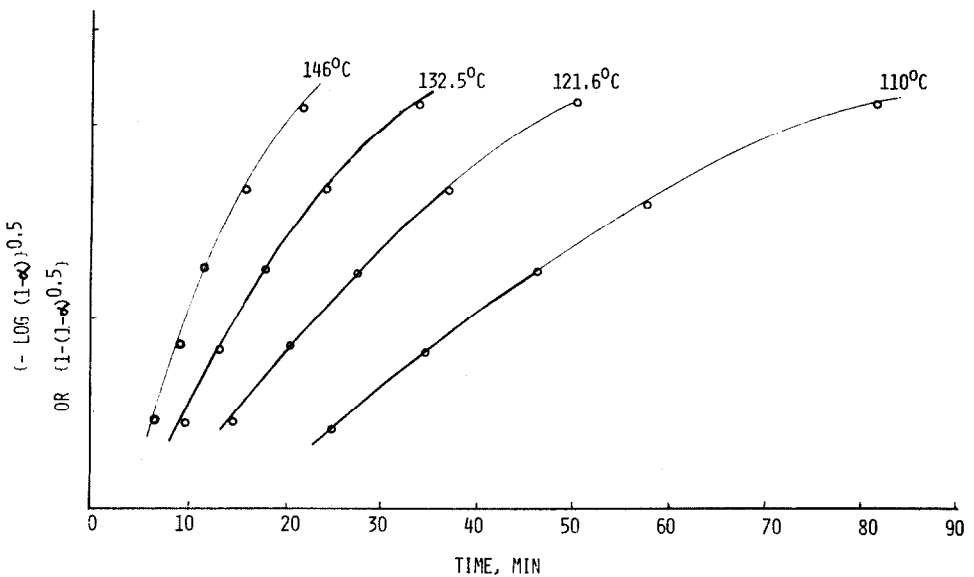
(1) ACTIVATION ENERGY OBTAINED FROM LOG $(\Delta\alpha/\Delta\tau)$ DATA (MANCHE-CARROLL PLOT)

(2) RATE CONSTANT IN MIN⁻¹ AT 40°C

(3) HALF-LIFE IN DAYS AT 40°C FOR FIRST ORDER REACTION

(4) VALUE FROM FIRST ORDER PLOT

(5) VALUE FROM KISHORE PLOT



cleavage of crosslink bonds by hydrolysis, consequently the diffusion of the NG plasticizer to the surface is facilitated. The ratio of the half-life in helium to nitrogen for the volatilization of NG in powdered CDB propellants parallels the ratio of their thermal conductivities. This was observed also with cylindrical plug samples. Thus this is convincing evidence that the mechanism for the volatilization of NG in these samples is thermal transport.

The overall order for the rate of volatilization of NG from powdered and cylindrical plugs of CDB propellant based on first order rate constants at 40°C is: aged CDB-1 > CDB-1 > CDB-3 > CDB-2 > aged CDB-2. This is the same order as powdered > cylindrical plugs and lower crosslink density > higher crosslink density.

Compensation Effect

A kinetic compensation effect was observed for the volatilization of NG from cylindrical plugs (figure 15) but not for powdered CDB samples. This is probably due to the difference in geometry of the two types of samples and the four-fold difference in sample mass i.e. 60 mgs (plugs) vs 15 mgs (powdered). A kinetic compensation effect is so called because it was observed with some reactions that a change in the activation energy was not accompanied by a corresponding change in the rate constant because of a compensating change in the pre-exponential factor. A linear relationship between the activation energy and pre-exponential factor implies a linear relationship or compensation between the enthalpy (ΔH) and entropy ($T\Delta S$) for the reaction (ref. 14). The compensation effect is given by the equation: $\log A = aE + b$ which resembles the Arrhenius equation $\log A = E/2.3RT + \log k$ where $a = 1/2.3RT$ and $b = \log k$. The parameters were found to be $a = 0.5$ and $b = -1.5$. Thus although the kinetic parameters varied for the different cylindrical plug samples of CDB propellants, the compensation parameters a and b remained the same. This is in agreement with Zsako's (ref. 15) observation that even though the kinetic parameters for individual runs may vary, the compensation parameters a and b will not vary for the whole series.

FIGURE 14: PLOT OF $\{-\log(1-\alpha)\}^{0.5}$ (AVRAMI-EROFEEV) OR $\{1-(1-\alpha)^{0.5}\}$ (CONTRACTING AREA) VERSUS TIME FOR VOLATILIZATION IN HELIUM OF NITROGLYCERIN IN A CROSSLINKED DOUBLE BASE PROPELLANT (CDB-3, CYLINDRICAL)

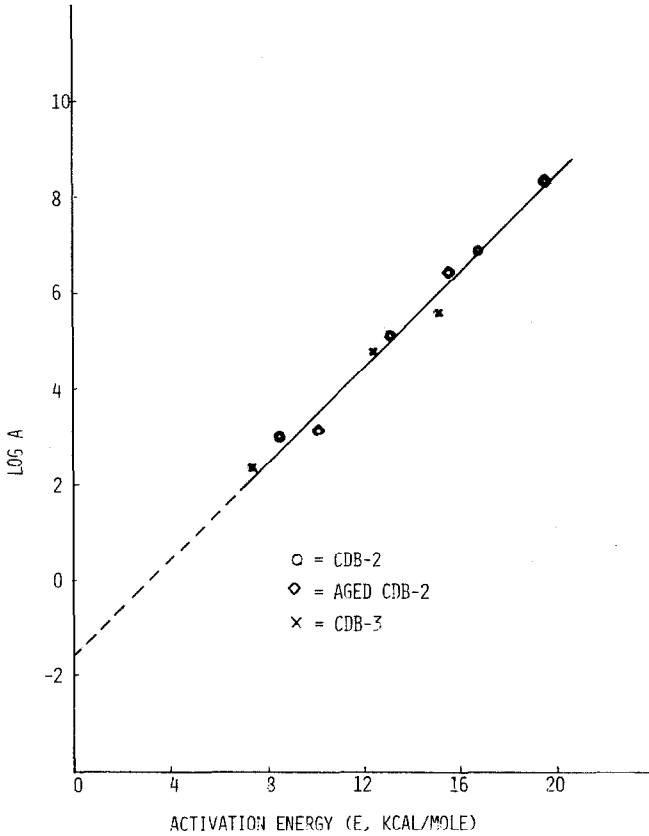


FIGURE 15: KINETIC COMPENSATION PLOT FOR ISOTHERMAL TG DATA IN VACUUM, HELIUM AND NITROGEN FOR VOLATILIZATION OF NITROGLYCERIN IN CROSSLINKED DOUBLE BASE PROPELLANTS (CDB-2 AND CDB-3, CYLINDRICAL)

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