

# **Thermal and Kinetic Studies of Trinitrotoluene (TNT) and Amatol Vis-a-Vis Oxygen Balance**



**By**

**JUNAID AKHTAR**

**School of Chemical and Materials Engineering (SCME)**

**National University of Sciences and Technology (NUST)**

**2016**

# **Thermal and Kinetic Studies of Trinitrotoluene (TNT) and Amatol Vis-a-Vis Oxygen Balance**



**JUNAID AKHTAR**

**NUST201464684MSCME67614F**

**This thesis is submitted as a partial fulfilment of the requirements for the  
degree of**

**MS In**

**Energetic Materials Engineering**

**Supervisor Dr. Abdul Qadeer Malik**

**School of Chemical and Materials Engineering**

**(SCME)**

**National University of Sciences and Technology**

**(NUST) H-12 Islamabad, Pakistan**

**August, 2016**



BISMILLAH IR-RAHMAN IR-RAHIM

"(I START) IN THE NAME OF GOD, MOST GRACIOUS, MOST MERCIFUL"

## **DEDICATION**

My research is dedicated to my beloved family whose great support enabled me to fulfill this tedious task.

# ABSTRACT

Trinitrotoluene (TNT) is considered as one of the most useable explosive for the military use but it has some drawbacks of negative oxygen balance which is about negative 74% which forms the unburnt carbon in the form of soot due to which maximum potential of the explosive cannot be explored. To address this problem 80/20 amatol has been used which has positive oxygen balance which comes out to be positive 1.2%. Due to this positive oxygen balance it has more blast effects than the TNT due to the high volume of gasses released after the detonation. In the study oxygen balance vis-a-vis thermal and kinetic parameters of the TNT and amatol has been analyzed. This study also highlights the effects of increasing heating rates on the temperature changes of the TNT and amatol. For thermal study of TNT and 80/20 amatol, DTA/TGA techniques have been used in the form of simultaneous thermal method. In case of TNT thermal analysis, it is found that with the increase in the heating rate thermal decomposition temperature and activation energy increases till heating rate of 20<sup>0</sup>C/min after that decomposition temperature and activation energy reduces at heating rate of 25<sup>0</sup>C/min. This effect is similar to the DDT phenomenon which takes place due to increase in heat rate due to which heat generated is more than the heat liberated which results in the increase of internal temperature and reduction in the activation energy, here as well, as the heating rate is increased beyond 20<sup>0</sup>C/min more heat is generated resulting in the reduction of activation energy of TNT. In case of amatol thermal analysis, it is found that with the increase in the heating rate there is increase in the thermal decomposition temperature and contrary to that it is found that there is decrease in the activation energy with the increase in the heating rate. Some of the reasons of such trends are thermal lag, furnace temperature, higher heat dissipation and heating rate. From the data it is found that TNT decomposition temperature is 240<sup>0</sup>C/min and that of amatol it comes out to be about 245<sup>0</sup>C/min which clearly shows that amatol is found to be more safe in handling than the TNT. In the nutshell, this study shows that amatol is having more blast effect than the TNT and also amatol is found to be more safe in handling due to the higher decomposition temperature than the TNT.

# ACKNOWLEDGEMENTS

I am deeply grateful to Almighty Allah for enabling me to complete my thesis which became possible due to His blessings.

I feel really honored to mention my supervisor Dr. Abdul Qadeer Malik who shed light of guidance and lead me to conclude this thesis, his guidance gave me a lot of confidence and resolve to complete my research. His dedication to impart in the students the will to undertake new projects has been great source of inspiration to select this challenging project.

I am very much thankful to Squadron Leader Zaheer ud din babar who gave me a lot of support and guidance for the research.

I am thankful to the Dean of Sciences Dr. Naghmana of Allama Iqbal Open University for letting me use the laboratory to complete my research.

I am thankful to Ms. Ayesha for training me on the DTG for quick completion of my work.

My special thanks to the laboratory technicians Shams and Khurram who were of great help for my work.

I am thankful to Shah Faisal for all his support during the work.

I am thankful to my unit 630 Explosive Ordnance Unit Especially Major Jamal Maruf for his all-out support which was vital for my work.

I am thankful to Ahsan and Aftab for their great support.

My special thanks to my family especially my wife who allowed me so much time to complete my work without which it would not have been possible.

**(JUNAID AKHTAR)**

# Index

<b>S.No.</b>	<b>Contents</b>	<b>Page</b>
<b>Chapter 1: Introduction</b>		
1.1	Explosives	1
1.2	Classification of Explosives	1
1.2.1	By Sensitivity	1
1.2.1.1	Primary Explosive	1
1.2.1.2	Secondary Explosive	2
1.2.1.3	Tertiary Explosive	2
1.2.2	By Velocity	2
1.2.2.1	Low Explosives	2
1.2.2.2	High Explosives	3
1.2.3	By Composition	3
1.2.3.1	Priming Composition	3
1.2.4	By Physical Form	4
1.2.5	Nuclear Explosives	4
1.3	Characteristics of Explosives	4
1.3.1	General	4

1.3.2	Availability and Cost	5
1.3.3	Sensitivity	5
1.3.4	Brisance and Power	6
1.3.5	Stability	6
1.3.6	Density	6
1.3.7	Hygroscopicity	6
1.3.8	Volatility	6
1.3.9	Toxicity	7
1.3.10	Electrical Discharge	7
1.3.11	Ignition Temperature	7
1.4	Kinetics of Explosive Reactions	8
1.5	Rate of Reaction	9
1.6	Kinetics of Thermal Decomposition	11
1.7	TNT as Effective Explosive	12
1.7.1	Drawbacks of TNT	13
1.8	Oxygen Balance of TNT	13
1.9	Aim of Study	15
1.10	Amatol	15
1.10.1	Properties of Amatol	16
1.10.2	Preparation of Amatol	18



## **Chapter-2 Thermal Analysis**

2.1	Thermal Analysis	21
2.2	Methods of Thermal Analysis	21
2.3	Analytical Techniques Used in Current Study	25
2.3.1	The TGA Technique	25
2.3.1.1	Applications of TGA	25
2.3.1.2	Processes Relating Weight	26
2.3.1.3	Working/Principle	27
2.3.1.4	Interpretation of TG and DTG Curves	28
2.3.2	Differential Thermal Analysis	29
2.3.2.1	Basics	29
2.3.2.2	Working/Principle	30
2.3.2.3	Apparatus	30
2.3.2.4	Requirements for Good Experiments	31
2.3.2.5	Factors Affecting the Heat Transfer	31
2.3.2.6	Physical and Chemical Changes	32
2.3.3	Simultaneous Thermal Analysis	33
2.3.4	Calculation of Kinetic Parameters	34

## **Chapter-3 Experimentation**

3.1	Methodology	36
-----	-------------	----

3.1.1	Thermal Analysis (DTG-60H by Shimadzu)	36
3.2.1	Features	37
3.2.2	Main Parts of Thermal Instrument	38
3.2.3	Specifications	39
3.2.4	Method Used	40
3.3	Sample Material	40
3.4	Specifications of Materials	40
3.5	Study Samples	40
3.6	Experimental Conditions	40
3.7	Experimental Procedure	41

## **Chapter-4 Results and Discussion**

4.1	TNT and 80/20 Amatol	42
4.2	SEM Analysis	42
4.3	Oxygen Balance of TNT	44
4.4	Oxygen Balance of Amatol	45
4.5	Discussion	46
4.6	Thermal Analysis of TNT H/Rate @ 5 °C/min	47
4.7	Thermal Analysis of TNT H/Rate @ 10 °C/min	51

4.8	Thermal Analysis of TNT H/Rate @ 15 °C/min	55
4.9	Thermal Analysis of TNT H/Rate @ 20 °C/min	59
4.10	Thermal Analysis of TNT H/Rate @ 25 °C/min	63
4.11.1	Comparison of DTA of TNT at Different H/Rates	67
4.11.2	Comparison of TGA of TNT at Different H/Rates	69
4.11.3	Comparison of Activation Energy of TNT at Diff H/Rates	71
4.13	Thermal Analysis of Amatol H/Rate @ 5 °C/min	72
4.14	Thermal Analysis of Amatol H/Rate @ 10 °C/min	76
4.15	Thermal Analysis of Amatol H/Rate @ 15 °C/min	80
4.16	Thermal Analysis of Amatol H/Rate @ 20 °C/min	84
4.17	Thermal Analysis of Amatol H/Rate @ 25 °C/min	89
4.18	Comparison of DTA curves of Amatol at Different H/Rates	92
4.19	Comparison of TGA curves of Amatol at Different H/Rates	94
4.20	Comparison of Activation energy of Amatol at Diff H/Rates	95
4.21	Comparison of TNT and Amatol	97
4.22	Conclusion	101
4.23	Future Recommendations	102

# ABBREVIATIONS

HMX	High Melting Explosive (Cyclotetramethylenetetranitramine)
RDX	Royal Development Explosive (Cyclotrimethylenetrinitramine)
AN	Ammonium Nitrate
AP	Ammonium per Chlorate
Ea	Activation Energy
DTA	Differential Thermal Analysis
TG	Thermogravimetry
DTG	Derivative Thermogravimetry
STA	Simultaneous Thermal Analysis
TNT	Trinitrotoluene

## LIST OF FIGURES

Fig 1	TG/DTA curve of 80/20 TNT with heating rate of 5 <sup>0</sup> C/min	47
Fig 2	DTA curve of 80/20 TNT with heating rate of 5 <sup>0</sup> C/min	48
Fig 3	TG curve of 80/20 TNT with heating rate of 5 <sup>0</sup> C/min	49
Fig 4	Graph for calculation of kinetic parameters of TNT with heating rate of 5 <sup>0</sup> C/min	50
Fig 5	TG/DTA curve of 80/20 TNT with heating rate of 10 <sup>0</sup> C/min	51
Fig 6	DTA curve of TNT at 10 <sup>0</sup> C/min Heating Rate	52
Fig 7	TG curve of TNT at 10 <sup>0</sup> C/min Heating Rat	53
Fig 8	Kinetic parameters of TNT at 10 <sup>0</sup> C/min H/Rate	54
Fig 9	TG/DTA curve of 80/20 TNT with heating rate of 15 <sup>0</sup> C/min	55
Fig 10	DTA curve of TNT with Heating rate 15 <sup>0</sup> C/min	56
Fig 11	TGA curve of TNT with Heating rate 15 <sup>0</sup> C/min	57
Fig 12	Kinetic parameters of TNT with heating rate of 15 <sup>0</sup> C/min	58

Fig 13	TG/DTA curve of TNT at 20 <sup>0</sup> C/min Heating Rate	59
Fig 14	DTA curve of TNT at 20 <sup>0</sup> C/min Heating Rate	60
Fig 15	TGA curve of TNT at 20 <sup>0</sup> C/min Heating Rate	61
Fig 16	Kinetic parameters of TNT at 20 <sup>0</sup> C/min Heating Rate	62
Fig 17	TG/DTA curve of TNT with Heating Rate 25 <sup>0</sup> C/min	63
Fig 18	DTA curve of TNT with Heating Rate 25 <sup>0</sup> C/min	64
Fig 19	TG curve of TNT with Heating Rate 25 <sup>0</sup> C/min	65
Fig 20	Kinetic parameters of TNT at heating rate of 25 <sup>0</sup> C/min	66
Fig 21	DTA curve of TNT at different heating rates	67
Fig 22	TGA curve of TNT at different heating rates	69
Fig 23	TG/DTA curve of Amatol with Heating Rate 5 <sup>0</sup> C/min	72
Fig 24	DTA curve of Amatol with Heating Rate 5 <sup>0</sup> C/min	73

Fig 25	TG curve of Amatol with Heating Rate 5 <sup>0</sup> C/min	74
Fig 27	TGA/DTA curve of Amatol with Heating Rate 10 <sup>0</sup> C/min	76
Fig 28	DTA curve of Amatol with Heating Rate 10 <sup>0</sup> C/min	77
Fig 29	TGA curve of Amatol with Heating Rate 10 <sup>0</sup> C/min	78
Fig 31	TGA/DTA curve of Amatol with Heating Rate 15 <sup>0</sup> C/min	80
Fig 32	DTA curve of Amatol with Heating Rate 15 <sup>0</sup> C/min	81
Fig 33	DTA curve of Amatol with Heating Rate 15 <sup>0</sup> C/min	82
Fig 35	TG/DTA curve of Amatol with Heating Rate 20 <sup>0</sup> C/min	85
Fig 36	DTA curve of Amatol with Heating Rate 20 <sup>0</sup> C/min	86
Fig 37	TGA curve of Amatol with Heating Rate 20 <sup>0</sup> C/min	87
Fig 39	TG/DTA curve of Amatol with Heating Rate 25 <sup>0</sup> C/min	89
Fig 40	DTA curve of Amatol with Heating Rate 25 <sup>0</sup> C/min	90
Fig 41	TG curve of Amatol with Heating Rate 25 <sup>0</sup> C/min	91
Fig 43	DTA curve of Amatol with different Heating Rates	93





# **CHAPTER 1**

## **1.1 EXPLOSIVES**

Explosives are highly volatile substances and they require utmost care in handling them for the safe operation. They have the ability to undergo reaction instantly. When explosion or blast occurs it results in the formation of great amount of potential energy which also results in the light, pressure, sound and heat [1]. The chemical energy (may be derived from TNT) or nuclear energy (may be derived from fissile isotopes of uranium-235) stored in the substance is changed to the potential energy by the reaction taking place. Explosives can be classified as under:

## **1.2 CLASSIFICATION OF EXPLOSIVES**

### **1.2.1 By sensitivity**

#### **1.2.1.1 Primary explosive**

Primary explosive is defined as the explosive which shows very high sensitivity to any initiating source such as impact, friction, heat or static electric potential etc. Initiation phenomenon requires relatively small energy. Primary explosives as a rule are compared to the PETN and are considered the one which are having more sensitivity than Pentaerythritol tetra nitrate [2]. Primary explosives can have the initiation with a hammer blow explaining its dire sensitivity, when we compare it to the PETN then we find that PETN can also have initiation by hammer blow so it is just a guideline for the primary explosive. On the other hand, there are some explosive which are very much prone to detonation and are extremely difficult to handle e.g. nitrogen triiodide. This explosive can have detonation with the alpha radiation and may be considered as one of the few very highly sensitive explosives.

Main purpose of the primary explosives is to use them as trigger for the secondary explosives because secondary explosives are hard to detonate without initiation from a

relative sensitive explosive. Blasting caps and percussion caps mainly comprise the primary explosive to form the initiating wave. Some of the primary high explosive are as under:

- Lead azide
- Manganese heptoxide
- Methyl ethyl ketone peroxide
- Ammonium permanganate

#### **1.2.1.2 Secondary explosive**

Secondary explosive may be considered as the explosive which requires more energy for initiation. This is due to the insensitivity of the secondary explosives which requires high energy for detonation. They are considered to be safe in handling in comparison to the primary explosives. Also they are safe in storage as well. Secondary explosives are initiated in explosive train by using primary explosive. Few explosives are

- TNT
- RDX

#### **1.2.1.3 Tertiary explosive**

Tertiary explosives are the one which are so insensitive that they require the intermediate explosive booster in addition to the primary explosive to cause the detonation. These explosives are known as the blasting agents. They are very safe in handling and are very economical to produce large quantities for use on large scale. This large scale usage includes the mining and construction operation. Tertiary explosive includes the ANFO.

## **1.2.2 By velocity**

### **1.2.2.1 Low explosives**

Low explosive is related with the rate at which detonation occurs. These are the one having decomposition rate at a speed which is less than the speed of sound. In low explosives flame front travels or deflagrates through the explosive at a speed which is very low as compared to the shock wave speed in case of high explosive. In low explosives deflagration phenomenon takes place whose rate ranges from few centimeters/seconds to about few hundred meters/seconds. In this case deflagration may occur at so much high speed to simulate the effects of detonation. Such are the cases taking place under confinements with high ranges of temperatures and pressures.

In the low explosives two substances such as oxidant and combustible material are mixed together to cause deflagration, which is at a rate very less than the rate of decomposition in high explosives. Use of low explosives is normally resorted to propellants. Low explosives are having the most of the important use as the propellants for which they have been employed extensively.

### **1.2.2.2 High explosives**

High explosives may be defined as the explosive in which when initiation takes place, shock wave travels through the explosive at supersonic speed and detonation takes place. Explosive velocity ranges from 3000m/s to 9000m/s when detonation takes place in high explosive. Detonation rate of trinitrotoluene is approximately 5800 m/s and 6700 m/s is detonation rate of detonating cord. High explosive is employed for the mining, demolition and military purposes, among these uses bulk of quantity is utilized for civil purposes such as mining.

## **1.2.3 By composition**

### **1.2.3.1 Priming composition**

Priming compositions may be defined as the one in which some sensitive explosives are combined with the other materials which reduces the sensitivity to the desired level. One of the example is conversion of primary explosive to wet state for the storage and transportation to avoid any accident due to the high sensitivity of primary explosives.

### **1.2.3 By physical form**

Explosives are produced in different physical forms and are characterized as per the different physical shapes it adopts after manufacturing. These are listed as:

- Pressings
- Castings
- Plastic or polymer bonded
- Putties (plastic explosives)
- Rubberized
- Extricable
- Binary
- Blasting agents
- Slurries and gels
- Dynamites

**1.2.5 Nuclear explosives** Nuclear explosives may be defined as the one in which large atomic nuclei are split / fissioned into two pieces resulting in the very huge amount of energy release [3]. Another type of nuclear reaction occurs when small atomic nuclei are fused together to make a large nucleus resulting in the release of very high quantity of energy. Explosive power as a result of atomic or nuclear explosion is not similar to the traditional explosive where chemical reaction takes place rather it is due to the nuclear reaction.

## **1.3 Characteristics of Explosives**

**1.3.1 General.** Since the development of explosives has started, huge number of explosives have been tested and experimented for the military use, but only few of them have been found useful and fulfilling the requirements as per the military use. This is due to the reason that these explosives have to meet certain characteristics which are required to meet the workability, handling and storage requirements [4]. Explosives which meet most of these requirements are then further used. Some of these characteristics are studied below which are:

### **1.3.2 Availability and cost**

Keeping in mind the huge quantity of explosive used for various purposes, the raw material used for the production of explosive must be cheaply available and that too in large quantity. Beside that production process must be simple and cost effective.

### **1.3.3 Sensitivity**

Sensitivity of explosive is a major parameter considered for the workability of explosive and there is range of sensitivity which new explosives should meet for the production and use at large scale. Explosives which are too much sensitive are dangerous in handling and explosives which are having high insensitivity are also not desirable due to the high risk of low workability in initiation.

Sensitivity of an explosive is greatly dependent upon the heat and friction to which explosive is subjected. Different methods used for determining the sensitivity of explosive include [5]:

- Impact

Standard weight is dropped from specific heights to explode the explosive and sensitivity is measured as per the distance a weight is dropped.

- Friction

An explosive may respond differently reaching to the highest level of explosion when a pendulum with weight is grazed over it measuring the frictional sensitivity.

- Heat

When temperature is raised and explosion takes place at some specific temperature this measures the heat sensitivity of explosive.

### **1.3.4 Brisance and power**

One of the main characteristic of the explosive is its shattering effect also called the brisance, and the amount of potential energy stored in it which generates the practical effects. It must be sensitive enough to have detonation by different means available such as friction or percussion etc. beside that it must have the ability to cause detonation or initiation to the other explosives as well.

### **1.3.5 Stability**

Stability of explosives is one of the most important factor which comes into play due to the requirement of storage for very extended times and also the environment in which storage is done. As the times are changing modern war strategies are resulting into new and adverse type of environments, demanding higher stability at wide ranges of environmental conditions.

### **1.3.6 Density**

As there is very limited space available in the round of munition, it highlights the importance of loading density, lesser the space available higher the loading density required. Greater densities also result into the higher detonation effects and greater destruction.

### **1.3.7 Hygroscopicity**

The ability to absorb the moisture is called as the hygroscopic, and plays vital role in the stability of any explosive as moisture reduces the sensitivity and reactivity. Explosive must absorb least of moisture to render it suitable for use.

### **1.3.8 Volatility**

Explosive must not be volatile for its safe handling and operation. Due to the higher volatility explosive may develop different defects such as separation of different elements of a mixture or generation of extra pressure in the round etc. This demands that explosive should not show more than the desired volatility under different environmental and storage conditions.

### **1.3.9 Toxicity**

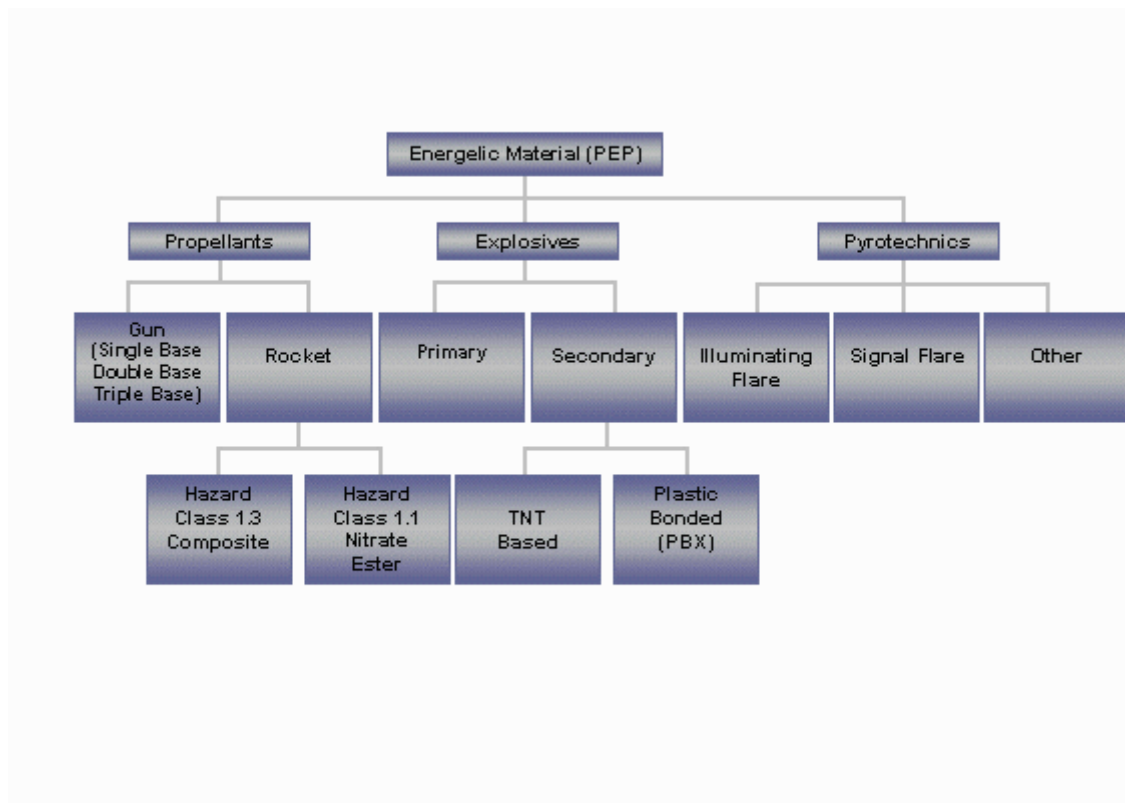
As explosive are chemical in nature so they have some of the toxicity but it must be kept in mind that any explosive used should have minimum toxicity and due care and attention must be paid to this characteristic for the explosive to be acceptable for use.

### **1.3.10 Electrical discharge**

Electrical discharge in any explosive can be very sensitive issue as this or static discharge may be very dangerous to cause an explosion which may render the explosive very unsafe for handling and operation so utmost care to be done address it.

### **1.3.11 IGNITION TEMPERATURES**

Ignition temperature is dependent on various factors among which rate, confinement and heating mechanism are important. Due to these factors there is no fixed temperature of ignition [6], however a range of temperature is always identified so that to avoid heating the explosive close to that range to avoid any undue explosion.



**Fig 1.1 : Classification of Energetic materials**

## **1.4 KINETICS OF EXPLOSIVE REACTIONS**

When chemical reaction takes place then it proceeds with some speed depending upon the reactants and conditions under which chemical reaction is taking place. This is referred to as the rate of chemical reaction and it relates to the kinetics in way that [7] “rate of change of chemical reactions is the kinetics of any chemical reaction”

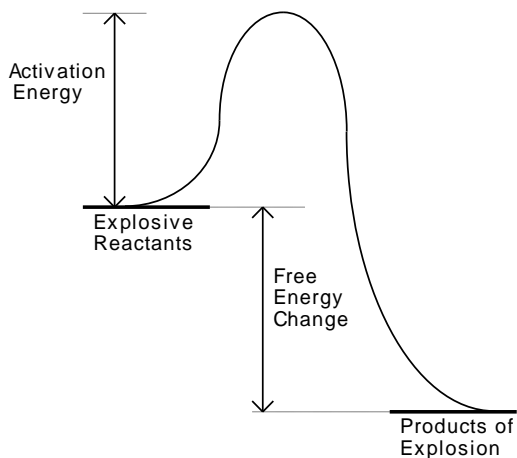
Rate of these chemical reactions vary from very fast such as explosion to very slow spread over long time such as rusting process of iron. When we consider the case of explosive reaction then rate of reaction is extremely quick and behaves differently under the influence of concentration and heat.

To initiate explosive a barrier of minimum energy is required to be crossed this barrier is called as the activation energy. Energy is provided by the initiator for the explosive chemical reaction which increases the temperature, as the temperature is increased it



forms the hotspots.

### ACTIVATION ENERGY



**Fig 1.2: Graphical Form of Activation Energy**

These hotspots generate the energy, if energy released is less than the activation energy then it will not allow any chemical reaction to take place and ultimately result in the killing of hotspot.

On the contrary the reaction will occur if energy produced by hotspot is larger than the activation energy and will ultimately lead to the detonation.

So we can safely state that activation energy is the amount of minimum energy to move the material to excited state to initiate the reaction and leading to the formation of explosive products along with huge energy quite higher in magnitude compared to the activation energy.

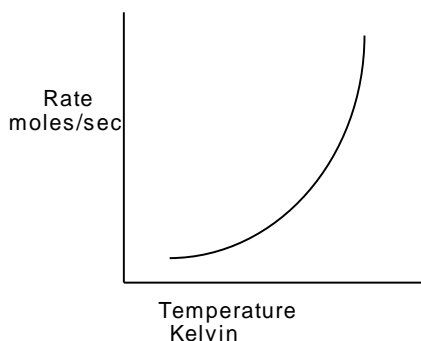
This activation energy relates the ease with which initiation of any explosive material can be done. The explosive material which has lower activation energy is easy to initiate and vice versa.

### 1.5 RATE OF REACTION

Rate of reaction is related to two very important factors which are the temperature and the activation energy [8], and can be measured by using these two factors.

Temperature and activation energy are directly related i.e. when we increase the temperature energy is transferred to the molecules in relation to the increase in temperature, in this way they increase in energy till they acquire the activation energy to start the chemical reaction.

This process is very well explained in the figure below:



**Figure 1.3: The effect of temperature on the rate of reaction**

This figure explains that as temperature is increased rate also increases giving direct relationship between the temperature and rate of reaction.

This relationship between rate of reaction and temperature is explained by the Arrhenius equation as shown below

$$k = Ae^{-E/RT}$$

Where

k is a constant for the rate of reaction,

A is a constant for a given material,

E is the activation energy in  $\text{kJ mol}^{-1}$ ,

T is the temperature in Kelvin and

R is the Universal Gas constant i.e.  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ .

In the above formula

A= is pre-exponential factor and is the (number of collisions/unit volume\*sec) among the molecules.

$e^{-E/RT}$  = Fraction of colliding molecules that result in a reaction.

List of some explosives with activation energy and collision factor is as under [8] :

<b>Type of Explosive</b>	<b>Activation energy E (kJ mol<sup>-1</sup>)</b>	<b>A (Collision factor)</b>
Primary explosives		
Mercury fulminate	105	10 <sup>11</sup>
Silver azide	167	
Lead azide	160	
<hr/>		
<b>Secondary explosives</b>	<b>Activation energy E (kJ mol<sup>-1</sup>)</b>	<b>A (Collision factor)</b>
Nitroglycerine	176	10 <sup>19</sup>
Tartly (crystalline)	217	10 <sup>22.5</sup>
PETN	196	10 <sup>19.8</sup>
RDX	199	10 <sup>18.5</sup>
Picric acid	242	10 <sup>22.5</sup>
TNT	222	10 <sup>19</sup>
HMX	220	10 <sup>19.7</sup>

From the above table we find that primary explosive requires less activation energy for the reaction to start and also have lower values of collision factor ‘‘A’’ compared to the secondary explosives. Lower values of activation energy also depict the sensitivity of explosive to the stimulus needed to initiate the explosive. For this reason, secondary explosives are less sensitive and require high energy to initiate them.

## **1.6 KINETICS OF THERMAL DECOMPOSITION**

Beside detonation one of the other phenomenon is of thermal decomposition which is faced by the explosives, this phenomenon takes place at lower temperature ranges compared to the detonation temperature. The importance of this phenomenon is highlighted more when we talk of stability and shelf life of explosive as these two are related to thermal decomposition.

We also extract from this phenomenon that how much the explosive is susceptible to the heating process. Isothermal conditions are used for the calculation of kinetic data in which rate of gas is measured which is released from the sample. This kinetic calculation is performed under controlled temperatures [9], which is explained by the formula below:

$$V = k^T + C$$

This formula explains the interaction of volume of gas with the rate of reaction

where

V = Gas evolved

T = Temperature in ° C

k = Rate of reaction constant

C = Constant

As rate of decomposition is dependent upon the temperature we find that decomposition becomes doubled for every temperature increase of 10 degrees centigrade leading up to 50 times in molten explosive. Storage conditions along with the impurities in the explosive play important role for the increase or decrease of rate of decomposition. Along with these factors moisture also plays vital role for the increase or decrease of rate of decomposition.

### **1.7 Trinitrotoluene (TNT) As Effective Explosive**

Trotyl, tolit, triton, tritol, trilit, and 1-methyl-2,4,6 trinitrobenzene are the different names with which trinitrotoluene is represented. Trinitrotoluene is considered as one of most effective explosive and has been in use after the second world war. It has several advantages which are its good thermal stability, power, safe handling, chemical

stability, low toxicity, good properties for melt casting (low melting point), good physical properties and compatibility with the other explosives.

TNT isomers are basically six in numbers among which alpha isomer is the one which carries great significance as far as effective explosive is concerned. This is primarily called as TNT and used as a military explosive. Other five isomers are given the name from Greek letters starting from beta till eta with an exception of zeta which is not included in isomers.

Trinitrotoluene is basically a crystalline compound which is yellow in color with molecular weight of 227, melting point ranging from 80 degrees centigrade to 81 degrees centigrade. It boils at 345 degrees centigrade at atmospheric pressure.

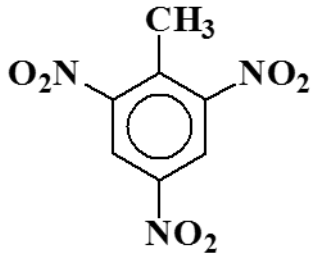
### **1.7.1 Drawbacks of trinitrotoluene TNT**

TNT is being extensively used as effective explosive after the second world war due to the good characteristics in handling and operation. But one of the drawback of TNT is its negative oxygen balance which has an effect on the performance reduction of this explosive. TNT negative oxygen balance is described below.

### **1.8 OXYGEN BALANCE OF TNT**

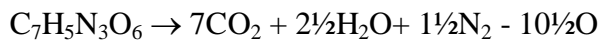
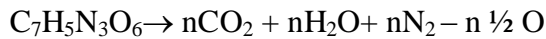
When detonation takes place, oxygen is utilized for the complete oxidation of explosive. If amount of oxygen is less for complete oxidation in any explosive, then it has negative oxygen balance [10]. On the other hand, if oxygen is present in excess of than required for the complete oxidation then the explosive has positive oxygen balance.

In case of TNT ( $C_7H_5N_3O_6$ ), it has negative oxygen balance persisting which results in the incomplete oxidation, which means detonation products are not completely converted to  $CO_2$ ,  $H_2O$ ,  $SO_2$ ,  $Al_2O_3$  etc.



**Figure 1.3: Structural formulae of TNT**

If we consider the complete oxidation takes place when TNT is detonated then it will completely transform to form gases like CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> and the equation will be as under



In the above equation negative sign has been shown with oxygen which indicates that excess of oxygen has been used compared to that available in the TNT explosive for the complete oxidation of products of detonation. Percentage of negative oxygen or deficient oxygen can be calculated as under:

TNT chemical formula is C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>6</sub>

So TNT molecular mass [11] is 227 (7 \* 12 + 5 \* 1 + 3 \* 14 + 6 \* 16 = 227)

Negative oxygen mass = -10.5 \* 16 = -168

Negative oxygen percentage = -168 \* 100 / 227 = -74%

### **1.8.1 CALCULATION OF THE OXYGEN BALANCE BY FORMULA**

An alternative method formula is shown below to calculate the oxygen balance, for which we use the general formula C<sub>a</sub>H<sub>b</sub>N<sub>c</sub>O<sub>d</sub>

$$\Omega = [d - (2a) - (b/2)] \times 1600/M$$

M = Molecular mass

It implies that in any explosive material there will be either negative oxygen balance or positive oxygen balance depending upon the presence of oxygen in the explosive. With

the help of this oxygen balance we can know which type of gasses are liberated on detonation. In case of less oxygen present in the explosive, toxic gases will be formed such as carbon monoxide which are not desirable and must be kept minimum.

Due to this negative oxygen balance TNT power is reduced somewhat, that is the reason amatol is formed by adding ammonium nitrate to TNT which has positive oxygen balance.

### **1.9 AIM OF STUDY**

TNT is considered as very reliable explosive for the military use yet it has one of the drawback of negative oxygen balance which results in the formation of unburnt carbon in the form of soot which in turn results in the decrease of heat of explosion. This matter can be discussed by using another explosive called as amatol for some of the specific bulk uses to replace TNT. Amatol is a mixture of TNT and ammonium nitrate, with this we can achieve two benefits, one of the benefit is to use ‘Amatol’ where negative oxygen balance of TNT is addressed by reducing the oxygen balance negativity by mixing TNT with ammonium nitrate due to which excessive oxygen contents in the ammonium nitrate bring good effect to the TNT negative oxygen balance. Secondly amatol's are less in cost as compared to the TNT so in this way economy can also be achieved beside enhancing the performance as compared to TNT.

Keeping in view the above, the objectives of the study are:

- a. Theoretical calculations of oxygen balance for TNT and Amatol
- b. Measurement of thermal effect and kinetic parameters of TNT at different heating rates and its comparison
- c. Measurement of thermal effect and kinetic parameters of Amatol at different heating rates and its comparison
- d. Comparison of thermal effect/ parameters of TNT and Amatol
- e. SEM analysis of TNT and Amatol

## 1.10 Amatol

Ammonium nitrate and TNT are mixed together to form a binary mixture known as amatol [12]. They are mixed in different percentages which are mentioned on the nomenclature e.g. 80/20 amatol contains 80% ammonium nitrate and 20% TNT. Melting of the mixture occurs at the TNT melting point being lesser as compared to the ammonium nitrate which remains solid at that temperature.

### 1.10.1 Properties of Amatol

- Some properties of different mixture compositions of amatol are shown in the table below as:

<b>Properties of Amatol</b>	<b>80/20 Amatol</b>	<b>60/40 Amatol</b>	<b>50/50 Amatol</b>	<b>45/55 Amatol</b>	<b>40/60 Amatol</b>
<b>Nitrogen content</b>	31.7%	28.4%	26.8%	25.9%	25.1%
<b>Oxygen balance to CO<sub>2</sub></b>	+ 1.20%	- 17.6%	-27.0%	-31.7%	-36.4%
<b>Oxygen balance to CO</b>	+ 11.06%	+2.13%	-2.32%	-4.55%	-6.78%
<b>Color</b>	Lt buff	Lt buff	Buff	Buff	Buff
<b>Melting point, °C</b>	-	-	81	-	-
<b>Heat of combustion at constant volume</b>	1,254	-	2,073	-	2,402

- To ascertain the sensitivity of amatol when comparing it with TNT the impact test data indicates:

Amatol	80/20	60/40	50/50	40/60
--------	-------	-------	-------	-------



Sensitivity to TNT	90 to 95	95 to 100	93 to 100	93 to 100
--------------------	----------	-----------	-----------	-----------

- When rifle bullet impact tests and pendulum friction tests were performed on amatol it remained unaffected.
- Explosion temperatures test conducted on various amatol configuration show that these values are less than that of TNT and are given as under:

Nomenclature	80/20 amatol	60/40 amatol	50/50 amatol
Temperature	280°C to 300°C	270°C	254°C to 265°C

- Some of the Characteristics of different amatol configurations are listed below in the table:

Nomenclature	80/20 Amatol	60/40 Amatol	50/50 Amatol	40/60 Amatol
Brisance by sand test	74%	90%	90%	94%
Brisance by fragmentation test	-	81% at density of 1.53 grams per cubic centimeter	82% at density of 1.55 grams per cubic centimeter	-
Power by Trauzl test	126%	-	116%	120%
Power by ballistic mortar test	130%	128%	123%	-
Detonation	5,300	6,200	6,400	6,550

velocity in meters per second at 1.59 to 1.6 grams per cubic centimeter				
---	--	--	--	--

### 1.10.2 Preparation of Amatol

Ammonium nitrate in ground and screened condition is heated in a mixing kettle with steam jacket from 90° to 95°C [13]. The ammonium nitrate used for this purpose should be very finely granulated with less than 0.25% water in it. At 95°C gradual addition of molten TNT is carried out with accurate quantity with the help of mechanical agitation. Mechanical agitation is carried out for about 15 minutes at the temperature of 95°C so that mixture is thoroughly blended. After that it is suitable for press loading and extrusion process. The explosive resembles the cast TNT and has resemblance to the wet brown sugar.

## REFERENCES

[1]

<http://webcache.googleusercontent.com/search?q=cache:RcSKVYXGDkUJ:www.innovateus.net/sc>

[2] [https://en.wikipedia.org/wiki/Explosive\\_material](https://en.wikipedia.org/wiki/Explosive_material)

[3] <http://www.encyclopedia.com/utility/printtopic.aspx?id=90667>

[4] <http://www.bsee.gov/Technology-and-Research/Technology-Assessment-Programs/Reports>

[5] [http://danpritchard.com/wiki/Explosive\\_material](http://danpritchard.com/wiki/Explosive_material)

[6] Gunners Mate Chapter 1 Explosives and pyrotechnics: <http://tpub.com/gunners/2.htm>

[7] THE CHEMISTRY OF EXPLOSIVES 2<sup>nd</sup> edition by Jacqueline Akhavan

[8] [http://www.e-reading.club/bookreader.php/141462/Akhavan\\_-\\_The\\_chemistry\\_of\\_explosives.pdf](http://www.e-reading.club/bookreader.php/141462/Akhavan_-_The_chemistry_of_explosives.pdf)

[9] <http://www.slideshare.net/M1CH4/j-akhavan-thechemistryofexplosivessecondebookfiorg>

[10] *The Chemistry of Explosives, Second Edition, Oxygen balance*

[11] <http://www.thirdwave.de/tech/explo/Warheads.pdf>

[12] DEPARTMENT OF THE ARMY TECHNICAL MANUAL Washington, D.C., 25

September 1990 MILITARY EXPLOSIVES

[13]

[www.freepyroinfo.com/Pyrotechnic/Pyrotechnic\\_Books/Tm\\_9\\_1300\\_214\\_U\\_S\\_Military\\_Explosives.pdf](http://www.freepyroinfo.com/Pyrotechnic/Pyrotechnic_Books/Tm_9_1300_214_U_S_Military_Explosives.pdf)

## **CHAPTER 2**

### **2.1 Thermal Analysis**

Thermal analysis may be defined as the branch of material science in which we deal with the properties of material in relation to the change in temperature. With the help of thermal analysis, we analyse many properties [1] of material which may be stiffness, volume change, rates of heat transfer, damping, dimension changes, mass increase or decrease etc. We also study the relationship of light and sound with the temperature changes. To sum up all we can say that all the changes taking place in materials due to changes in temperature are studied.

In order to perform the thermal analysis, we generally have the control over the temperature, whose rate is altered to suit our experiment or analysis design. This alteration of temperature [2] in an organised manner helps us to extract information on the material behaviour to the temperature changes.

One of the major factor which comes into play while performing the thermal analysis is the environment in which experiment or analysis is being carried out. As the environment have pivotal role on the results outcome and can change altogether with the change in the environment. Environment for the thermal studies is controlled by using inert gas such as helium or nitrogen, as per the requirement their input is controlled. Beside that air is also used as environment to check the reaction of material with the environment.

### **2.2 Methods of Thermal Analysis**

- **Thermogravimetry (TG)**

In this method heat is supplied to the sample as per our requirement and weight of the sample is recorded with the change or rise in the temperature

- **Isobaric mass-change determination**

In this method sample is subjected to heat change program and during this heating

process we keep the constant partial pressure and measure the weight of sample to analyze the changes

- **Evolved gas detection (EGD)** (MASS)

In this method we heat a sample as per the desired program, due to this heating gas is produced which is detected and measured for the analysis.

- **Evolved gas analysis (EGA)**

In this method when we heat a sample it results in the formation of volatile products which are detected and analysis is carried out.

- **Emanation thermal analysis**

In this method radioactive emanation is detected as a result of heating as per the required program and analysis is done.

- **Thermoparticulate analysis**

Measurement of particulate matter is carried out which is formed as a result of heating done to a sample.

- **Heating or cooling curve determination** (Temperature)

In this method heating of sample is carried out which result in the increase of sample temperature which is noted and analyzed. Inverse heating rate curves are also formed in it.

- **Differential thermal analysis (DTA)** (Temperature)

In this method heating of sample and reference material is done and we measure the temperature difference among the sample and reference.

- **Differential scanning calorimetry (DSC) (Enthalpy)**

In this method we carry out heating of both sample and reference material and then we note the difference in energy inputs taking place in both the sample and reference material for further analysis.

- **Thermodilatometry (Dimensions)**

In this method as a sample is heated it results in the change in the dimension of sample which is noted and analyzed. For this experiment load to the sample should be negligible.

- **Thermomechanical measurement (Mechanical characteristics)**

In this method heating of sample is carried out as per the requirement and measurement of deformation occurring to the sample as a result of heating is recorded and analyzed. This experiment is performed under non oscillatory loading to the sample.

- **Dynamic thermomechanical measurement (Mechanical characteristics)**

In this method sample is heated as per the program during this heating changing taking place in damping or modulus are recorded. This experiment is carried out by subjecting the sample under the oscillatory loading.

- **Thermosonimetry (Acoustic characteristic)**

In this method heating of the sample is carried out and then changes occurring to the sound emitted by the sample as result of rise in temperature are recorded and analyzed.

- **Thermoacoustimetry (Acoustic characteristics)**

In this method heating of sample is carried out as per the program then measurement of

characteristics of imposed acoustic waves is done as the increase of temperature in the sample takes place.

- **Thermometry** (Optical characteristics)

In this method heating of the sample is carried out as per the program and as a result of increase in temperature optical characteristics are recorded.

- **Thermoelectrometry** (Electrical characteristics)

In this method heating of the sample as per the program is carried out and changes taking place in the electric characteristics are recorded and analyzed.

- **Thermomagnetometry** (Magnetic characteristics)

In this method heating of the sample is carried out as per the program and then we measure the magnetic susceptibility of the sample as a result of increase in temperature of the sample.

- **Multiple techniques**

- **Simultaneous Techniques**

In this method of analysis, we apply different techniques of analysis at the same time to extract the results. One of the most common use is the application of Thermogravimetry analysis and Differential thermal analysis.

- **Coupled Simultaneous Technique**

In this method of analysis, coupling of two or more techniques is carried out so that analysis can be carried out one after the other without giving pause. It is the most efficient technique to extract quick results for example we can use of differential



thermal analysis coupled with the mass spectrometry.

- **Discontinuous Simultaneous Techniques**

In this technique multiple methods are applied for the analysis but the sample is inserted one after the other and is not done in a continuous manner. For that sample is obtained from the chromatography and then inserted into the differential thermal analyzer for the further analysis.

## **2.3 Analytical Techniques Used in Current Study**

### **2.3.1 The TGA Technique**

- TGA is used to analyse the changes occurring to the weight with the changes in the temperature [3] under the controlled atmosphere where nitrogen, air or helium is used for the atmosphere management.
- Different type of materials [4] ranging from ceramics, plastics, inorganic materials, to metals etc. can be observed for changes with the temperature.
- The experimentation can be performed ranging from ambient temperature to about 1500 degree centigrade as per the instrument specification.
- Samples which are analysed have the weight limits ranging from 1mg to 150 mg or so depending upon the instrument capacity.
- Sensitivity of 0.01 mg exists for the weight change.
- Samples for the experimentation are placed in the powder or small pieces' form.

#### **2.3.1.1 Applications of TGA**

TG has find its utility in vast fields relating to science and technology due to its capability to analyze [5] different type of materials and provide quantitative data to that effect. Important applications are listed below:

▶ **Thermal Stability:** Thermal stability of different materials is analyzed and decomposition taking place under the controlled environment is noted to extract the behavior of matter.

▶ **Material characterization:** Materials can be identified by relating their TG profiles.

▶ **Compositional analysis:** Under the controlled environment and temperature, components of the matter are removed to analyze the composition [6] of different materials.

▶ **Simulation of industrial processes:** It can simulate the industrial reactor in the miniature form where balance furnace is used in the form of a small reactor.

▶ **Kinetic Studies:** Thermal data extracted from the thermal analysis is used further to lead to the kinetics studies.

▶ **Corrosion studies:** Oxidation processes or material reaction with the gases can be used to provide data for the corrosion studies.

▶ **Material preparation:** This process can be used for the preparation of materials as it exposes different stages of decomposition under different environments with the changing temperatures.

### 2.3.1.2 Processes Relating Weight

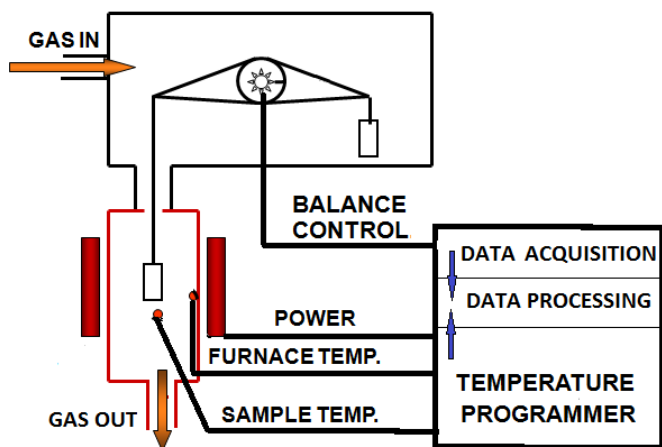
Various processes relating to weight gain and loss [7] which take place during experimentation are as under:

<b>Process</b>	<b>Activity</b>	<b>Activity</b>
Adsorption	<b>Weight gain</b>	
Absorption	<b>Weight gain</b>	
Desorption		<b>Weight loss</b>
Drying		<b>Weight loss</b>

Dehydration		<b>Weight loss</b>
Desolvation		<b>Weight loss</b>
Vaporisation		<b>Weight loss</b>
Decomposition		<b>Weight loss</b>
Solid-solid reactions		<b>Weight loss</b>
Solid-gas reactions	<b>Weight gain</b>	
Oxidation	<b>Weight gain</b>	

### 2.3.1.3 Working / Principle

As the temperature is increased, changes takes place in sample mass which is measured by using thermobalance. In TG main reliance is on the accurate measurement of the mass change, temperature, and changes in temperature. TGA comprises of a precision balance with pan for loading of sample and programmable furnace. This furnace is used to control the heating process during experimentation. Sample chamber atmosphere is controlled by the inert gas to offset any unwanted or undesirable reaction. Weighing of sample is done continuously during the experiment when heating of sample is done continuously. As the temperature is increased different processes such as decomposition etc. takes place.



## **Figure 2.1 schematic thermobalance instrumentation**

### **2.3.1.4 Interpretation of TG and DTG curves**

Actual TG curves obtained may be classified into various types as illustrated in Fig. 5. Possible interpretations are as follows [8].

Type (i) curve. This curve states that over the complete temperature range the sample remained stable and no reaction took place.

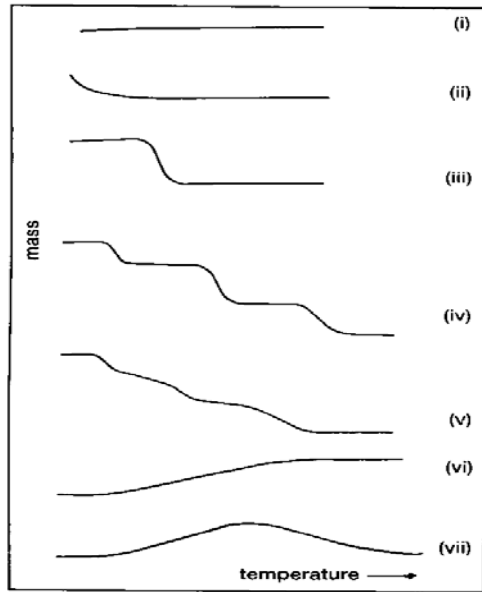
Type (ii) curve. This curve depicts buoyancy mechanism, where mass loss is rapid.

Type (iii) curve depicts single stage decomposition has taken place and is used to investigate the kinetics of reaction.

Type (iv) curve states that multi stage decomposition phenomenon has taken place with stable intermediates. Curve is used to determine the kinetics of reaction at all stages.

Type (v) curve shows the phenomenon of multi stage decomposition but here stable intermediates are not present making such curve.

Type (vi) curve. This curve shows an increase in the sample weight depicting the reaction of the sample with the surrounding atmosphere such as oxidation process taking place in metals. Type (vii) curve. This curve states increase in weight of sample due to oxidation which on the later stage decomposes at high temperature.



**Fig 2.2: TG Curves/Profiles**

## **2.3.2 Differential Thermal Analysis**

### **2.3.2.1 Basics**

- In the differential thermal analysis, sample and the inert reference material both are placed in the similar environment and are provided heat in similar manner to note or record the temperature difference that develops between these two materials.
- DTA is based on the comparison principal where difference between temperature of two materials is compared to extract the quantitative data.
- DTA detects the different transformations i.e. any alteration in specific heat or enthalpy of transition is detected and recorded.
- Sample and the reference material are subjected to similar heat flow in the DTA technique.
- The differential temperature obtained from the process is then placed on graph against the temperature or the time called as thermogram or DTA curve.

### **2.3.2.2 Working/ principle**

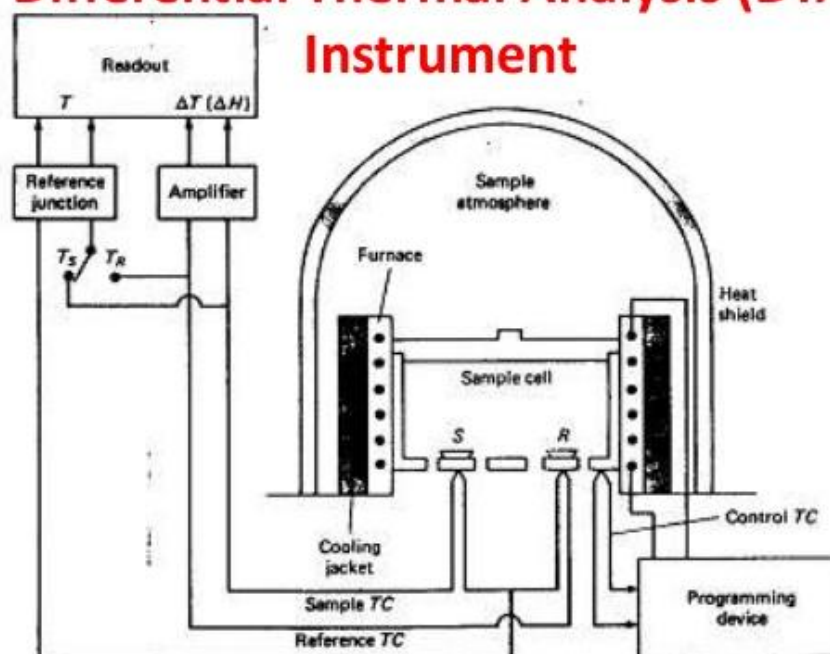
Temperature of the sample and the inert reference material is measured by using the thermocouples attached to the sample and reference material holder. Sample and reference material temperature difference is detected as the temperature is raised with the start of experiment. Amplification of the signal is done so that thermal change of the sample in relation to the inert material can be recorded. Thermogram or DTA curve is then obtained by plotting the temperature difference against the time or temperature increase. Different thermal changes and processes relating to the physical and chemical changes are reflected by different peaks on the DTA curve and are interpreted to extract the information. During the experimentation similar conditions are provided for both the sample and the inert reference material to get the most accurate results.

### **2.3.2.3 APPARATUS**

DTA apparatus mainly consists of following:

- Sample holder with the thermocouples, ceramic or metallic block, sample container.
- Furnace
- Temperature programmer
- Recording system

## Differential Thermal Analysis (DTA) Instrument



***Endothermic*** - heat flows into the sample.  
***Exothermic*** - heat flows out of the sample.

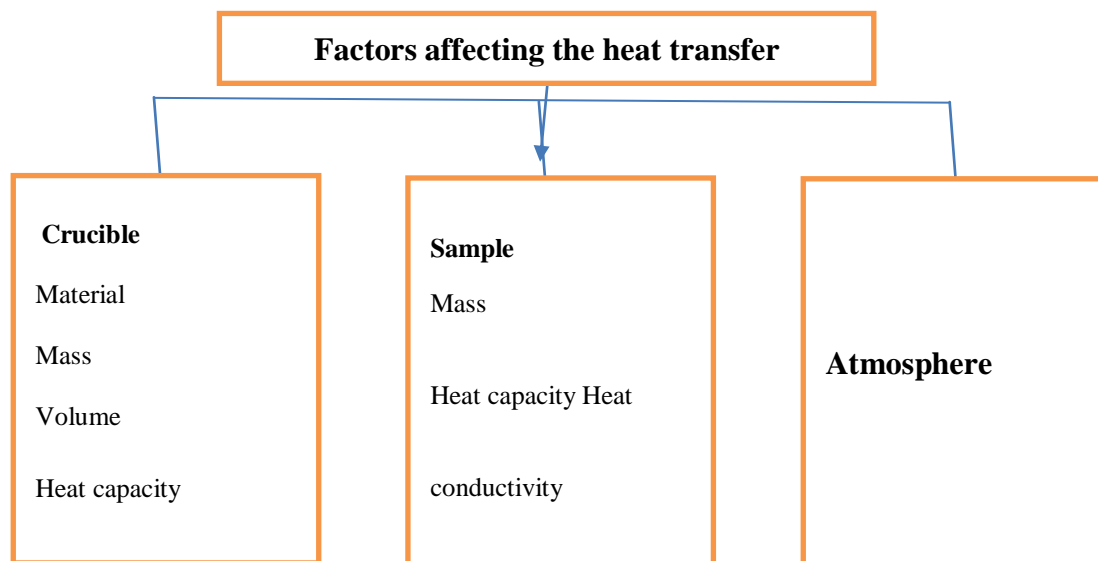
Fig 2.3: DTA Instrument

### 2.3.2.4 Requirements for Good Experiment

Following are the important requirements to be met for the good experimental results:

- Requirement of very high level of purity for the sample to be used for the experiment.
- In order to have large contact area and good equilibrium, there is requirement of using very fine grained powder for the experiment
- To achieve the reaction completeness, we should ensure maximum time at any temperature during the experiment.

### 2.3.2.5 Factors affecting the heat transfer



### 2.3.2.6 Physical and Chemical Changes

- Physical changes taking place with the type of reactions are listed below:

Physical Changes	Type of Reaction
Adsorption	exothermic
Desorption	endothermic
A change in crystal structure	endo – or exothermic
Crystallization	exothermic
Melting	endothermic
Vaporization	endothermic
Sublimation	endothermic

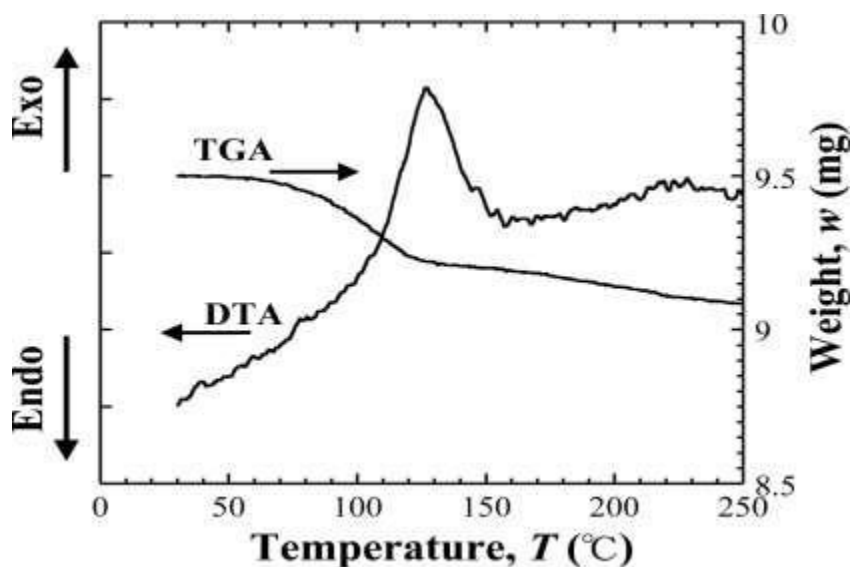
- Chemical changes with the type of reaction are listed below:



Chemical Changes	Type of Reaction
Oxidation	exothermic
Reduction	endothermic
Break down reactions	endo – or exothermic
Chemisorption	exothermic
Solid state reactions	endo – or exothermic

### 2.3.3 SIMULTANEOUS THERMAL ANALYSIS

We have amply shed light on the TGA and DTA techniques above for the experimentation on separate basis. With the advent of new technology now these two techniques have been joined together in one instrument and is called as the Simultaneous thermal analysis (STA). The sample under study is kept at the similar test conditions and the combined results of TGA and DTA are obtained simultaneously. The results of STA can be very useful as both the curves i.e. differential temperature vs sample temperature and the other curve for weight loss vs sample temperature are obtained to analyze and extract results.



### **Fig 2.4: TGA/DTA Curve**

With the help of this simultaneous analysis we can also determine different processes taking place without any weight loss such as crystallization process etc.

In our study we have used this technique to study the amatol to extract thermal profiles and then further used these thermal profiles to perform kinetic study.

#### **2.3.4 CALCULATION OF KINETIC PARAMETERS**

In order to perform the kinetic calculations to study 80/20 amatol, the results obtained from the simultaneous thermal analysis have been used in which TG/DTA curves have been recorded. For that purpose, Horowitz and Metzger Method has been used to determine the activation energy, order of reaction, and enthalpy which has been further used to determine other kinetic parameters.

In order to use the Horowitz and Metzger Method we use the thermal profile obtained by thermal analysis. For that we find the temperature at maximum rate of decomposition which is denoted as  $T_s$  and is calculated by using the formula as:

$$T_s = W_t / W_o = 1/e$$

**Where**

**e = Exponential**

**W<sub>o</sub> = Initial sample weight**

**W<sub>t</sub> = Sample weight at T temperature**

**T<sub>s</sub> = Reference temperature**

In the second step curve fitting program has been used to find activation energy, order of reaction and enthalpy.

## REFERENCES

- [1] Brown M. E., Introduction to Thermal Analysis, Techniques and applications, 1998, CHAPMAN AND HALL New York
- [2] Daniels, T. (1973) Thermal Analysis, Kogan Page, London
- [3] Duval, C. (1963) Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 2nd edition
- [4] J. Sestak, Thermophysical properties of solids, Academia, Prague, 1984
- [5] <http://www.globalspec.com/reference/36940/203279/chapter-3-thermogravimetry-tg>
- [6] Keatch, C. J. and Dollimore, D. (1975) An Introduction to Thermogravimetry, Heyden, London, 2nd edition
- [7] <http://www.andersonmaterials.com/tga.html>
- [8] [http://thanma.web.auth.gr/files/Thermogravimetry\\_TG.pdf](http://thanma.web.auth.gr/files/Thermogravimetry_TG.pdf)

## CHAPTER 3

### EXPERIMENTATION

#### 3.1 METHODOLOGY

The methodology adopted to perform this study is as under:

- Preparation of samples
- Thermal analysis using Shimadzu DTG-60H
- SEM analysis
- Extraction and interpretation of results
- Kinetic study by **Horowitz and Metzger Method** using **Curve Fitting Program**

#### 3.2 THERMAL ANALYSIS (DTG-60H by Shimadzu)

To conduct the thermal analysis, DTG-60H by Shimadzu has been used which utilizes the differential top pan balance which has the ability to carry out simultaneous measure of temperature changes and mass changes between the sample and inert reference sample. It is suitable for all type of materials including organic and inorganic substances. It analysis sample for temperature ranging from ambient to 1500 degree centigrade. Some of the features of this equipment are shown below:



**Fig 3.1: DTG-60H by Shimadzu**

### 3.2.1 Features

- **Stability and High Sensitivity**

The differential balance in the DTG-60 series is of the Roberval style, where the sample and reference are located above the balance at the top of two separate detectors. This design prevents changes in sensitivity from thermal expansion, enables high-precision thermogravimetric measurements, and minimizes baseline drifts caused by buoyancy or convection during the heating process.

- **Wide Measurable Mass and Differential Thermal Ranges**

The advanced balance, high-quality detectors, and excellent furnace temperature distribution combine to provide a measurable mass change of  $\pm 500$  mg, a mass readability of  $0.1 \mu\text{g}$ , a maximum sample quantity of 1 g, and a measurable differential thermal range of  $\pm 1,000 \mu\text{V}$ .

- **Automated Measurement up to 24 Samples**

The compact, built-in auto sampler of the DTG-60A and DTG-60AH models can hold up to 24 samples for continuous data acquisition. After setup of a master file, automatic analysis and printing is performed according to the preset conditions in the template.

- **Integrated Cooling and Controlled Atmospheres**

The built-in cooling fan and low-mass furnace combine to create quick cooling between measurements. Reactive gases are supplied directly to the sample area and an inert gas purges the balance. By incorporating a FC-60A atmosphere control unit, the software can be used to switch reactive gases during a temperature program.

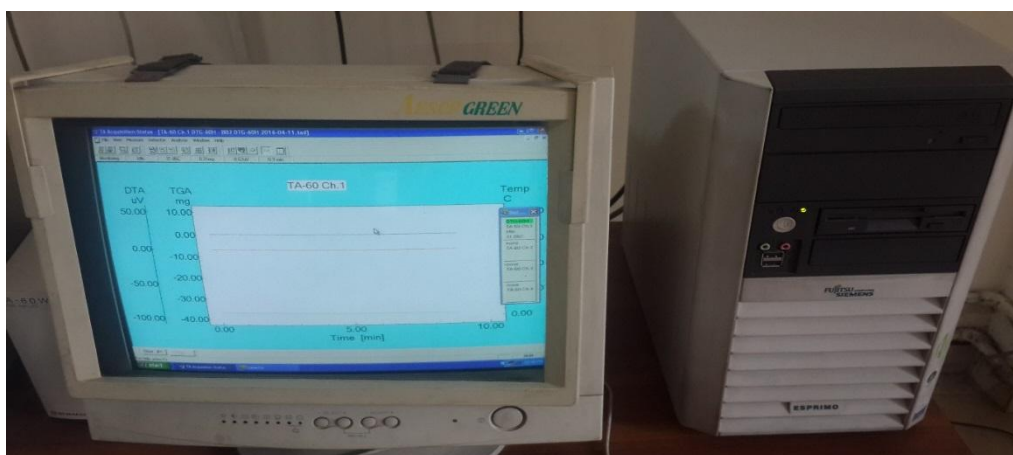
- **Controlled by TA-60WS Thermal Analysis Workstation**

The TA-60WS thermal analysis workstation connects the DTG-60 series and the computer. Intuitive data acquisition software controls the DTG-60 series and optional

accessories, such as the FC-60A atmosphere control unit. In addition, the TA-60WS and data acquisition software can be used to simultaneously control up to four Shimadzu thermal analysis instruments of any type.

- **Software Compliant with Analytical Laboratory Regulations and US FDA 21 CFR Part 11**

A software version that complies with US FDA 21 CFR Part 11, electronic record and electronic signature (ER/ES) regulations, and PIC/S GMP guidelines is available.



**Fig 3.2: Profile Screen**

### **3.2.2 MAIN PARTS OF THERMAL INSTRUMENT:**

- two plug-in detectors and set of crucibles (aluminium, platinum)
- lighted LCD display for temperature and signal
- operation panel for direct access for emergency stop and service tasks
- remote system functions
- self-diagnostics by software
- three gas connectors
- built in cooling fan allows controlled cyclic runs between 50 °C and 1500 °C
- auto-cleaning function



**Fig 3.3: Thermal Analyzer**

### **3.2.3 Specifications:**

- Balance type: Parallel Guide Differential Top Pan
- Weight range:  $\pm 500\text{mg}$
- Weight Readability:  $0.001\text{ g}$
- DT Range:  $\pm 1000\mu\text{V}$
- Sample Quantity :1 g max in gross weight
- Fully controlled atmosphere (air or inert gas) for various applications
- Temperature range: Room Temperature to  $1500^{\circ}\text{C}$
- Heating rate:  $\pm 0.01$  to  $\pm 99.9^{\circ}\text{K}/\text{min}$  at  $0.1^{\circ}\text{K}$  intervals
- Temp reproducibility  $0.1^{\circ}\text{K}$
- Temp accuracy:  $0.1^{\circ}\text{K}$
- TG readability:  $0.1\ \mu\text{g}$
- Dynamic range:  $\pm 1000\ \mu\text{V}$
- DTA sensitivity:  $0.1\ \mu\text{V}$

### **3.2.4 METHOD USED**

For the study multiple experiments were carried out by varying the heating rate and keeping the 80/20 amatol composition similar by using DTG equipment. Simultaneous use of TG/DTA was done to perform the thermal analysis, during which weight loss data and with the other thermal phenomenon like decomposition etc. with the changes in temperature were recorded. Profiles were recorded with the passage of time to note down changes taking place in the sample. From the profile it can be determined whether exothermic or endothermic reactions are taking place with the increase in temperature in systematic manner. The data of decomposition peak is further used to insert values in battery software to find the values of activation energy and further kinetic parameters.

### **3.3 Sample Material**

For the thermal experimentation following samples have been used:

- a. Trinitrotoluene (TNT)
- b. Ammonium Nitrate

**3.4 SPECIFICATIONS OF MATERIALS** Ammonium nitrate with 99.5 % purity was used so that very realistic results could be obtained

### **3.5 STUDY SAMPLES**

Following samples are used for carrying out the thermal and kinetic study:

**Sample No 1** Ammonium nitrate

**Sample No 2** Ammonium Nitrate 80 %, TNT 20 %

**Sample No 3** TNT

### **3.6 EXPERIMENTAL CONDITIONS**

Following conditions are used for carrying out the study:

- a) Sample Mass 5 mg  $\pm$ 1



- b) **Temperature Range** Ambient temperature - 400°C
- c) **Heating Rate**
  - a. Experiment 1 5°C/min
  - b. Experiment 2 10°C/min
  - c. Experiment 3 15°C/min
  - d. Experiment 4 20°C/min
  - e. Experiment 5 25°C/min
- d) **Atmosphere** Nitrogen
- e) **Flow Rate** 20 ml/Min
- f) **Pan Material** Alumina Crucibles

To carry out the study heating rate was varied for the experiments by keeping rest of all the conditions same. Main purpose of this is to provide similar conditions to analyze the behavior of 80/20 amatol.

**3.7 EXPERIMENTAL PROCEDURE** Initializing of the equipment was carried out in which all the readings of weight and energy were zeroed, after that equipment is tested with the reference material alumina for accuracy determination of equipment. Then sample to be analyzed is placed in the pan and pan is placed on the stand. Nitrogen atmosphere is maintained in the equipment with the flow of 20 ml/min. Equipment automatically weighs the sample and temperature range is set from ambient temperature to 400 ° C. Then after setting the heating rate, start button is pressed to start the experiment. Weight and energy profile is recorded with the passage of time, and variations in energy and weight are recorded. Exothermic and endothermic curves are recorded along with the weight loss curve. These weight loss and energy changes curve are noted simultaneously till decomposition of sample takes place. The decomposition curve data is inserted in the battery software to extract kinetic parameters by Horowitz and Metzger Method. After that further experiments are performed by changing the heating rate.

## **CHAPTER 4**

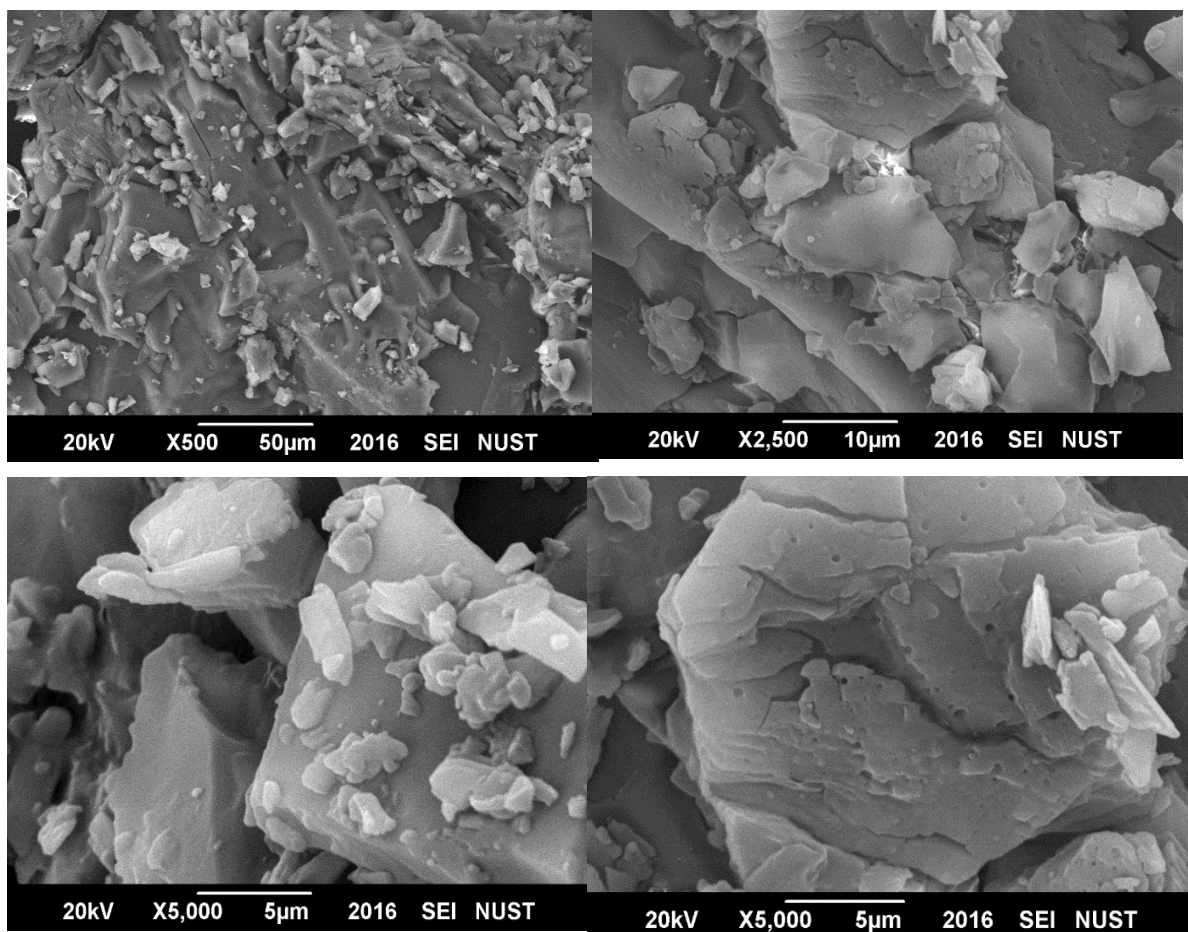
### **RESULTS AND DISCUSSION**

#### **4.1 Trinitrotoluene (TNT) AND 80/20 AMATOL**

In the study TNT and 80/20 amatol have been analyzed for the oxygen balance vis-a-vis thermal and kinetics properties. In this regard oxygen balance of both the amatol and TNT have been calculated and discussed. For the thermal studies of TNT and 80/20 amatol experimental determination of the TG curves along with the DTA curves simultaneously has been done and results have been analyzed. After the thermal calculations this thermal data has been used to find the kinetics of TNT and 80/20 amatol by using Horowitz and Metzger Method by inserting data into curve fitting program. SEM analysis is also performed to get the closer view of both the TNT and 80/20 amatol.

#### **4.2 SEM ANALYSIS OF TNT**

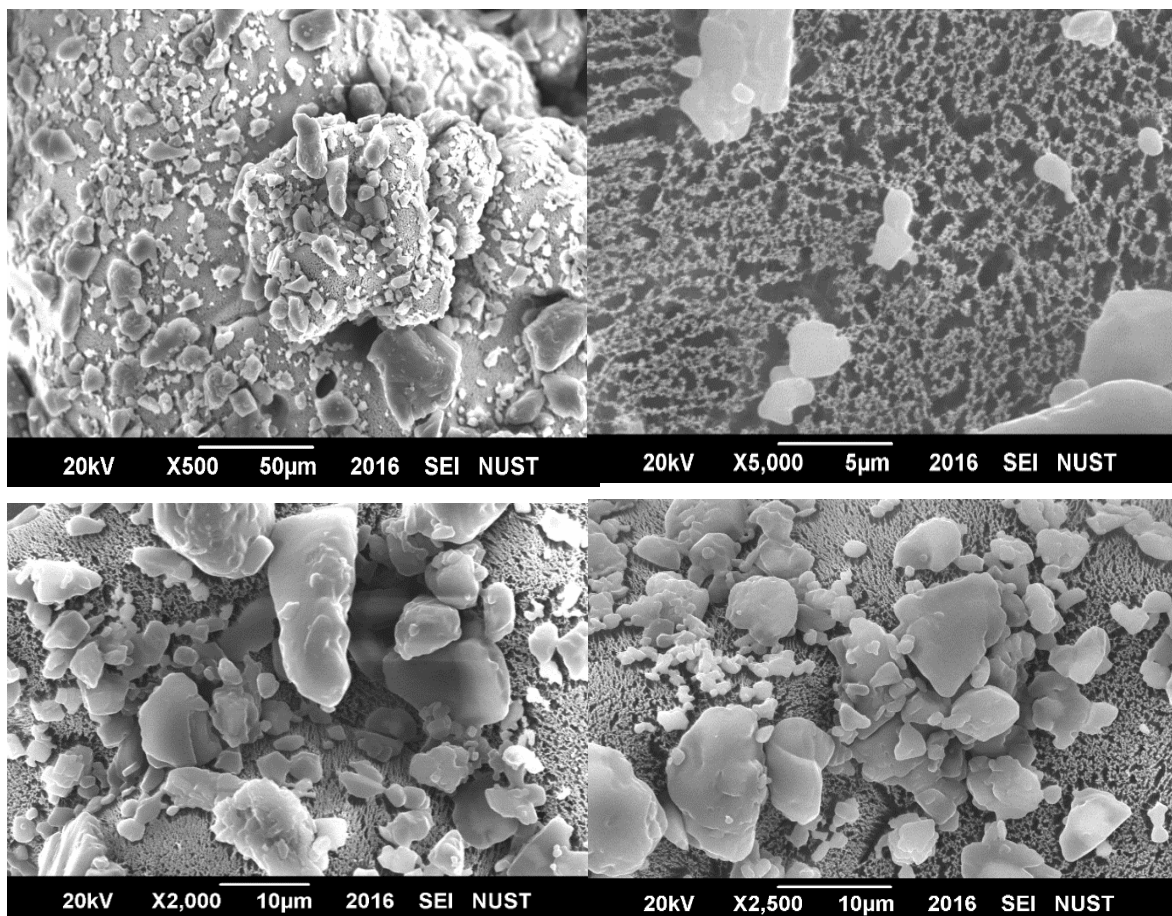
We have performed the SEM analysis of the trinitrotoluene (TNT) to ascertain the physical micro structure, porosity, mixing and the particle sizes range. From the figures below it is found that TNT has smooth background with the particle sizes varying from half micrometer to about 50 micrometers. Due to size variation or non-uniformity in the particles there is unsymmetrical structure. In the structure there is almost very less porosity visible due to which oxidizing ability of the TNT is reduced. As it is found that some of the particle sizes are large due to which exposed surface area of the TNT is reduced and limits the high oxidizing character.



#### 4.2.1 SEM ANALYSIS OF 80/20 AMATOL

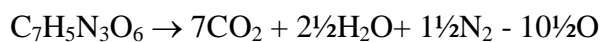
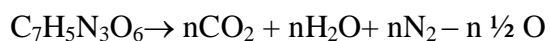
SEM analysis of the 80/20 amatol has been carried out to ascertain its micro structure, porosity, uniformity etc. so that one can understand the physical character of the sample and how it responds to the energy input. From the figure below it is found that uniform mixing of the ammonium nitrate and trinitrotoluene has been carried out. It is found that structure is mesoporous with the diameter sizes ranging from 2nm to 50 nm and it has uniformly distributed porous structure. In the amatol structure it is found that gaps are interconnected. The structure has high surface area due to which the oxidizing potential of the amatol is increased manifold. Due to the interconnection of gaps and evenly distributed

porous structure its ability to oxidize rapidly is greatly enhanced.



### 4.3 OXYGEN BALANCE OF TNT

If it is considered that the complete oxidation takes place when TNT is detonated then it will completely transform to form gases like CO<sub>2</sub>, H<sub>2</sub>O and N<sub>2</sub> and the equation will be as under



In the above equation negative sign has been shown with oxygen which indicates that

excess of oxygen has been used compared to that available in the TNT explosive for the complete oxidation of products of detonation. Percentage of negative oxygen or deficient oxygen can be calculated as under:

TNT chemical formula is  $C_7H_5N_3O_6$

So TNT molecular mass is 227 ( $7 * 12 + 5 * 1 + 3 * 14 + 6 * 16 = 227$ )

Negative oxygen mass =  $-10.5 * 16 = -168$

Negative oxygen percentage =  $-168 * 100 / 227 = -74\%$

#### 4.3.1 CALCULATION OF THE OXYGEN BALANCE BY FORMULA

An alternative method formula is shown below to calculate the oxygen balance, for which general formula  $C_aH_bN_cO_d$  is used.

$$\Omega = [d - (2a) - (b/2)] \times 1600/M$$

M = Molecular mass

TNT chemical formula is  $C_7H_5N_3O_6$  so by inserting values in the above equation oxygen balance of TNT can be calculated.

$$\Omega = [6 - 2 * 7 - 5/2] * 1600/227$$

$$\Omega = -74\%$$

#### 4.4 OXYGEN BALANCE OF AMATOL

Amatol has major advantage over TNT having being positive oxygen balance which increases the effectiveness of amatol over oxygen deficient explosives. Chemical formula of amatol is given as:

Name	Composition	Formula
AMATOL	80/20 nitrate/TNT Ammonium	$C_{0.62}H_{4.44}N_{2.26}O_{3.53}$

To calculate the oxygen, balance the equation given below is as:

$$\Omega = [d - (2a) - (b/2)] \times 1600/M$$

Where a = 0.62, b = 4.44, c = 2.26, d = 3.53

And M = molecular weight = 92

$$\Omega = [3.53 - 2 * 0.62 - 4.44/2] * 1600/92$$

$$\Omega = 1.2 \%$$

#### 4.5 DISCUSSION

It implies that in any explosive material there will be either negative oxygen balance or positive oxygen balance depending upon the presence of oxygen in the explosive. With the help of this oxygen balance it can be known which type of gasses are liberated on detonation. In case of less oxygen present in the explosive, toxic gases will be formed such as carbon monoxide which are not desirable and must be kept to minimum.

Due to this negative oxygen balance TNT power is reduced somewhat, that is the reason amatol is formed by adding ammonium nitrate to TNT which has positive oxygen balance. Comparison of amatol with TNT by Tiger Predictions method is done which shows that:

Explosive	Density (g/cc)	Detonation Velocity (m/sec)	P (katm)	T (°K)	Gas (moles/kg)
TNT	1.650	6989	208	2904	25.70
AMATOL	1.643	8054	257	1806	36.37

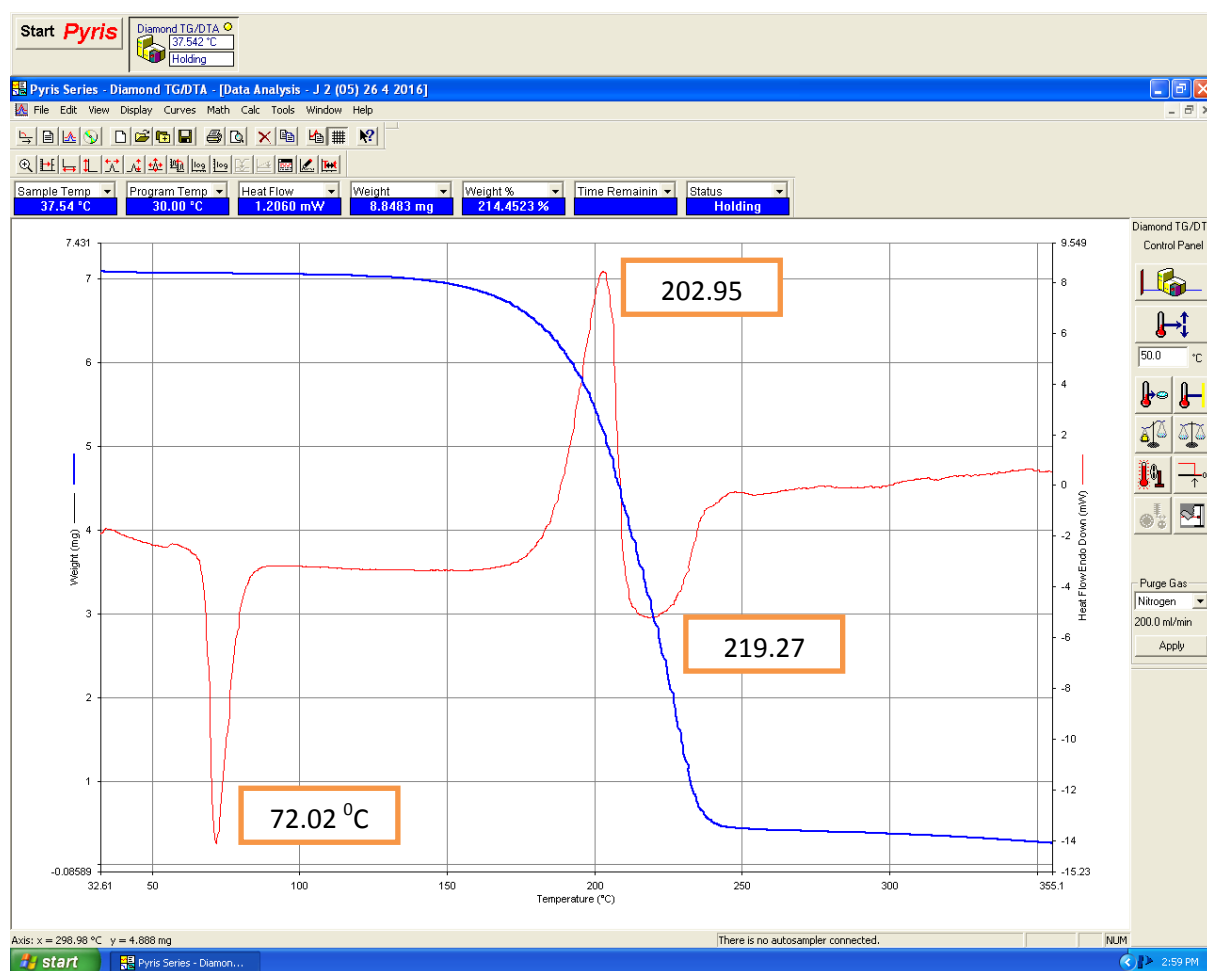
TIGER Predictions of Explosive Properties for Ideal Behaviour

From the above table it is found that gas produced by the amatol is much higher than the TNT which brings more effectiveness to the amatol being positive oxygen balance explosive.

## RESULTS

### 4.6 THERMAL ANALYSIS OF TNT AT HEATING RATE OF 5 °C

Thermal analysis of TNT was carried out by keeping heating rate at 5 °C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400 °C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.



**Fig:4.1 TG/DTA curve of TNT with Heating Rate 5 °C/min**

Note: Approximately 4% carbon is leftover in the form of soot

## DTA Curve

DTA curve of the TNT is shown below with the heating rate of 5 °C /min, where three peaks in the profile are found. First endothermic peak appears at 72.02 °C which reflects the phase transformation taking place. Second exothermic peak appears at the temperature of 202.95 °C which is due to the chemical reaction taking place in the TNT which is accompanied by the weight loss evident from the TGA curve. In the last it is found that endothermic peak appears at the temperature of 219.27 °C which is the decomposition peak resulting in the sample complete utilization.

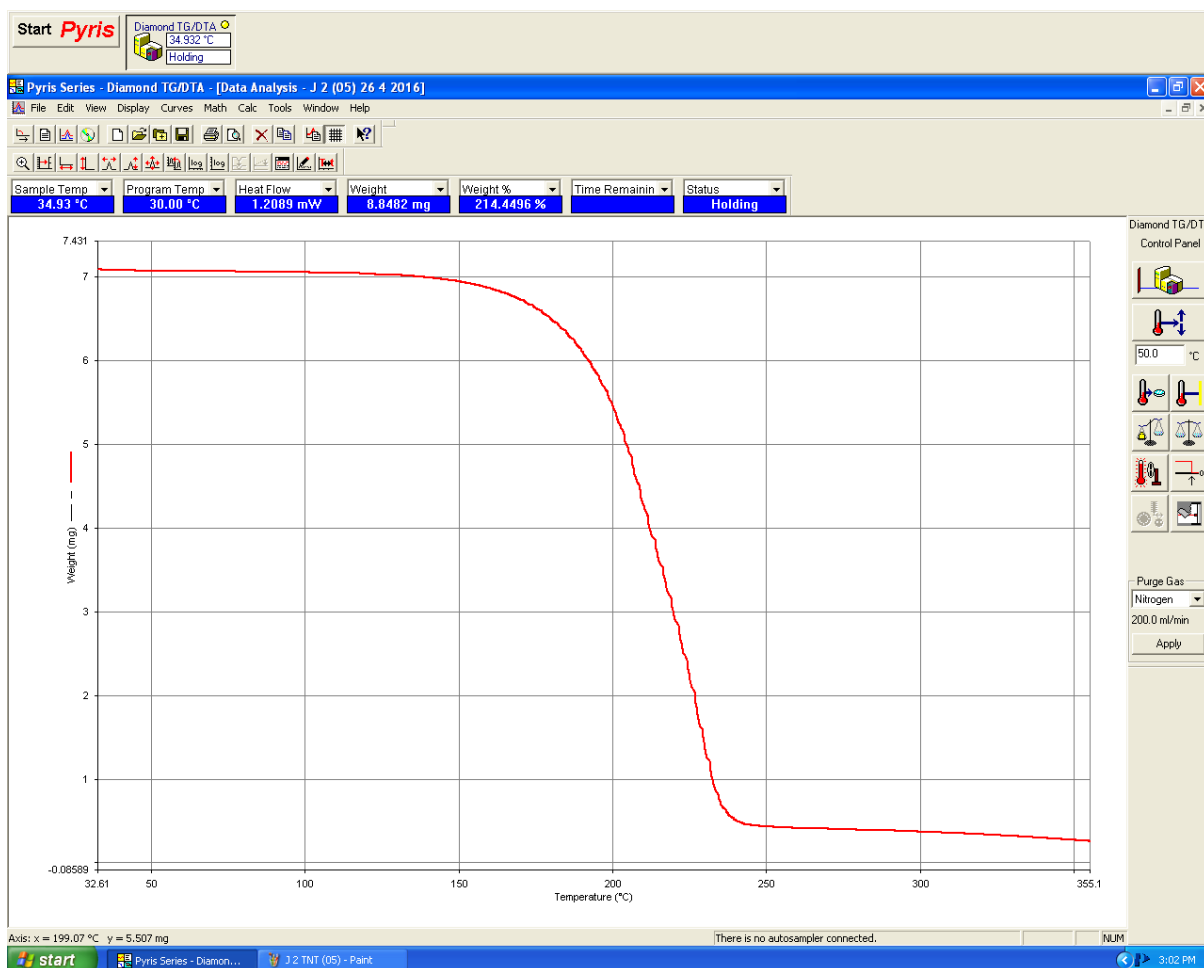


**Fig:4.2 DTA curve of TNT with Heating Rate 5 °C/min**



## TG Curve

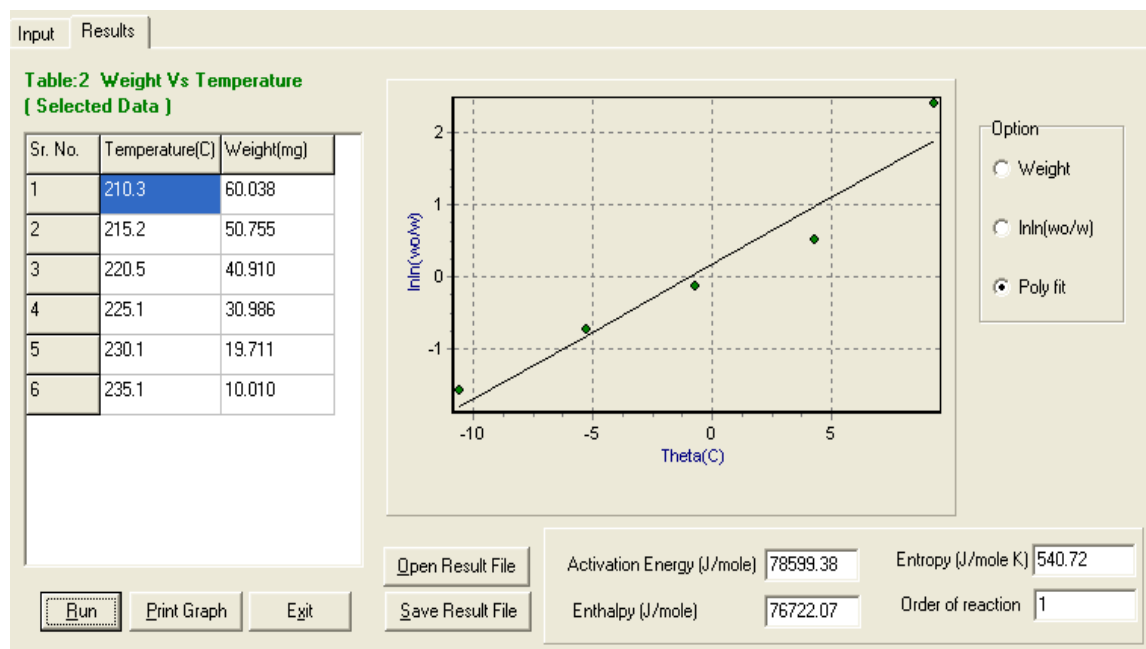
Below TGA profile with the heating rate of  $5\text{ }^{\circ}\text{C}$  is shown it is found that single stage decomposition process takes place. Plateau stage exists till the temperature of about  $140\text{ }^{\circ}\text{C}$  up till where weight remains constant but after that weight drops in single stage and all weight is consumed at the temperature of about  $240\text{ }^{\circ}\text{C}$ .



**Fig:4.3 TG curve of TNT with Heating Rate  $5\text{ }^{\circ}\text{C}/\text{min}$**

## KINETIC PARAMETERS

To calculate the kinetic parameter of the amatol with the heating rate at  $5^{\circ}\text{C}/\text{min}$  in the nitrogen atmosphere graph is shown below.

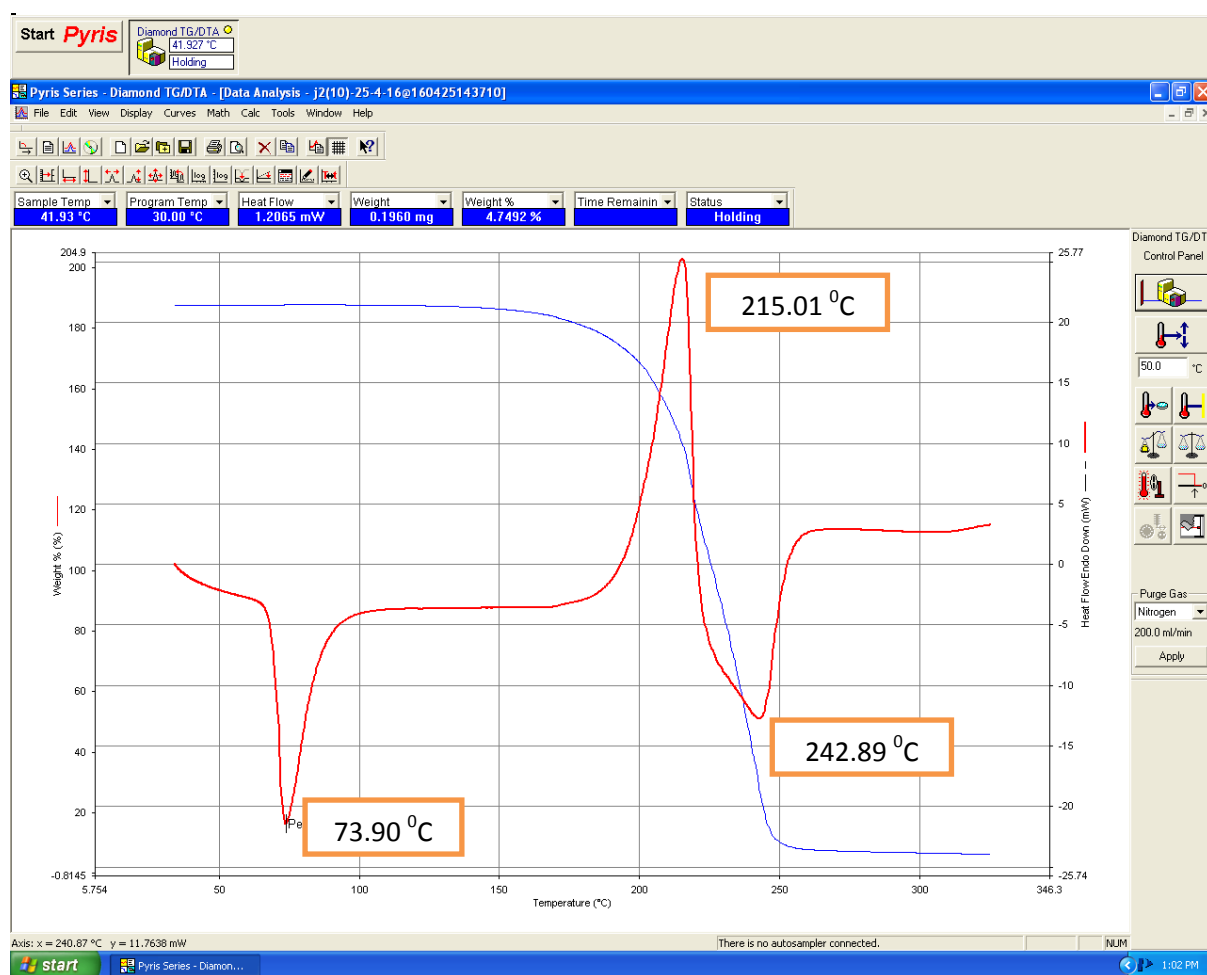


**Fig:4.4 Graph for calculation of kinetic parameters of TNT with heating rate of  $5^{\circ}\text{C}/\text{min}$**

The data obtained from the thermal experiment is inserted in the curve fitting program and graph is obtained between  $\ln\ln(w_0/w)$  and  $\Theta(\text{C})$  which shows a straight line. Order of reaction comes out to be 1 and activation energy is calculated as 78 KJ/mole.

## 4.7 THERMAL ANALYSIS OF TNT AT HEATING RATE OF 10 °C

Thermal analysis of TNT was carried out by keeping heating rate at 10 °C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400 °C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.

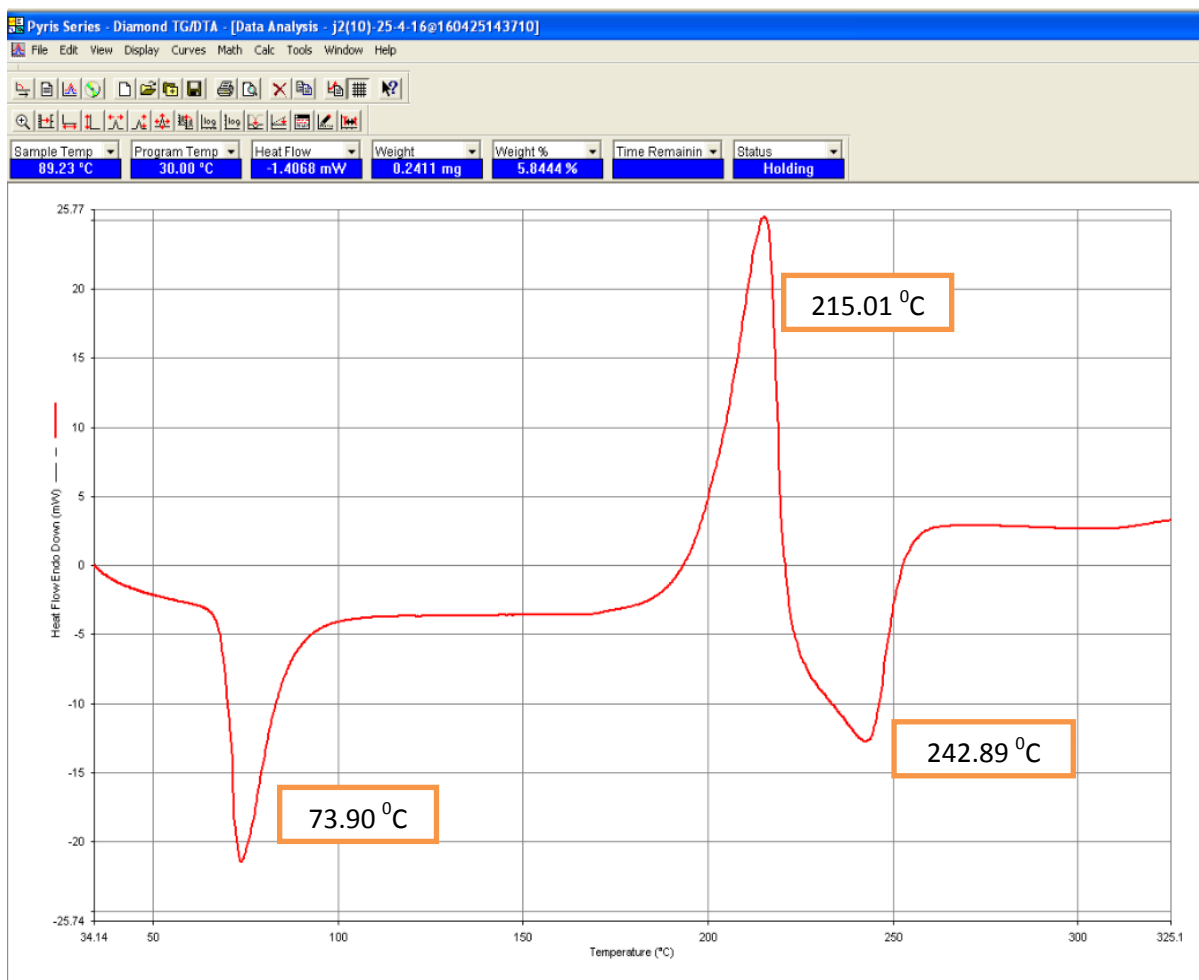


**Fig:5 TGA/DTA curve of TNT with Heating Rate 10 °C/min**

Note: Approximately 4% carbon is leftover in the form of soot

## DTA Curve

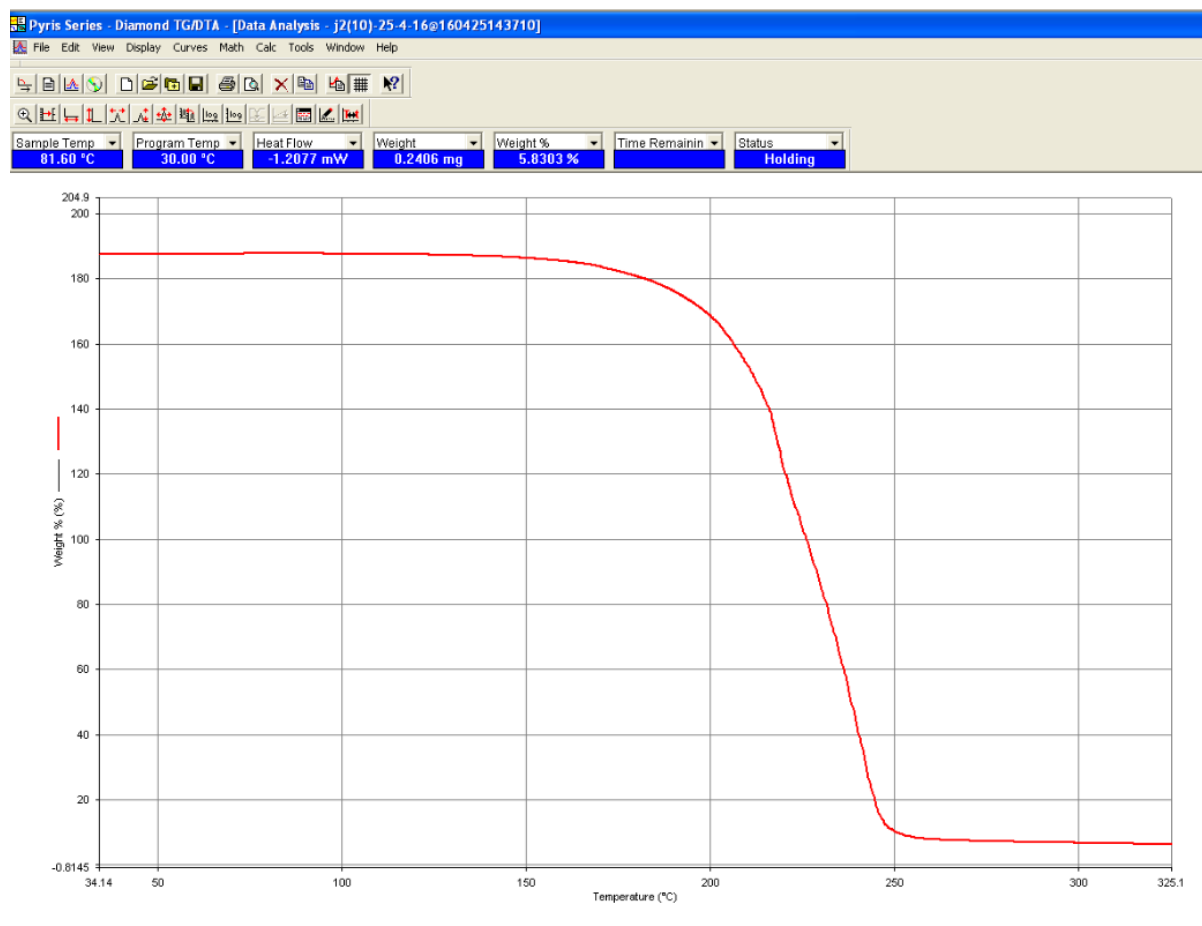
In the DTA curve below it is found that first endothermic peak appears at the temperature of about  $73.90^{\circ}\text{C}$  which reflects the phase transformation process. Then second peak appears at the temperature of about  $215^{\circ}\text{C}$  which is due to the chemical reaction as weight starts falling beside this peak start. In the last it is found that the endothermic decomposition peak appears at the temperature of  $242.89^{\circ}\text{C}$ .



**Fig:6 DTA curve of TNT with Heating Rate  $10^{\circ}\text{C}/\text{min}$**

## TGA Curve

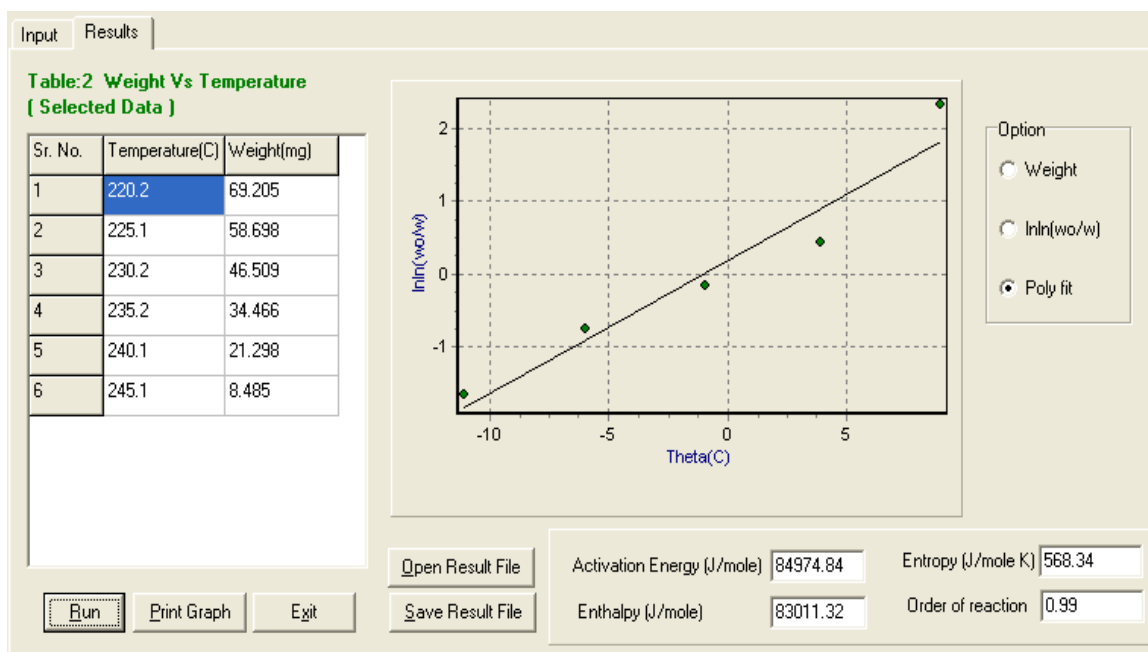
TGA curve is shown below at the heating rate of  $10\text{ }^{\circ}\text{C}$  which exhibits a plateau profile till the temperature of about  $148\text{ }^{\circ}\text{C}$  after that it is found that dip in the curve occurs which sharpens after the first quarter. Which means weight drop starts at about  $148\text{ }^{\circ}\text{C}$  and is completely consumed when it reaches at the temperature of about  $255\text{ }^{\circ}\text{C}$ .



**Fig:7 TGA curve of TNT with Heating Rate  $10\text{ }^{\circ}\text{C}/\text{min}$**

## KINETIC PARAMETERS

To calculate the kinetic parameter of the amatol with the heating rate at  $10^0$  C/min in the nitrogen atmosphere graph is shown below.



**Fig:8 Graph for calculation of kinetic parameters of amatol with heating rate of  $10^0$  C/min**

The data obtained from the thermal experiment is inserted in the curve fitting program and graph is obtained between  $\ln(w_0/w)$  and  $\Theta$  (C) which shows a straight line. Order of reaction comes out to be 1 and activation energy is calculated as 84 KJ/mole. So it is seen that with the increase in the heating rate activation energy has increased.

## 4.8 THERMAL ANALYSIS OF TNT AT HEATING RATE OF 15 °C

Thermal analysis of TNT was carried out by keeping heating rate at 15 °C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400 °C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.



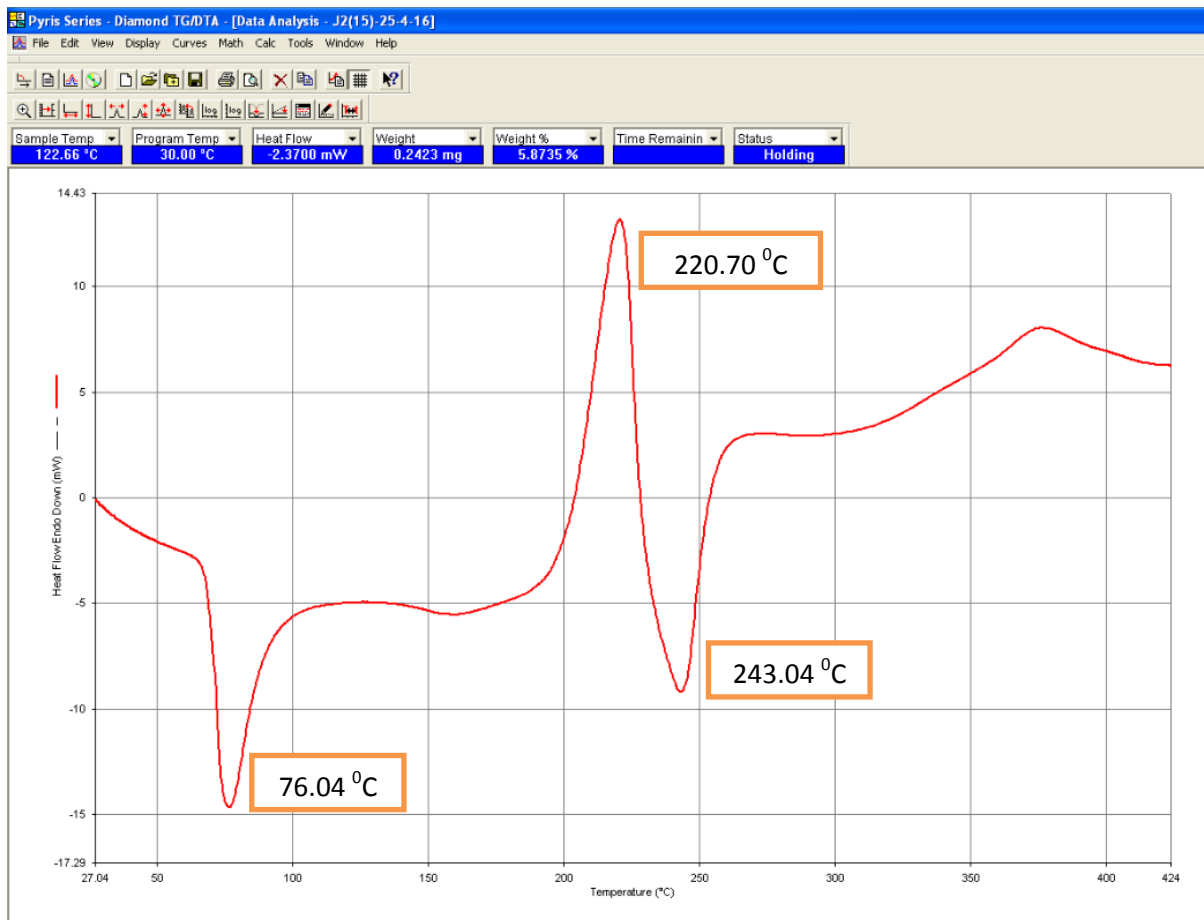
**Fig:9 TGA/DTA curve of TNT with Heating Rate 15 °C/min**

Note: Approximately 4% carbon is leftover in the form of soot

### DTA Curve

DTA curve of the TNT is shown below at the heating rate of 15 °C which shows

first endothermic peak at the temperature of 76.04 °C. This shows the solid phase transformation taking place. Then a second exothermic peak at the temperature of about 220.70 °C is found which shows chemical reaction taking place and is followed by the third endothermic decomposition peak over which sample is completely consumed.



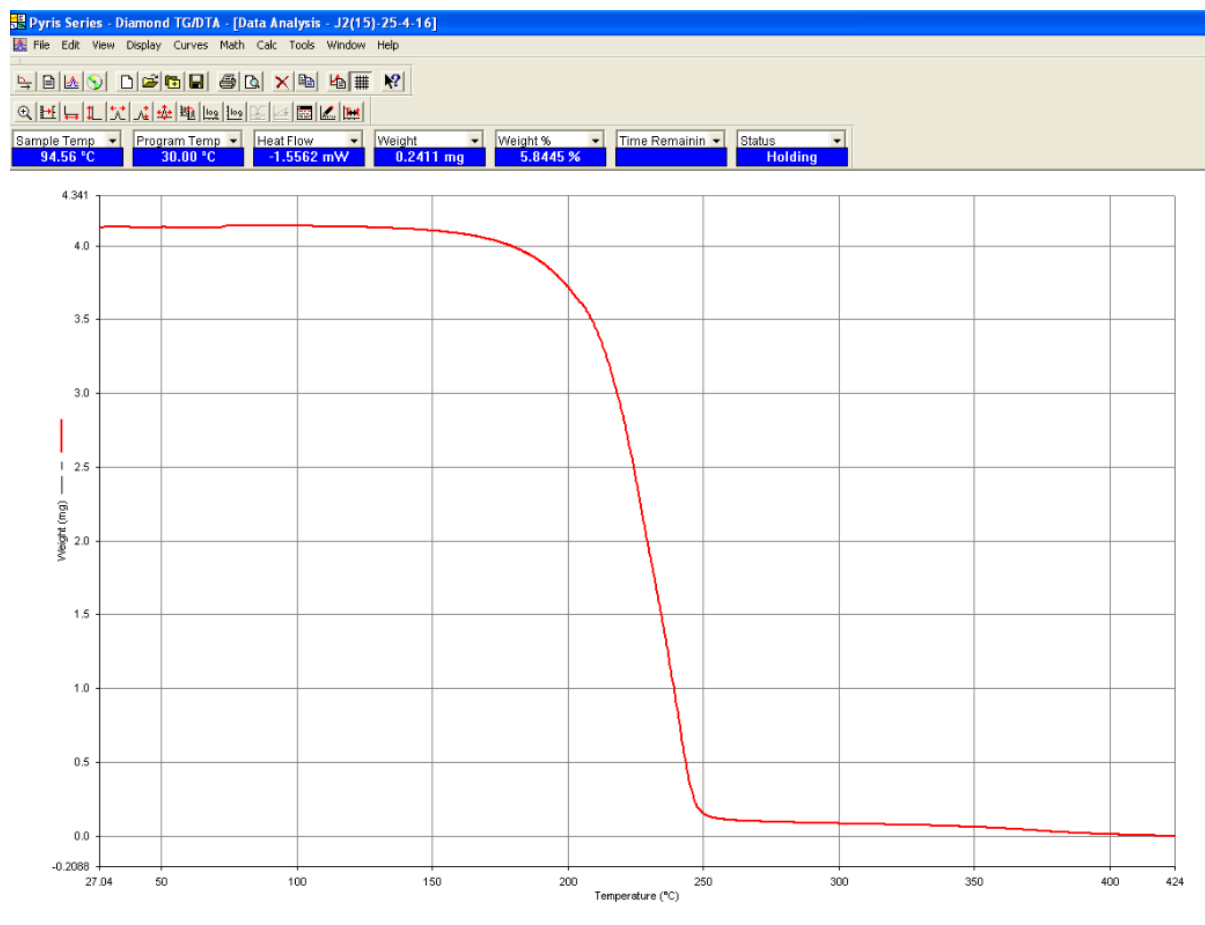
**Fig:10 DTA curve of TNT with Heating Rate 15 °C/min**

### TGA Curve

TGA profile shown below is recorded at the heating rate of 15 °C which shows the plateau profile till the temperature of about 150 °C after which profile drops showing decrease in the weight of the TNT. Weight is completely consumed when the temperature of about 257 °C is reached. Decomposition takes place in single



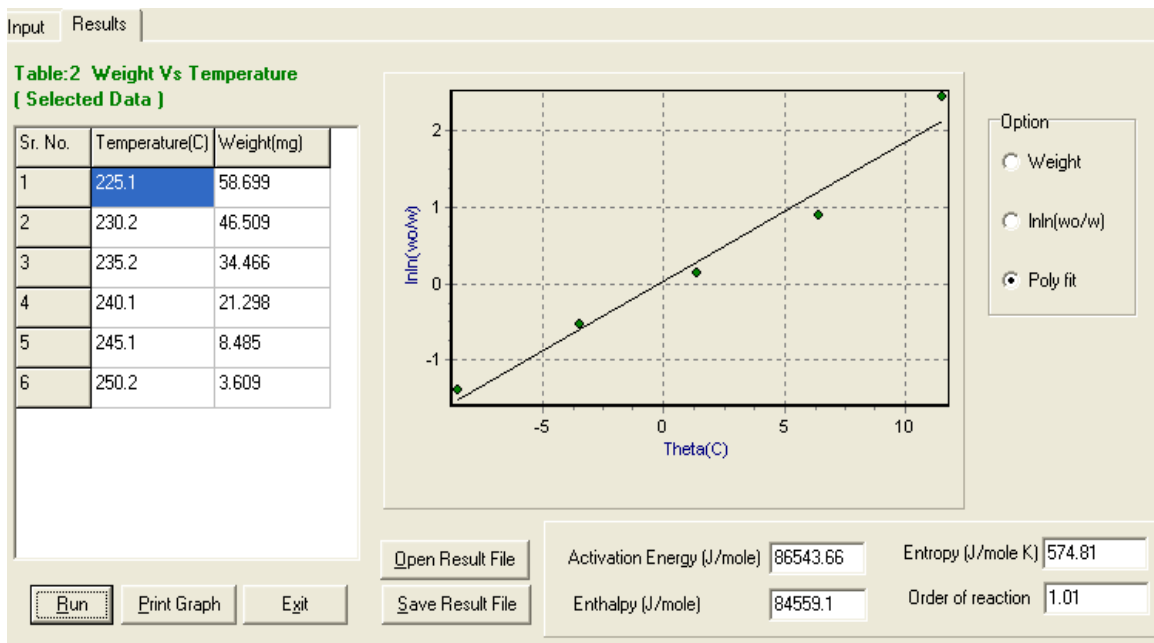
stage as shown in the profile below.



**Fig:11 DTA curve of TNT with Heating Rate 15<sup>0</sup> C/min**

### **KINETIC PARAMETERS**

To calculate the kinetic parameter of the amatol with the heating rate at 15<sup>0</sup> C/min in the nitrogen atmosphere graph is shown below.

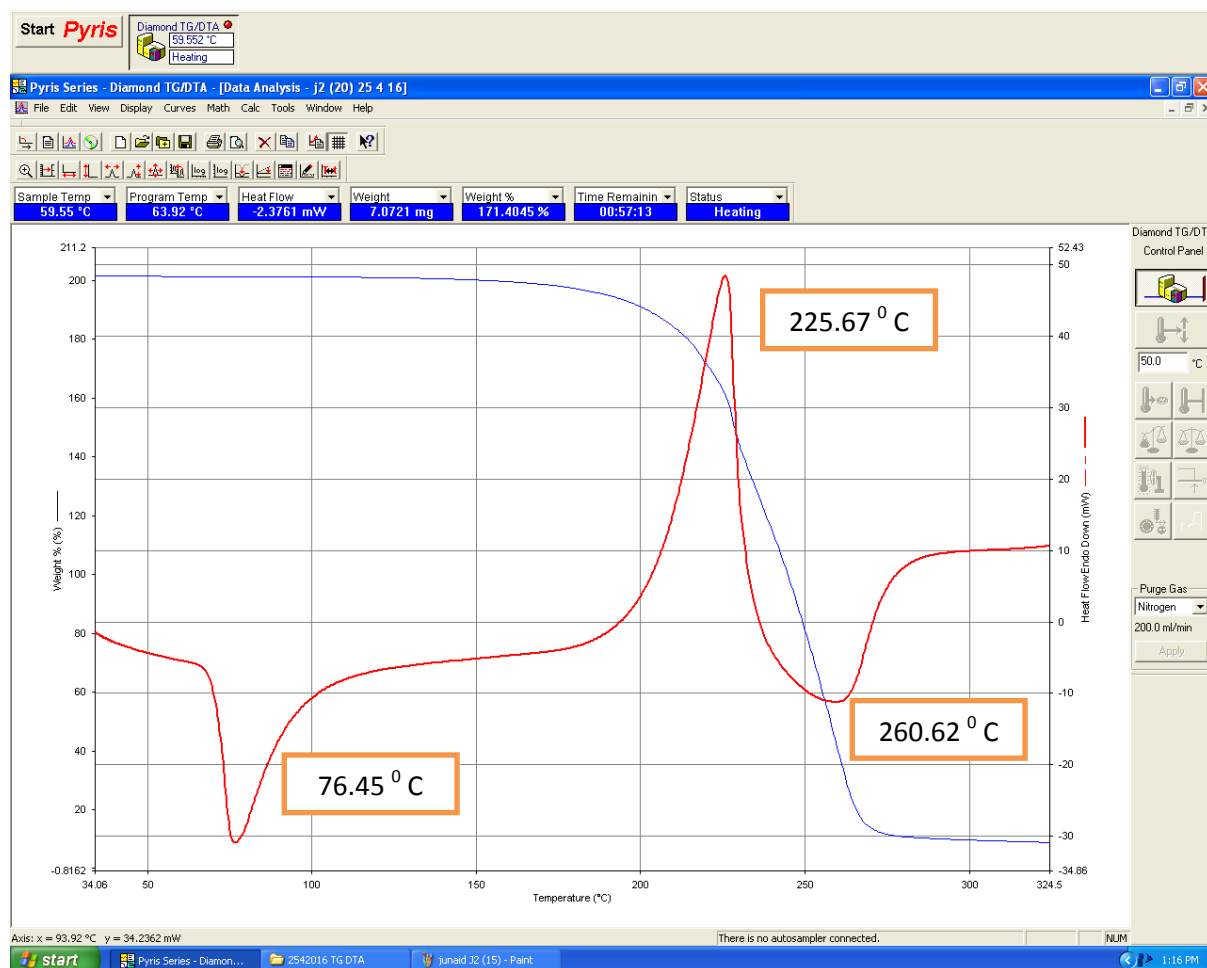


**Fig:12 Graph for calculation of kinetic parameters of amatol with heating rate of 15<sup>0</sup> C/min**

The data obtained from the thermal experiment is inserted in the curve fitting program and graph is obtained between lnln(wo/w) and Theta (C) which shows a straight line. Order of reaction comes out to be 1 and activation energy is calculated as 86 KJ/mole. Increase in the activation energy has been found at heating rate of 15<sup>0</sup> C/min as compared to the previous experiment with heating rate at 10<sup>0</sup> C/min. This is due to the slight change in the TGA curve due to the increasing heating rate.

#### 4.9 THERMAL ANALYSIS OF TNT AT HEATING RATE OF 20 °C

Thermal analysis of TNT was carried out by keeping heating rate at 20 °C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400 °C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.



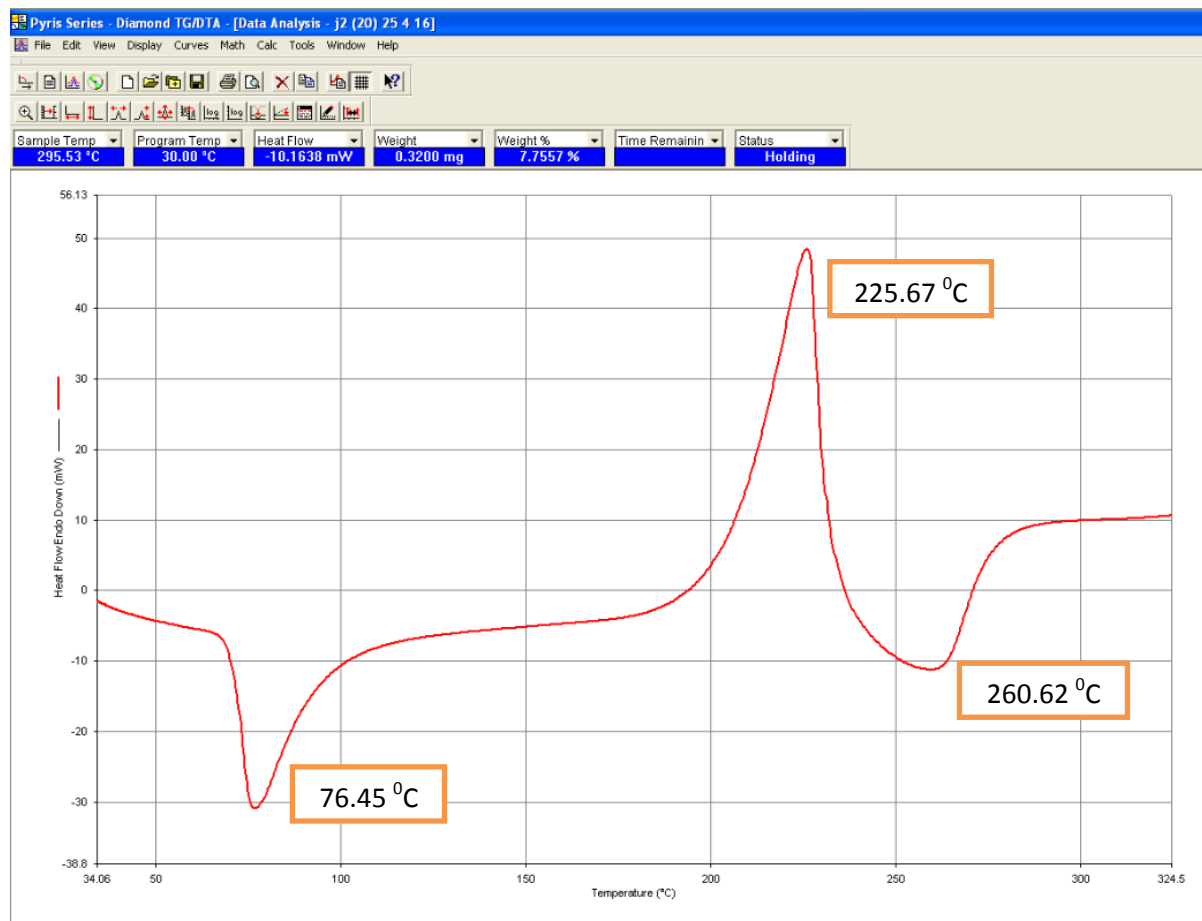
**Fig:13 TG/DTA curve of TNT with Heating Rate 20 °C/min**

Note: Approximately 4% carbon is leftover in the form of soot

#### DTA CURVE

DTA curve shown below is recorded at the heating rate of 20 °C. Profile shows first

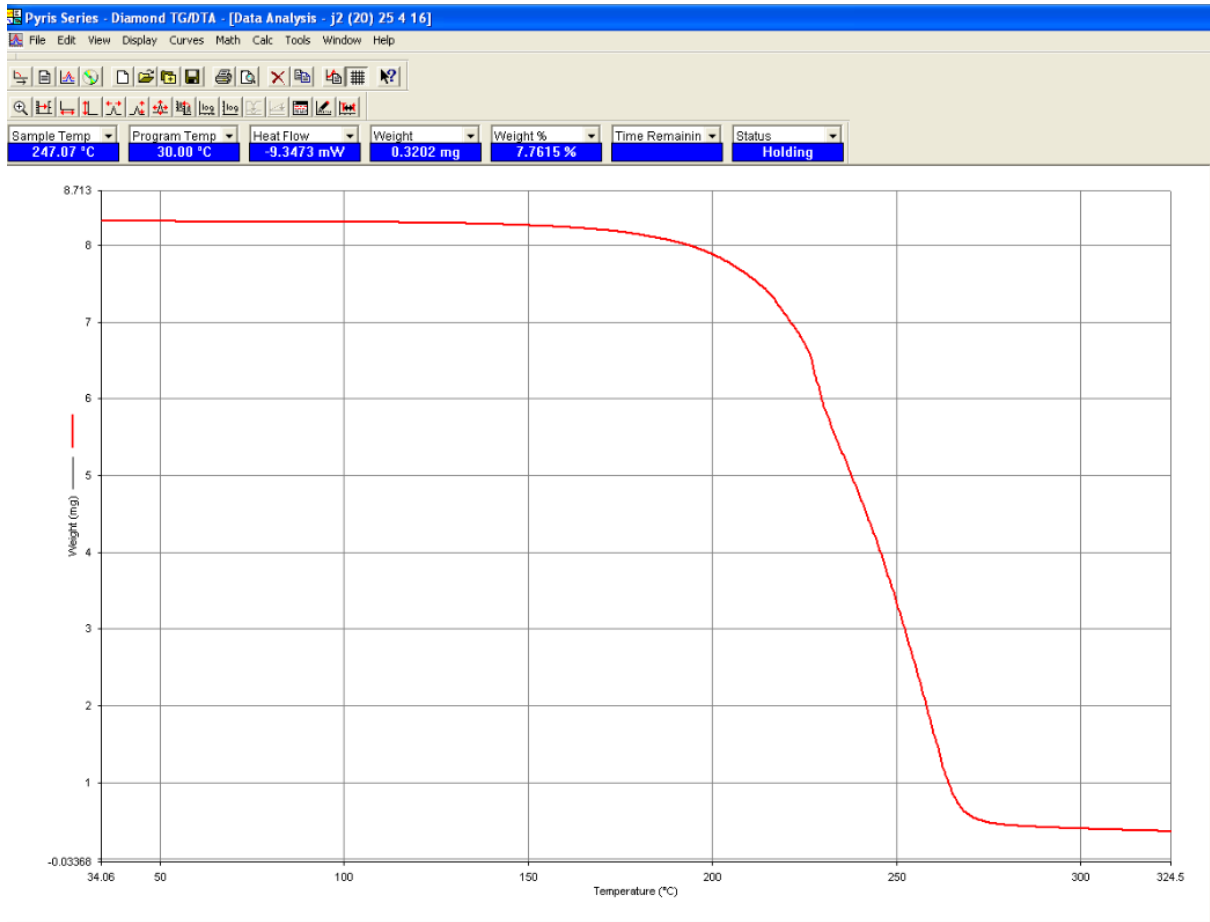
endothermic peak appears at the temperature of about 76.45 °C which shows the solid phase transformation taking place. Second exothermic peak appears at the temperature of about 225.67 °C which shows chemical reaction has taken place which further leads to the third endothermic decomposition peak over which TNT is completely decomposed.



**Fig:14 DTA curve of TNT with Heating Rate 20 °C/min**

### TGA CURVE

TGA curve shown below is recorded at the heating rate of 20 °C. The curve shows that it is a single stage decomposition phenomenon. TGA curve shows plateau phenomenon till it reaches the temperature of about 170 °C after which weight drops and peak drops sharply after the first quarter. Sample is completely consumed at the temperature of about 175 °C at which weight of TNT becomes zero.

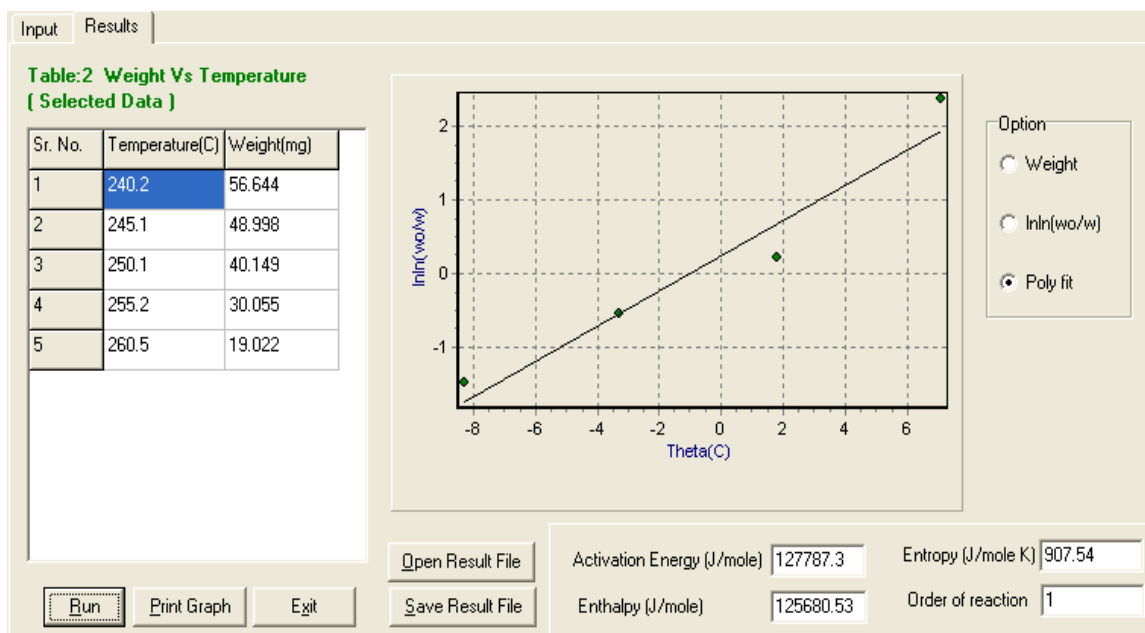


**Fig:15 DTA curve of TNT with Heating Rate 20<sup>0</sup> C/min**

Note: Approximately 4% carbon is leftover in the form of soot

## KINETIC PARAMETERS

To calculate the kinetic parameter of the amatol with the heating rate at  $20^{\circ}\text{C}/\text{min}$  in the nitrogen atmosphere graph is shown below.

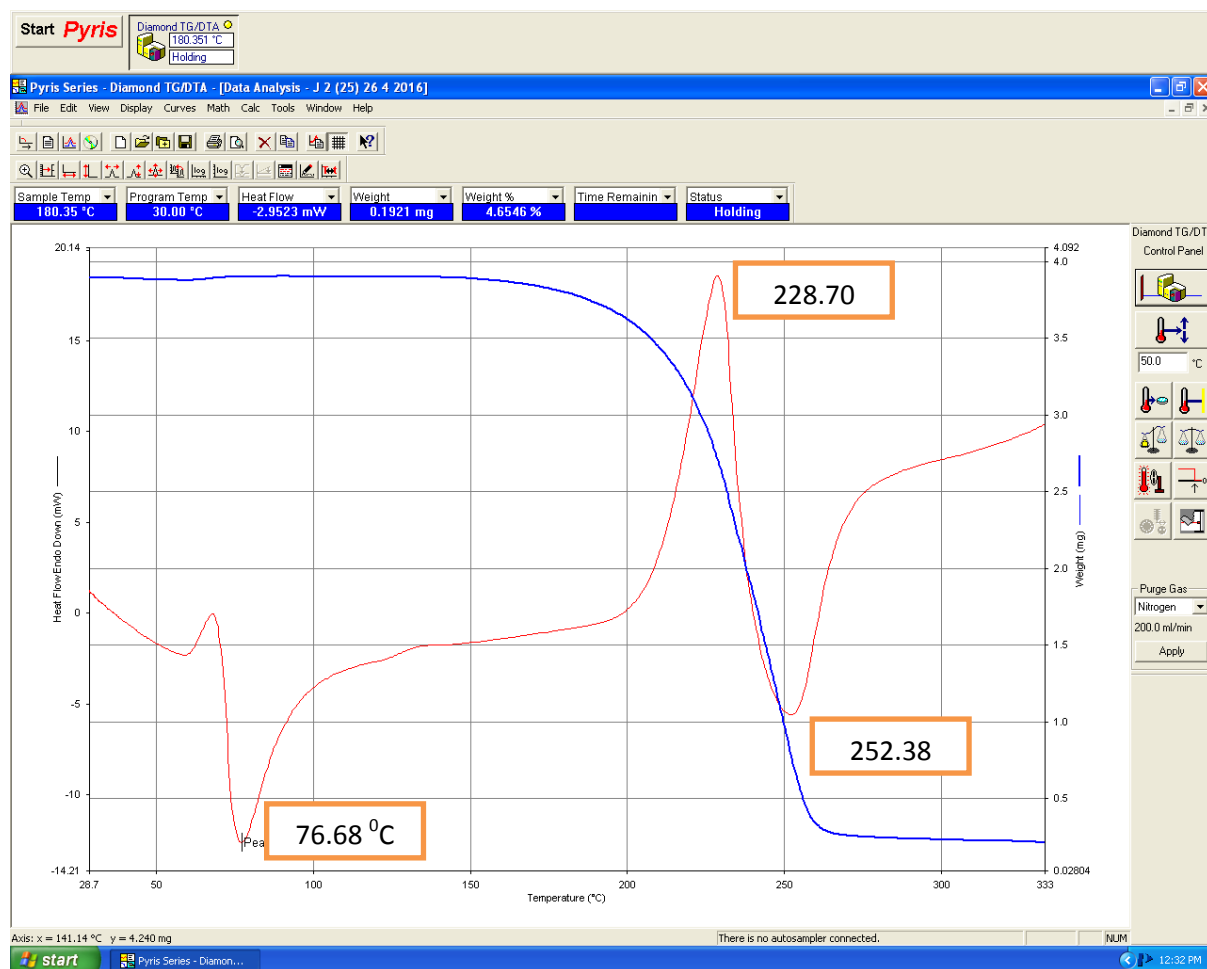


**Fig:16 Graph for calculation of kinetic parameters of amatol with heating rate of  $20^{\circ}\text{C}/\text{min}$**

The data obtained from the thermal experiment is inserted in the curve fitting program and graph is obtained between  $\ln(w_0/w)$  and  $\Theta(\text{C})$  which shows a straight line. Order of reaction comes out to be 1 and activation energy is calculated as 127 KJ/mole. Increase in the activation energy has been found at heating rate of  $20^{\circ}\text{C}/\text{min}$  as compared to the previous experiment with heating rate at  $15^{\circ}\text{C}/\text{min}$ . This is due to the slight change in the TGA curve due to the increasing heating rate.

#### 4.10 THERMAL ANALYSIS OF TNT AT HEATING RATE OF 25 °C

Thermal analysis of TNT was carried out by keeping heating rate at 25 °C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400 °C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.

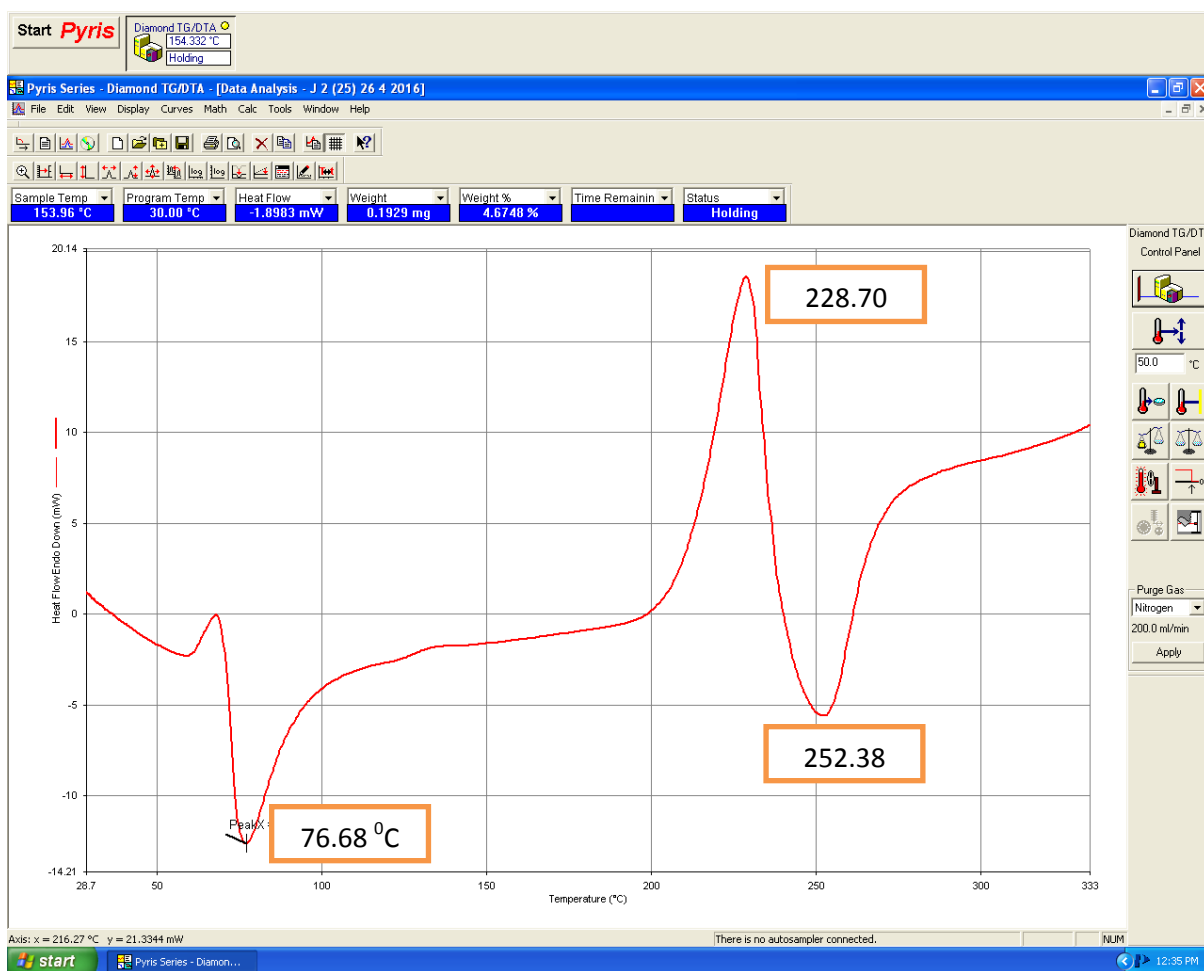


**Fig:17 TG/DTA curve of TNT with Heating Rate 25 °C/min**

Note: Approximately 7.5 % carbon is leftover in the form of soot

## DTA CURVE

DTA curve shown below is recorded at the heating rate of 25 °C/min. The curve shows a small exothermic peak followed by the endothermic peak at the temperature of about 76.68 °C. Then we find an exothermic peak at the temperature of about 228.70 °C which shows the occurrence of chemical reaction. At the end an endothermic decomposition peak at the temperature of about 252.38 °C is recorded over which TNT is fully decomposed.

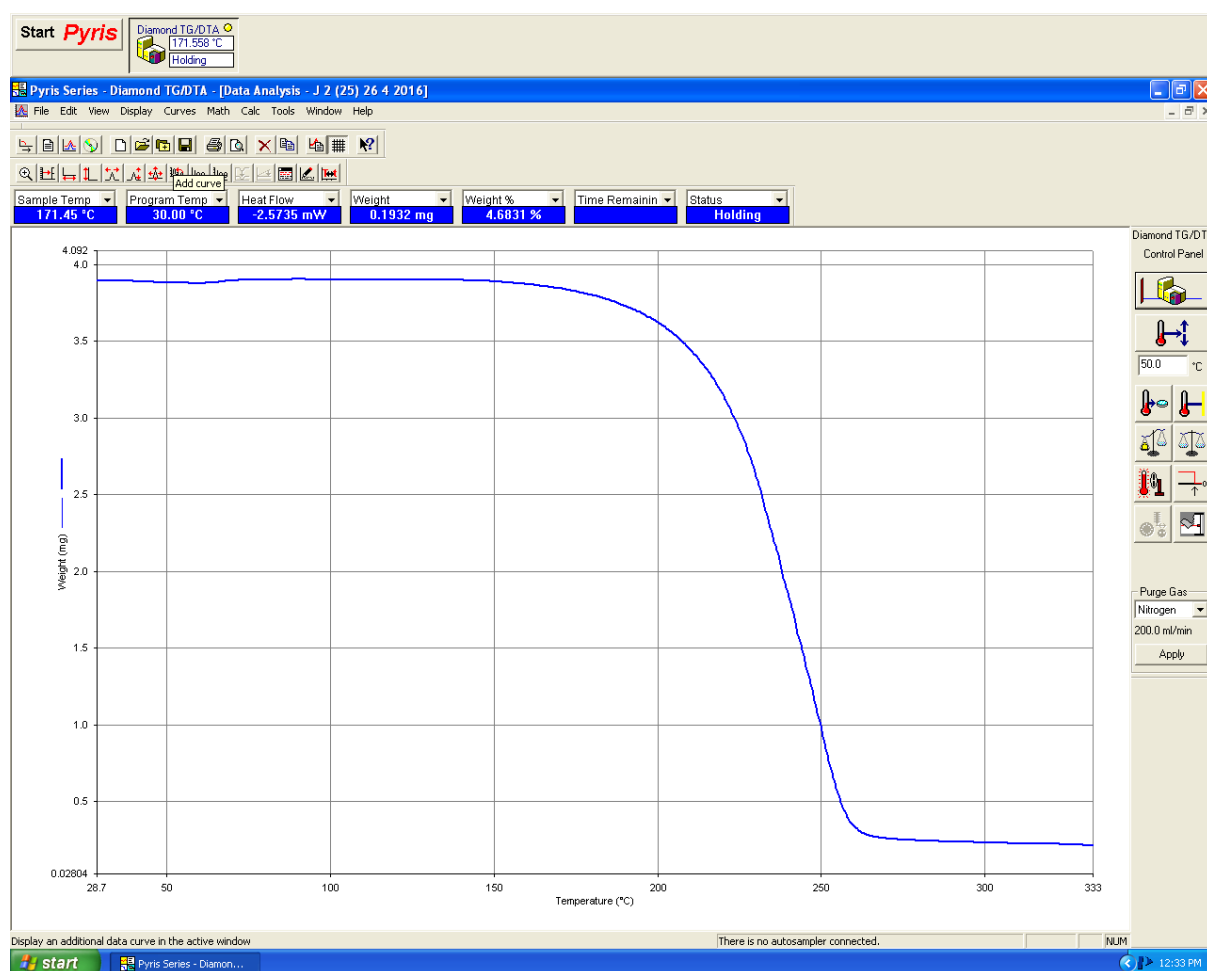


**Fig:18 DTA curve of TNT with Heating Rate 25 ° C/min**



## TGA CURVE

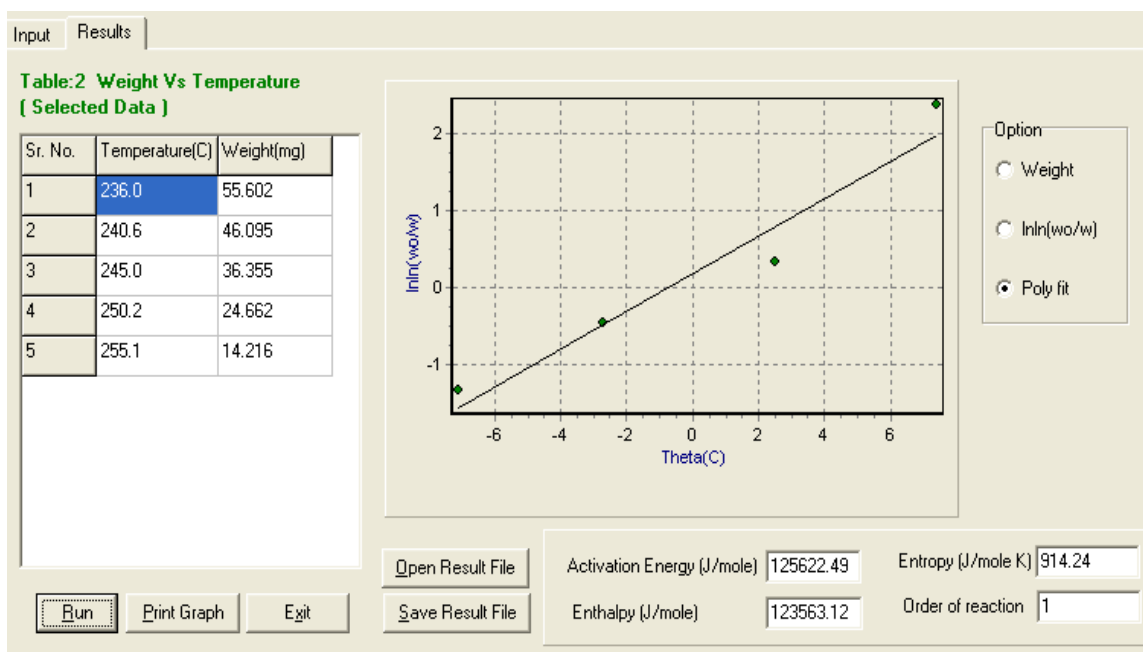
The profile shown below is TGA curve recorded at the heating rate of 25 °C/min. The curve shows the process of decomposition is single stage. Plateau profile is shown till the temperature of about 160 °C till that point weight of the sample remains unchanged. After that dip in the profile is evident which becomes steeper after the first quarter. This dip continues till the temperature of about 260 °C is reached and TNT is completely decomposed at this temperature.



**Fig:19 TG curve of TNT with Heating Rate 25<sup>0</sup> C/min**

## KINETIC PARAMETERS

To calculate the kinetic parameter of the amatol with the heating rate at 25<sup>0</sup> C/min in the nitrogen atmosphere graph is shown below.



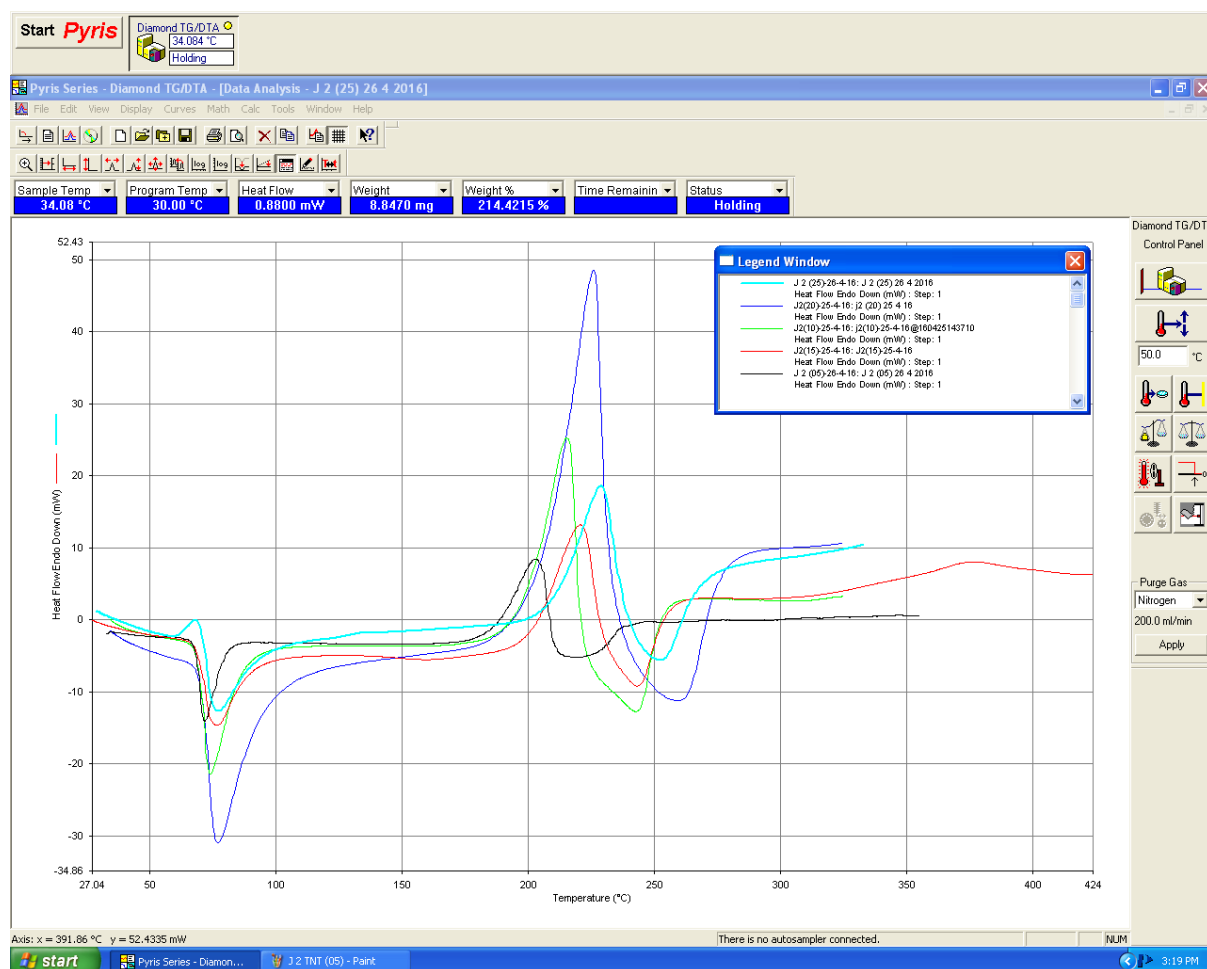
**Fig:20 Graph for calculation of kinetic parameters of amatol with heating rate of 25<sup>0</sup> C/min**

The data obtained from the thermal experiment is inserted in the curve fitting program and graph is obtained between  $\ln\ln(w_0/w)$  and  $\Theta$  (C) which shows a straight line. Order of reaction comes out to be 1 and activation energy is calculated as 125 KJ/mole. Decrease in the activation energy has been found at heating rate of 25<sup>0</sup> C/min as compared to the previous experiment with heating rate at 20<sup>0</sup> C/min. This shows the inverse trend of decrease in the kinetic parameters after reaching to the heating rate of 25<sup>0</sup> C/min

## 4.11 DISCUSSION

### 4.11.1 Comparison of DTA curves of TNT at Different Heating rates

The experiments were conducted on the TNT with the varying rates of heating which were 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min respectively. Profiles of DTA of all the heating rates in the figure below is shown.



**Fig:21 DTA curve of TNT with different Heating Rates**

From the graph it is found that with the increase in the heating rate all the three peaks are showing the variations for which a table has been shown below to evaluate the differences taking place due to the increase in the heating rate. When compare the first endothermic peak representing the solid phase transformation with the different heating rates it is found

that with the increase in the heating rate peak temperature for all the consecutive curves increases. Now when compare the second exothermic peaks with the increasing heating rates it is found that temperature also increases for the peak temperature for all the consecutive curves. When compare the third endothermic peaks which are decomposition peaks it is found that for the heating rates of 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min there is increase in the temperature of peaks with the increasing rate but when reach to the heating rate of 25 °C/min then it is found that there is decrease in the peak temperature.

### Comparison of DTA curves at Different Heating rates

Heating Rate	1st Endo Peak ( $\pm 1$ )	2 <sup>nd</sup> Exo Peak ( $\pm 1$ )	3 <sup>rd</sup> Decomposition Peak ( $\pm 1$ )
5 °/min	72.02 °C	202.95 °C	219.27 °C
10 °/min	73.90 °C	215.01 °C	242.89 °C
15 °/min	76.04 °C	220.70 °C	243.04 °C
20 °/min	76.45 °C	225.67 °C	260.62 °C
25 °/min	76.68 °C	228.70 °C	252.38 °C

Ideally speaking the heating rate should not have an effect on the melting peak of the mixture, however the results show that melting point has shifted to the higher temperature with the increasing heating rate. This behavior of increase in the temperature of the peak temperature with the increase in the heating rate is due to following reasons

**a. Thermal lag phenomenon**

It occurs due to the non-uniform heating of the sample caused by the thermal lag. The sample is exposed for less time for the specific heating rate at higher heating rate [1]. Similar effects have been observed in other researches as well [2].

**b. Influence of the Furnace Atmosphere**

The mechanism of many chemical reactions are influenced by the atmosphere and in particular by the gas pressure. With increasing partial pressure reaction moves to the higher temperature. With the higher partial pressure DTA effects are more

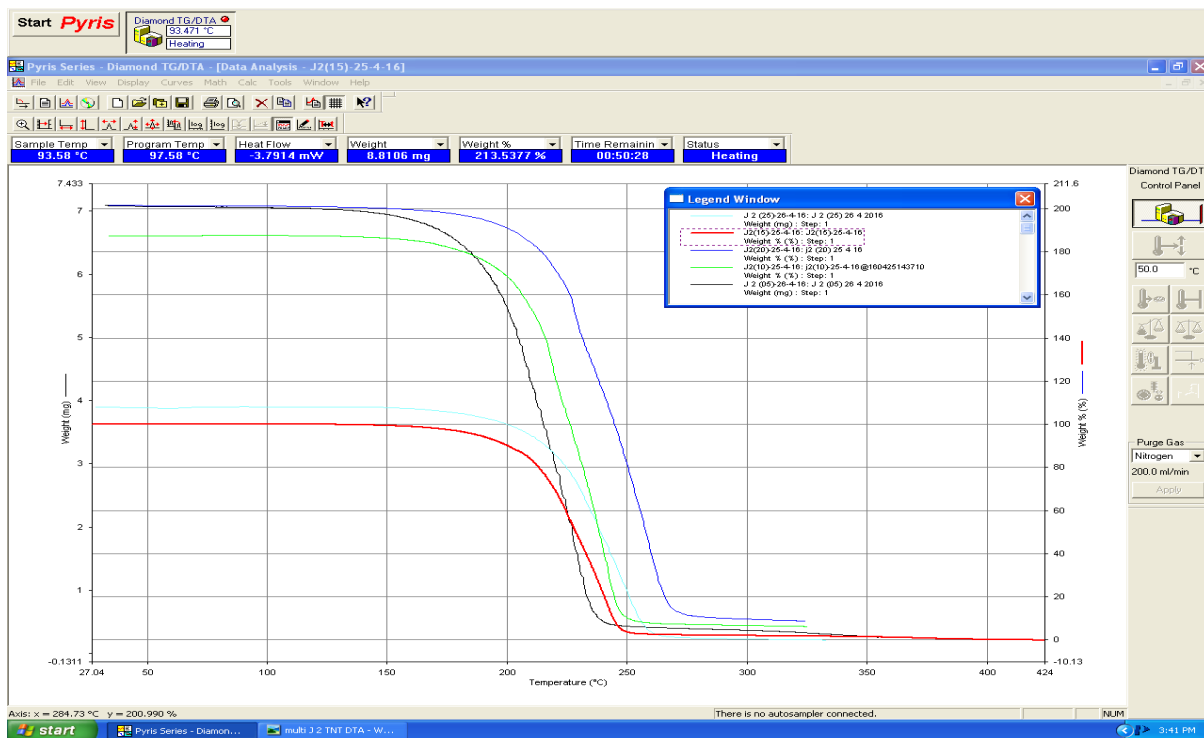
pronounced [3]. Steam formed by the decomposition reaction diffuses slower into the furnace atmosphere than new steam is produced.

**c. Influence of the Heating Rate**

As the heating rate is increased temperature rises quickly, causes less time for the substance transition, thus chemical reactions move to higher temperatures. In addition, there is local change in the furnace atmosphere and on the sample surface, as reaction rate is linked with the temperature increase [4]. Higher the heating rate higher will be gases output, lower will be gases diffusion rate in the atmosphere which will increase the partial pressure thus increasing the decomposition temperature.

**4.11.2 Comparison of TG curves of TNT at Different Heating rates**

The experiments were conducted on the TNT with the varying rates of heating which were 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min respectively. Profiles of TGA of all the heating rates in the figure below are shown.



**Fig:22 TGA curve of TNT with different Heating Rates**

From the comparative profile it is found that with the variation in the heating rate there is change in the temperature at which sample is completely decomposed. The table shown below shows the decomposition temperature at increasing heating rate. It is found that with the increasing heating rate from 5 °C/min, 10 °C/min, 15 °C/min and 20 °C/min there is increase in the decomposition temperature but when the experiment is done at 25 °C the decrease in the temperature occurs at which decomposition takes place.

**Comparison of TG curves of TNT at Different Heating rates**

Heating Rate	Decomposition Temperature (± 0.5)
5 °/min	240
10 °/min	255

15 °/min	257
20 °/min	275
25 °/min	265

a. **Higher Heat Dissipation**

It may be explained that at a higher heating rate, heat is dissipated more conveniently so decomposition process starts at the higher temperatures and also have the higher heat of diffusion. [5]

b. **Thermal lag phenomenon**

It occurs due to the non-uniform heating of the sample caused by the thermal lag. The sample is exposed for less time for the specific heating rate at higher heating rate [1]. Similar effects have been observed in other researches as well [2].

#### **4.11.3 Comparison of Activation Energy of TNT at Different Heating Rate**

From the table shown below it is evident that with the increase in the heating rate there is increase in the activation energy when TNT kinetic parameters are observed. It is found from the kinetic parameters i.e. activation energy that for the heating rate from 5<sup>0</sup>/min to 20<sup>0</sup>/min, activation energy increases but for the heating rate of 25<sup>0</sup>/min activation energy shows decrease in the value. This behavior can be resembled with the DDT phenomenon where in the start heat produced is less which increases with the confinement leading to the detonation. Likewise, in case of TNT, as the heating rate is increased to 25<sup>0</sup>C/min heating rate is increased to the level after which activation energy starts reducing. It shows that as the heating rate is increased then energy produced is so much more than the energy dissipated and it also overcomes the thermal lag due to which activation energy starts reducing at higher heating rate in TNT.

<b>Heating Rate</b>	<b>Activation Energy (± 2)</b>
5 <sup>0</sup> /min	78.6 KJ/mole

10 °/min	84.9 KJ/mole
15 °/min	86.5 KJ/mole
20 °/min	127.7 KJ/mole
25 °/min	125.6 KJ/mole

#### **4.12 THERMAL STUDIES OF AMATOL**

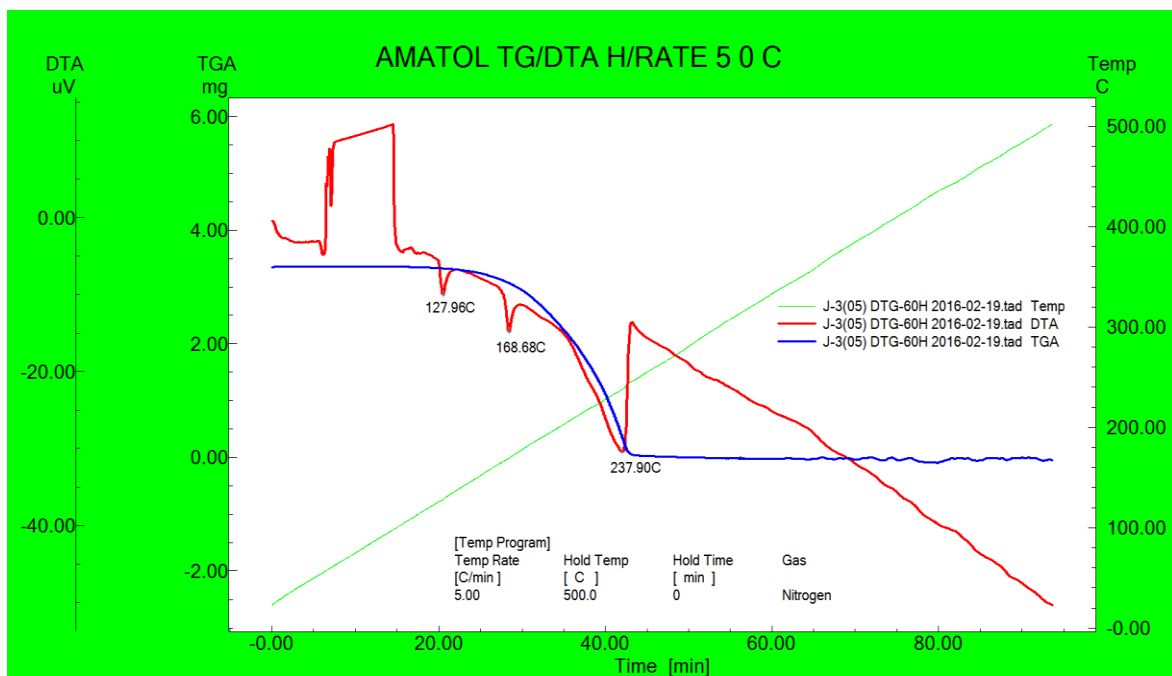
Thermal analysis of 80/20 amatol has been carried out by using the DTG – 60H equipment by Shimadzu. Simultaneous study method of TG/DTA have been utilized for our study. We have used 80/20 amatol sample with varying rate of heating i.e. 5 ° C ,10 ° C, 15 ° C, 20 ° C and 25 ° C. Experiments were conducted in nitrogen atmosphere by maintaining flow of 20 ml/min with the temperature range from ambient temperature to 400 ° C.

## **RESULTS**

#### **4.13 THERMAL ANALYSIS OF AMATOL AT HEATING RATE OF 5 °C**

Thermal analysis of amatol was carried out by keeping heating rate at 5 ° C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 500 0 C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.

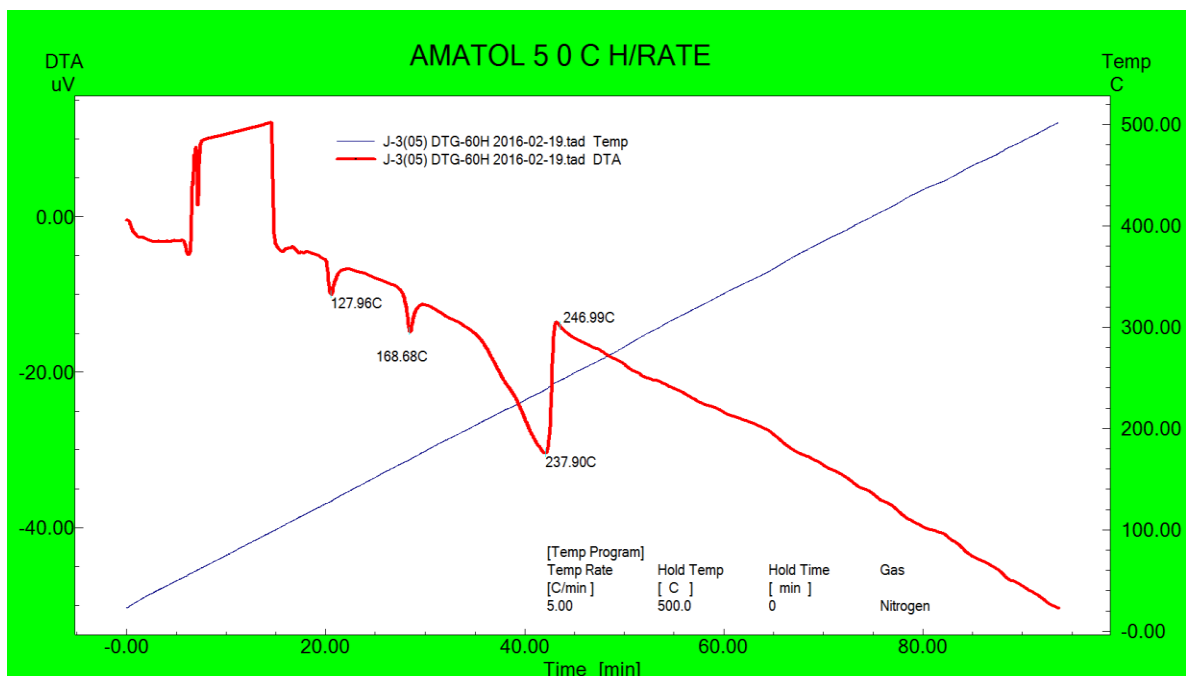




**FIG:23 TG/DTA curve of 80/20 Amadol with heating rate of 5<sup>0</sup> C/min**

### DTA CURVE

Thermal analysis of amatol has been carried out from room temperature to 500<sup>0</sup> C for which profile has been shown below for DTA curve. DTA curve shows that one exothermic region at the beginning is evident after that three endothermic peaks are shown. First peak appears at 127<sup>0</sup> C which shows a solid state phase transformation taking place in about twenty minutes after the start of the experiment. Second endothermic peak appears at 168<sup>0</sup> C which shows the occurrence of melting point. The third and the most prominent endothermic peak appears at 237<sup>0</sup> C which is basically the thermal decomposition peak showing the decomposition of amatol. It starts after right after the second peak at about 170<sup>0</sup> C and terminates at about 247<sup>0</sup> C.

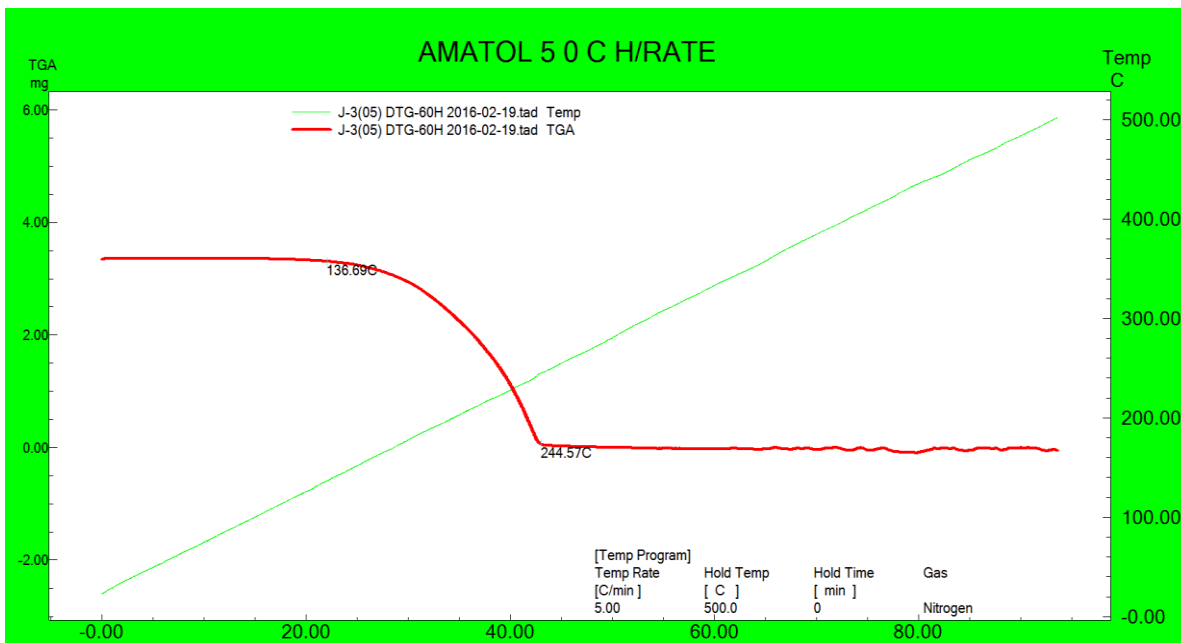


**FIG:24 DTA curve of 80/20 Amatol with heating rate of 5 °C/min**

Note: Approximately 2 % carbon is leftover in the form of soot

### TG CURVE

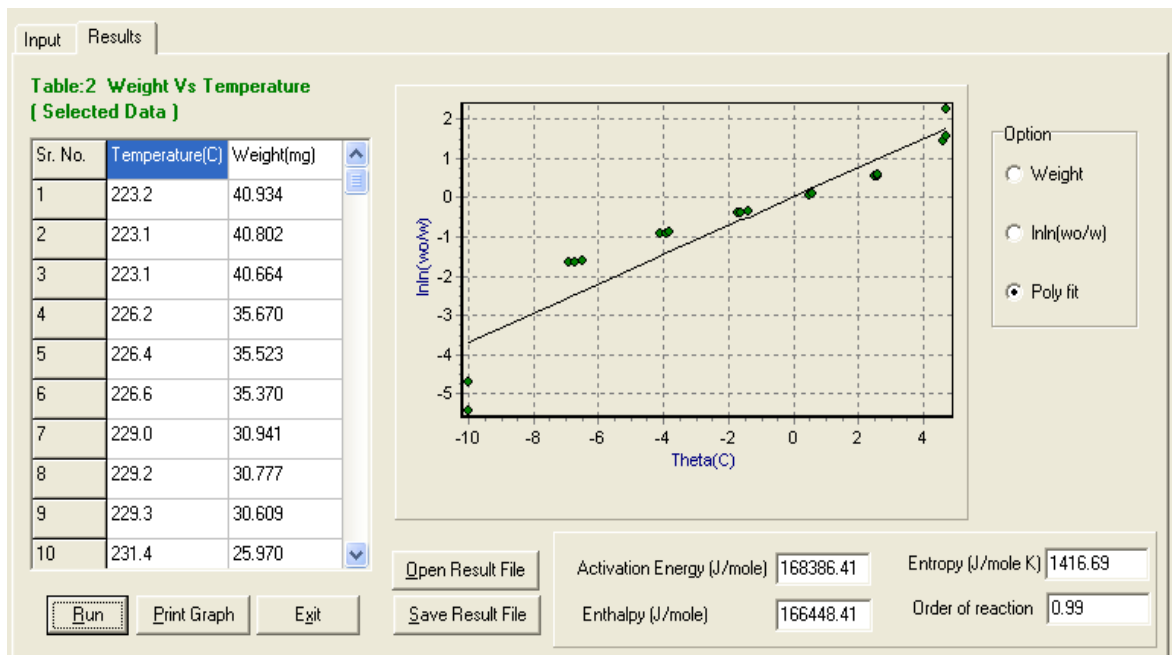
Amatol TG curve is shown below to analyze the effect of temperature which shows that decomposition of amatol takes place in single stage. TG curve can be divided into two distinct regions, one is plateau and the second is procedural decomposition temperature. The plateau region is the one which shows no change of mass during the increase of temperature which lasts till the second peak. The curve shows that weight loss starts with the second endothermic peak at about 168 °C which can be called as the procedural decomposition temperature, which is completed at about 244 °C. As the decomposition takes place weight loss is slow in the start but it increases significantly at the later stage. In our study procedural decomposition temperature is very important as our kinetic study is dependent upon the curve which becomes almost straight after the decomposition starts till it is completely consumed.



**FIG:25 TG curve of 80/20 Amatol with heating rate of 5 ° C/min**

### **KINETIC PARAMETERS**

In order to calculate the kinetic parameters, curve fitting program based on the Horowitz and Metzger Method has been used. For this graph has been shown which shows a straight line for which data obtained by the TG curve has been inserted into the battery software.



**Fig:26 Graph for calculation of kinetic parameters of amatol with heating rate of 5<sup>0</sup> C/min**

Calculation of the activation energy of the amatol with the heating rate of 5<sup>0</sup> C/min in the nitrogen atmosphere has been done and found that activation energy comes out to be 168 KJ/mole. Order of reaction for it is found to be 0.99.

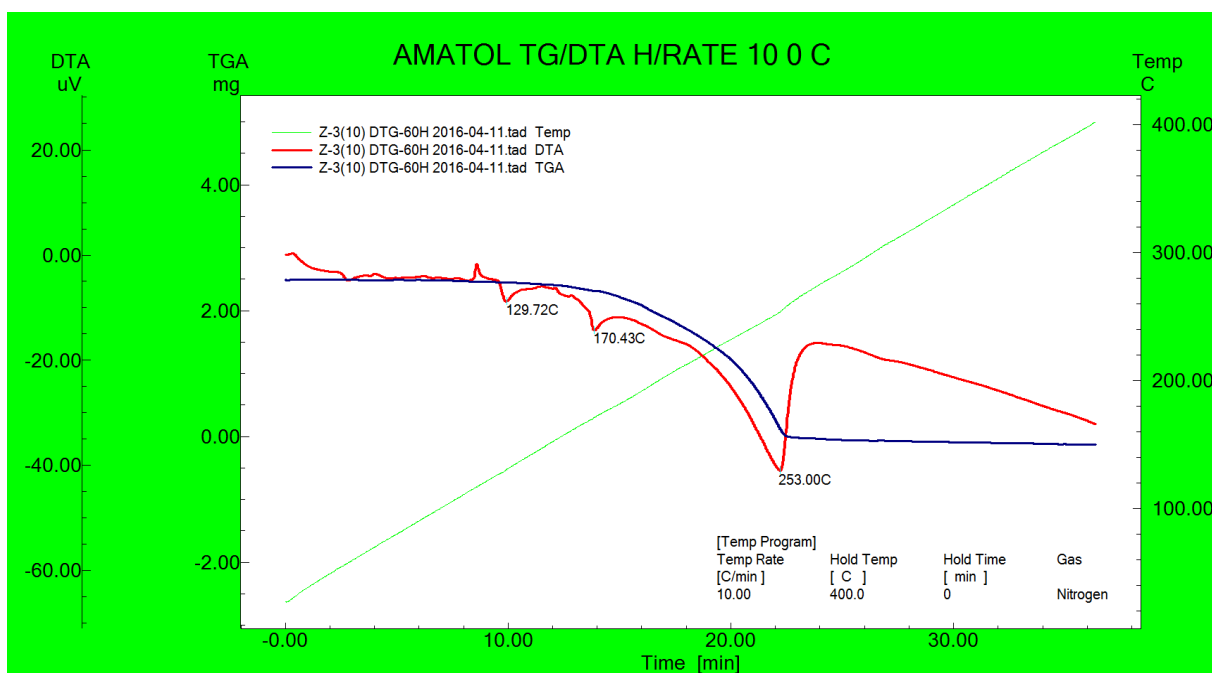
## DISCUSSION

Thermal and kinetic analysis of the 80/20 amatol has been carried out. In the thermal study we have performed the experiment by keeping heating rate at 5<sup>0</sup> C/min. The profile shows three main endothermic peaks, first peak showing the solid phase transformation at about 127<sup>0</sup> C. Second peak appears at about 168<sup>0</sup> C showing the melting point of the amatol. It was also found that till this point weight of sample remains unchanged and is denoted as plateau. After the second peak there is immediate dipping down of TGA and DTA curve leading to the decomposition of the sample with highest endothermic peak appearing at the temperature of 237<sup>0</sup> C. TG curve shows that weight of the sample becomes zero at about the temperature of 244<sup>0</sup> C. With this thermal data obtained experimentally the kinetic parameters of amatol were calculated showing the order of reaction to be 0.99 and activation energy to be 168 KJ/mole.

#### 4.14 THERMAL ANALYSIS OF AMATOL AT HEATING RATE OF 10<sup>0</sup>C

Thermal analysis of amatol was carried out by keeping heating rate at 10<sup>0</sup> C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400<sup>0</sup> C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.

#### RESULTS



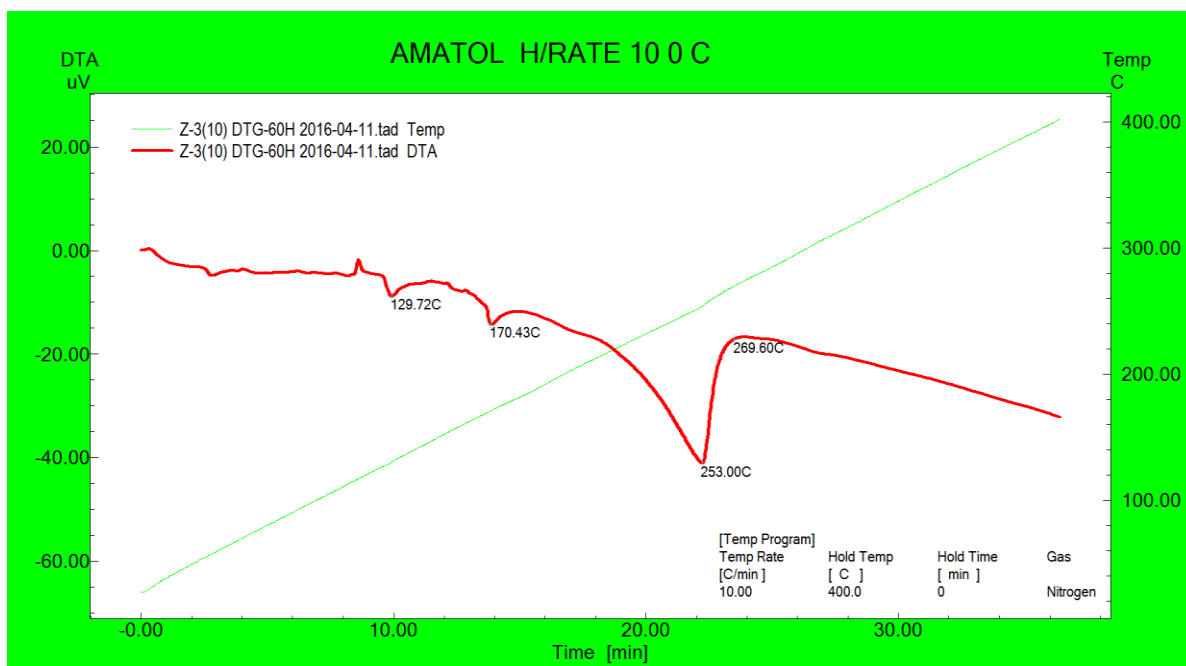
**FIG:27 TG/DTA curve of 80/20 Amatol with heating rate of 10<sup>0</sup> C/min**

Note: Approximately 2 % carbon is leftover in the form of soot

#### DTA CURVE

The DTA profile of the amatol at the heating rate of 10<sup>0</sup> C shows that profile has first portion of exothermic peak after that there are three endothermic peak. It is found that by increasing the heating rate from 5<sup>0</sup> C/min to 10<sup>0</sup> C/min there is slight change in the peaks. First endothermic peak changes its position and takes place at about 129<sup>0</sup> C as compared to 127<sup>0</sup> C which shows the solid state transformation taking place. Second endothermic peak

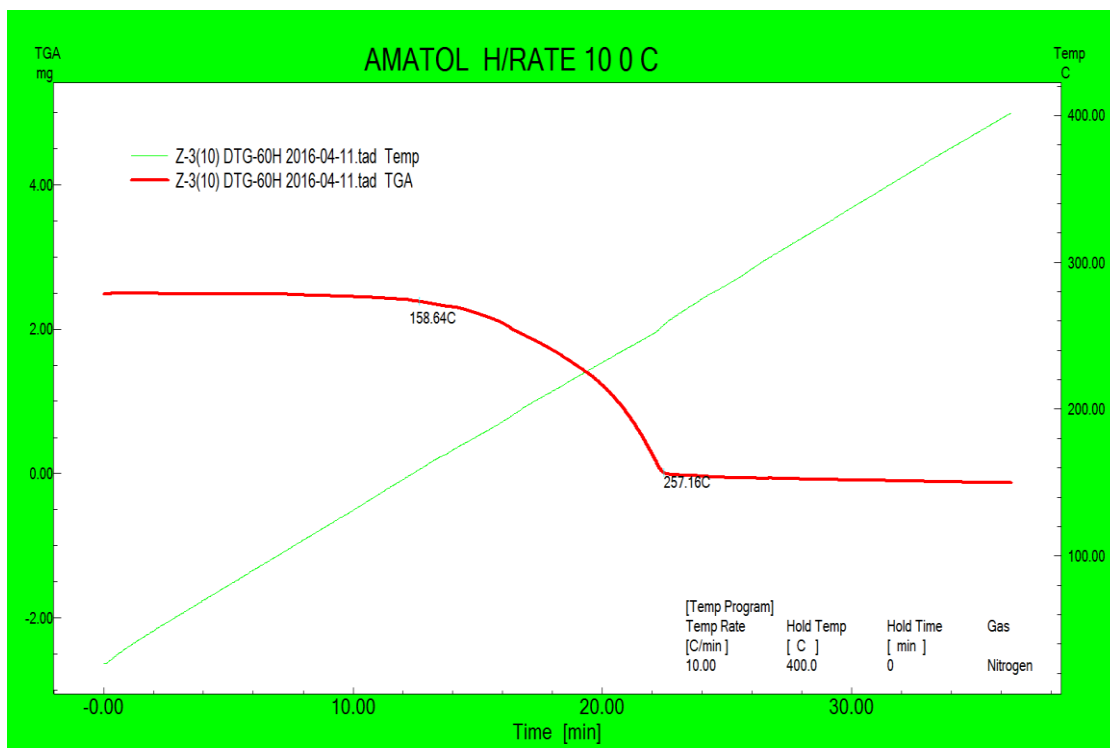
occurs at about 170 °C at the rate of 10 °C/min in comparison of 168 °C at rate of 5 °C/min which shows the melting point of the amatol. The third peak occurs at about 253 °C which shows the decomposition peak of the amatol. From the profile it was found that procedural decomposition temperature starts at about 170 °C which leads to the complete consumption of the amatol.



**Fig:28 DTA curve of amatol at 10 °C/min Heating Rate**

### TGA CURVE

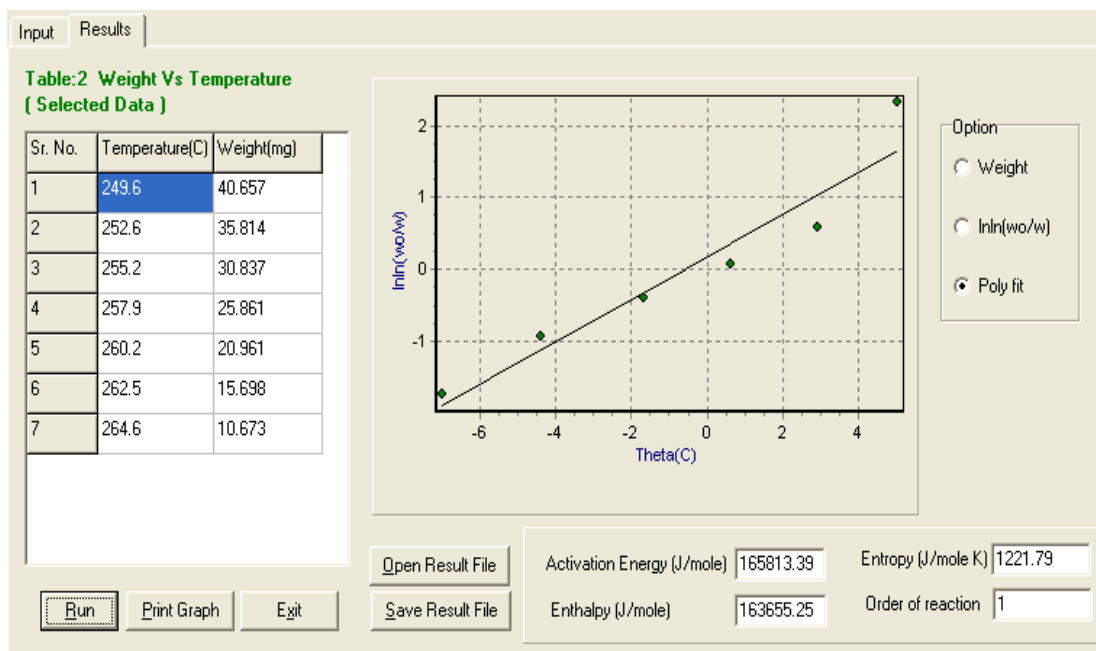
TGA curve of the amatol at heating rate of 10 °C/min is shown below. This profile states that plateau portion of the curve leads up to 170 °C. Up till this portion weight of the amatol remains almost constant after that decomposition temperature starts and weight loss starts which is slow in the start and it increases at the later stage making a straight line till complete decomposition has taken place. It was found that complete weight loss occurs at about 253 °C which is 16 °C higher as compared to the heating rate of 5 °C/min which depicts a little change in the profile.



**Fig:29 TG curve of amatol at 10<sup>0</sup> C/min Heating Rate**

### **KINETIC PARAMETERS**

To calculate the kinetic parameter of the amatol with the heating rate at 10<sup>0</sup> C/min in the nitrogen atmosphere graph is shown below.



**Fig:30 Graph for calculation of kinetic parameters of amatol with heating rate of  $10^0$  C/min**

The data obtained from the thermal experiment is inserted in the curve fitting program and graph is obtained between  $\ln(w_0/w)$  and  $\Theta$  (C) which shows a straight line. Order of reaction comes out to be 1 and activation energy is calculated as 165 KJ/mole. Decrease in the activation energy has been found at heating rate of  $10^0$  C/min as compared to the previous experiment with heating rate at  $5^0$  C/min. This is due to the slight change in the TGA curve due to the increasing heating rate.

## DISCUSSION

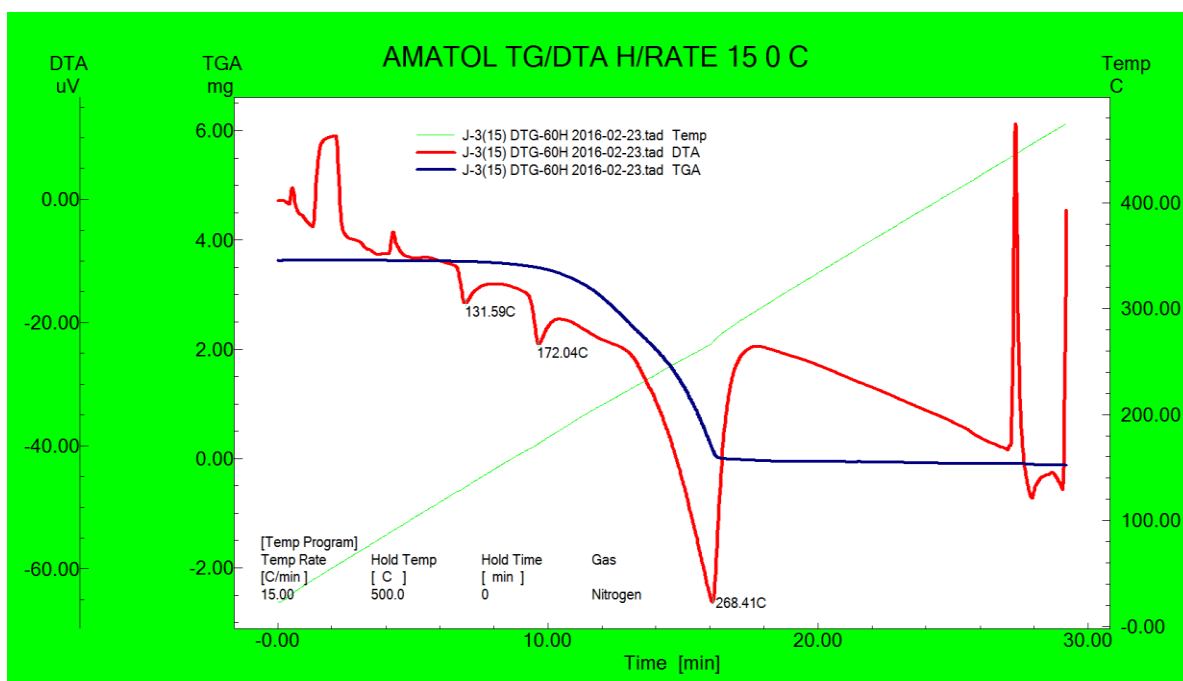
Thermal and kinetic analysis of amatol at heating rate of  $10^0$  C/min shows a lot of information regarding thermal and kinetic behavior. Thermal experiments show that there is increase in the temperature at which three endothermic peaks occur. It is found out that there is great difference in the decomposition temperature of amatol at the heating rate of  $10^0$  C/min which is  $253^0$  C as compared to the  $237^0$  C at the heating rate of  $5^0$  C/min. TG curve also shows changes in the plateau and the decomposition point where all the weight of sample is consumed. The temperature comes out to be  $257^0$  C at which all sample is consumed in comparison of  $244^0$  C temperature at the heating rate of  $5^0$  C/min. The



kinetic study by using the Horowitz and Metzger method shows that activation energy is calculated as 165 KJ/mole which has reduced from 168 KJ/mole at the heating rate of 10<sup>0</sup> C/min.

#### 4.15 THERMAL ANALYSIS OF AMATOL AT HEATING RATE OF 15<sup>0</sup> C

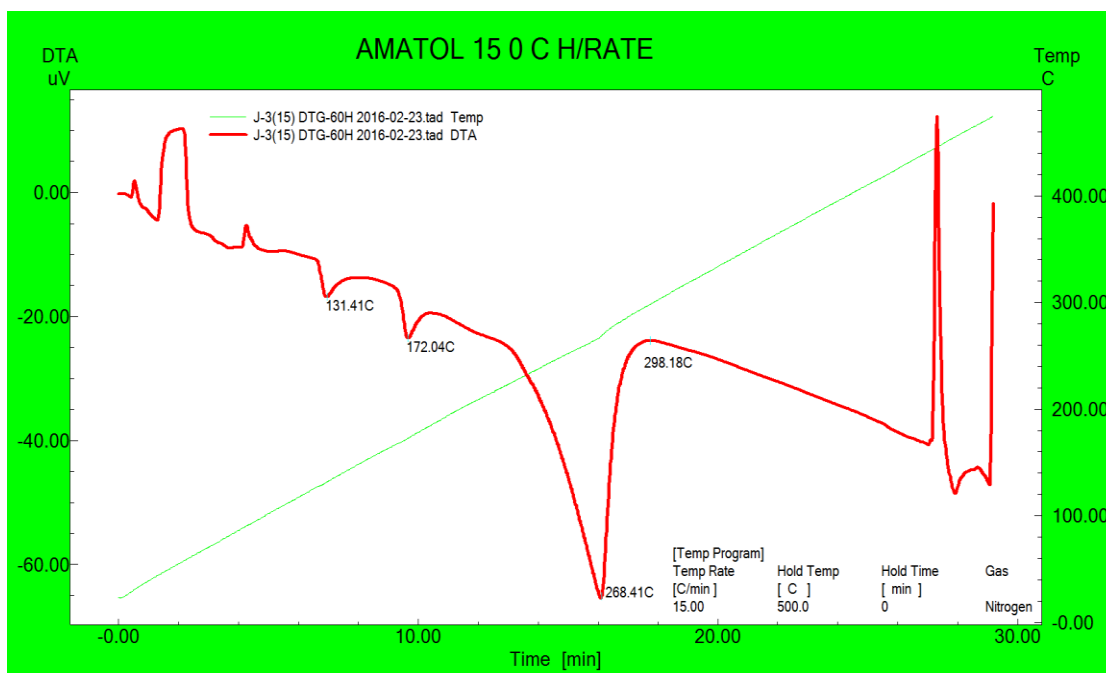
Thermal analysis of amatol was carried out by keeping heating rate at 15<sup>0</sup> C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 500<sup>0</sup> C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. Discussion will be done for the DTA and TG curve separately for analysis.



**FIG:31 TG/DTA curve of 80/20 Amatol with heating rate of 15<sup>0</sup> C/min**  
Note: Approximately 2 % carbon is leftover in the form of soot

## DTA CURVE

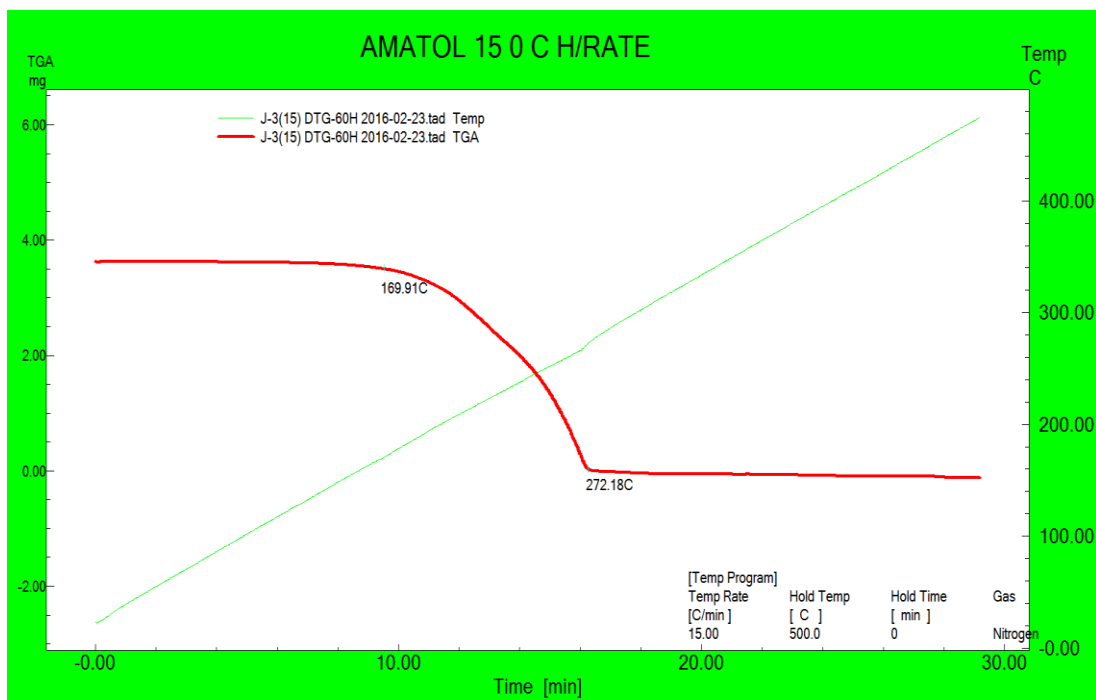
DTA profile of amatol is shown below with the heating rate of  $15^{\circ}\text{C}/\text{min}$ . For this experiment nitrogen atmosphere has been kept with the nitrogen flow of  $20\text{ ml}/\text{min}$ . It was found that first portion of the profile is showing exothermic peaks after that there are three endothermic peaks. First endothermic peak appears at the temperature of  $131^{\circ}\text{C}$ , which shows the solid state phase transformation with no change taking place in the weight of the amatol. Then second peak occurs at the temperature of  $172^{\circ}\text{C}$  which signifies the melting point of the amatol. After the second peak we see the dip in the profile which leads to the highest peak at the temperature of  $268^{\circ}\text{C}$ . This highest peak shows the decomposition of the amatol over which sample is completely consumed. Start temperature of the procedural decomposition peak is about  $175^{\circ}\text{C}$  which terminates at about  $298^{\circ}\text{C}$ .



**Fig:32 DTA curve of amatol with Heating rate  $15^{\circ}\text{C}/\text{min}$**

## TG CURVE

TGA profile of the amatol at heating rate of 15 ° C/min with nitrogen flow of 20 ml/min is shown below. In the plateau region of the profile where weight of the sample remains unchanged lasts till the temperature of about 169 ° C. After that there is a dip in the profile which shows slight slope in the beginning which increases significantly at the end to the temperature of 272 ° C. At this temperature all the sample under the study is consumed.



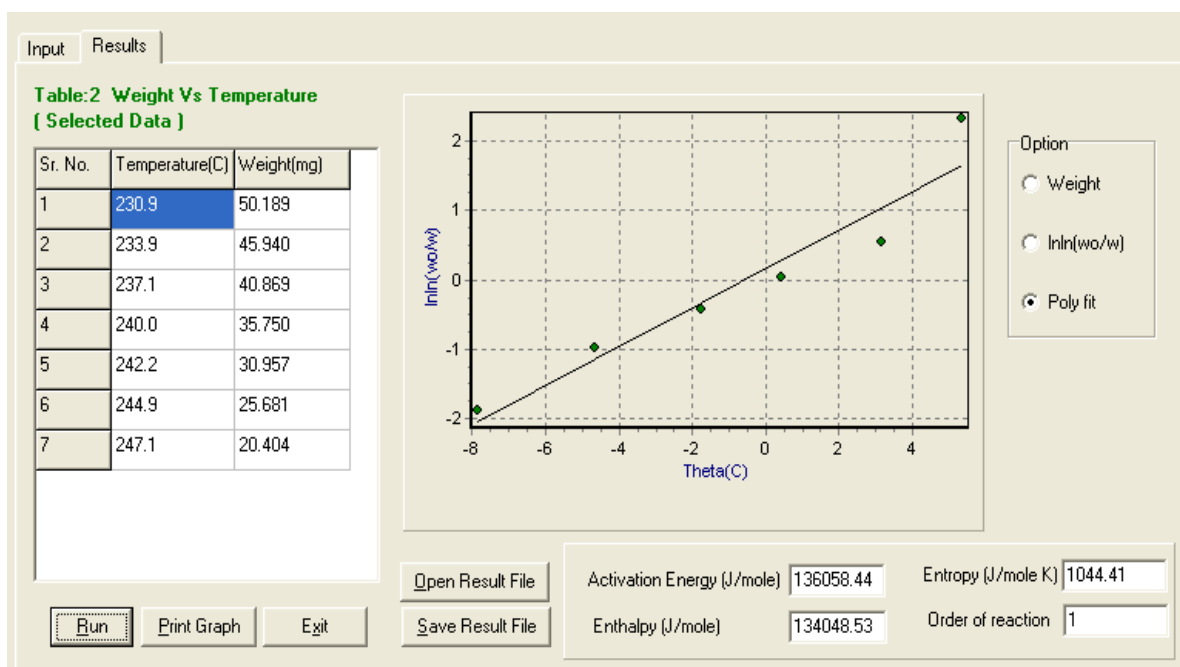
**Fig:33 TGA curve of amatol with Heating rate 15 ° C/min**

## KINETIC PARAMETERS

The kinetic parameter profile of the amatol at the heating rate of 15 ° C/min is shown below. The data of the thermal experiment is used in the curve fitting program to calculate the activation energy.

The activation energy of the amatol comes out to be 136 KJ/mole for the amatol at the heating rate of 15 ° C/min which has further decreased from 165 KJ/mole at

the heating rate of  $10^0$  C/min. The order of reaction comes out to be 1 for the reaction.



**Fig:34 Graph for calculation of kinetic parameters of amatol with heating rate of  $15^0$  C/min**

## DISCUSSION

Thermal analysis of the amatol at the heating rate of  $15^0$  C/min was carried out which revealed initial portion of the profile with the exothermic curves which then leads to the three endothermic peaks terminating with the decomposition of the sample. First endothermic peak occurred at the temperature of  $131^0$  C which resulted due to the solid phase transformation with no change in the weight of the sample. The second endothermic peak appears at the temperature of  $170^0$  C which signifies the melting point of the sample till this point weight of the sample remains unchanged resulting into the plateau portion of the TGA profile. Immediately after the second endothermic peak we observe that TGA profile starts showing the dip in the curve showing the reduction in the weight of the sample which is clear indication of the decomposition process. Third endothermic reaches

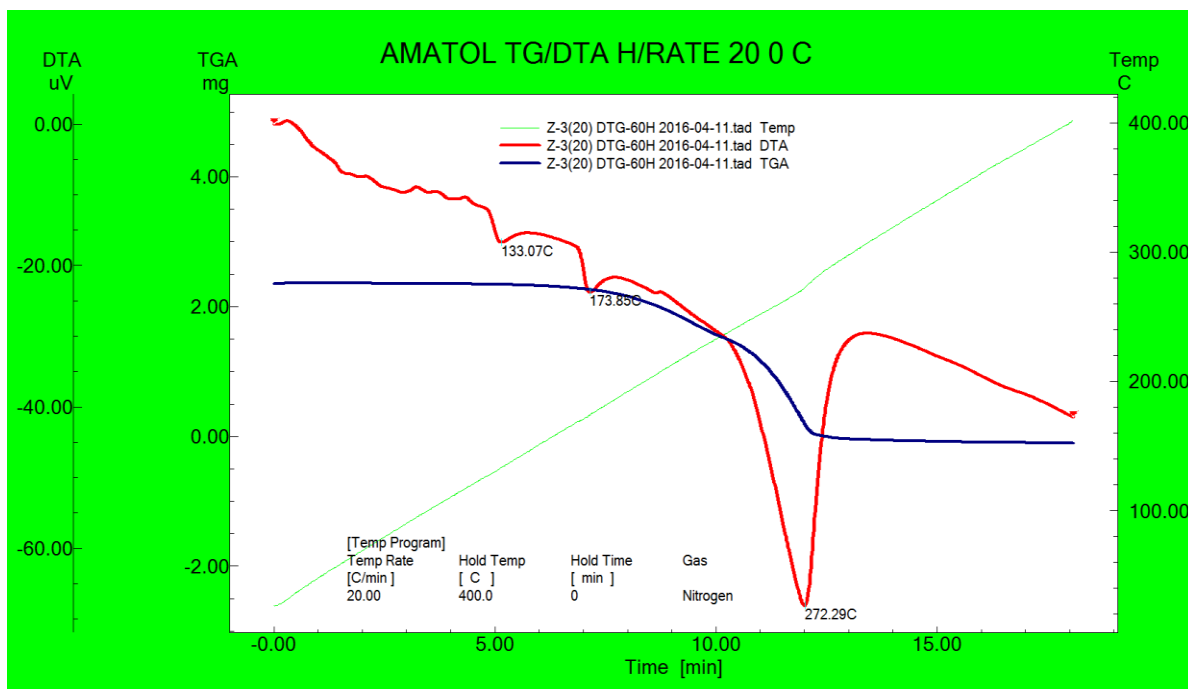
to the peak at the temperature of about 268 °C. At this stage when the sample has completely decomposed the temperature becomes about 272 °C at the TGA curve. When comparing the TGA and DTA profile obtained by this experiment with the experiment conducted at the heating rate of 10 °C/min it is found that there is increase in the temperature of all the three endothermic peaks in the DTA curves. Also when compared the two TGA curves it was found that there is increase in the decomposition temperature with the higher heating rate.

The data from the thermal analysis was then used in the curve fitting program to extract the value of activation energy depicting the kinetic parameters. Activation energy was calculated to be 136 KJ/mole. When comparing this value with the value of the activation energy at the heating rate of 10 °C/min we found that activation energy value has decreased at 15 °C/min heating rate.

#### **4.16 THERMAL ANALYSIS OF AMATOL AT HEATING RATE OF 20 °C**

Thermal analysis of amatol was carried out by keeping heating rate at 20 °C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400 °C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be

discussed separately for analysis.

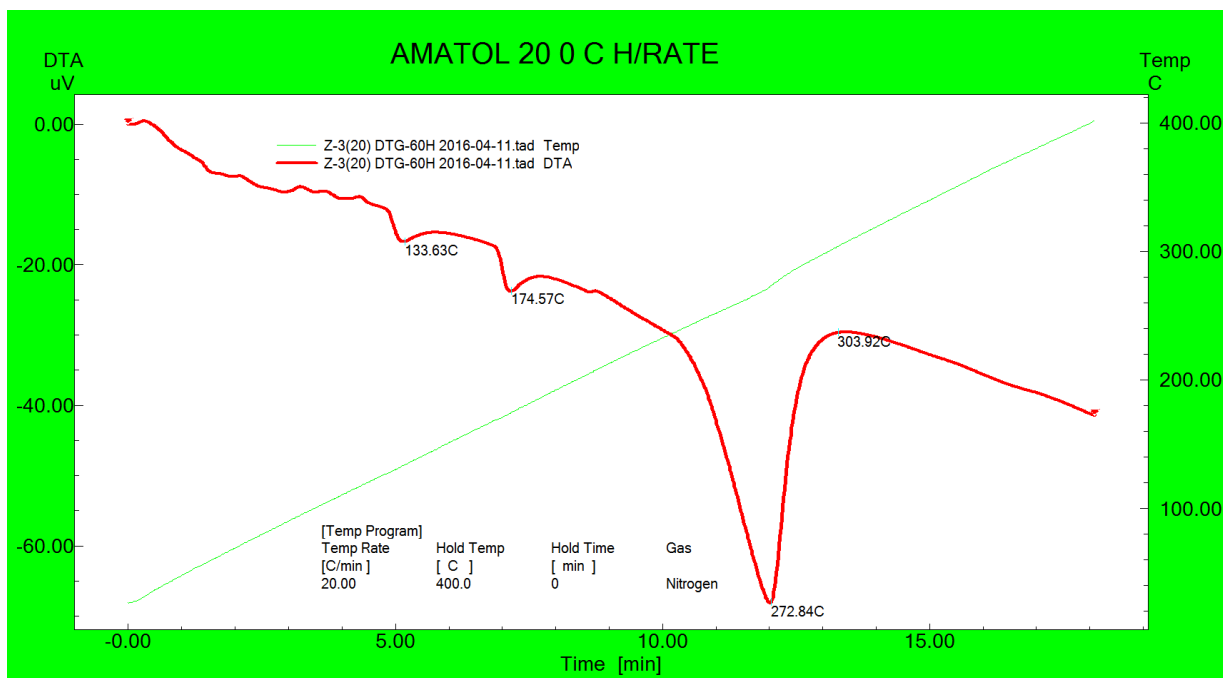


**Fig:35 TG/DTA curve of amatol at 20<sup>0</sup> C/min Heating Rate**

Note: Approximately 2 % carbon is leftover in the form of soot

### DTA CURVE

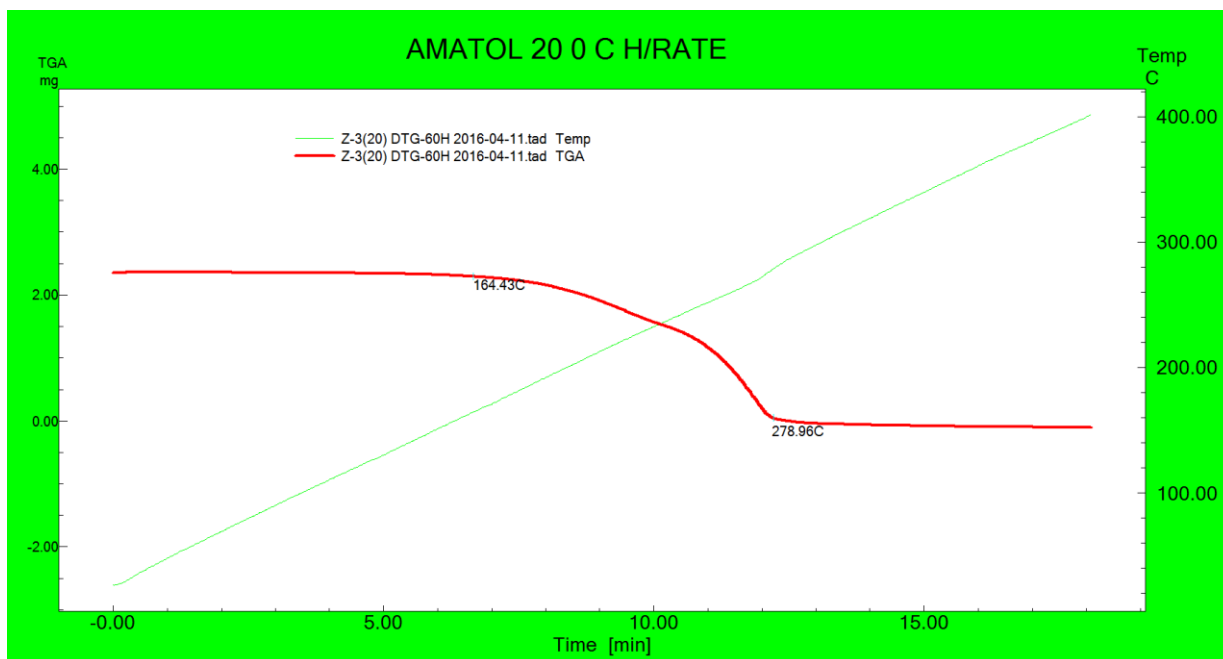
The DTA profile of amatol at 20<sup>0</sup> C/min is shown below. This profile was obtained in the nitrogen atmosphere. In the profile we find three distinct endothermic peaks, among these peaks first peak appears at 133<sup>0</sup> C which shows phase transformation. Second peak appears at 174<sup>0</sup> C which is showing the melting point transition. After the second peak, we find third and highest peak appears which is the procedural decomposition peak which starts after the second peak and terminates at about 303<sup>0</sup> C.



**Fig:36 DTA curve of amatol at 20<sup>0</sup> C/min Heating Rate**

### TG CURVE

TGA profile of the amatol at 20<sup>0</sup> C is shown below. This profile shows the similar curve as have been seen in the previous cases with different heating rates. The decomposition process is single stage with the difference in the start and termination temperature as compared to the previous curves of amatol at different heating rates. From the profile it is found that weight loss starts after the melting point is reached at about 174<sup>0</sup> C and complete sample is consumed in the process at the temperature of 278<sup>0</sup> C.

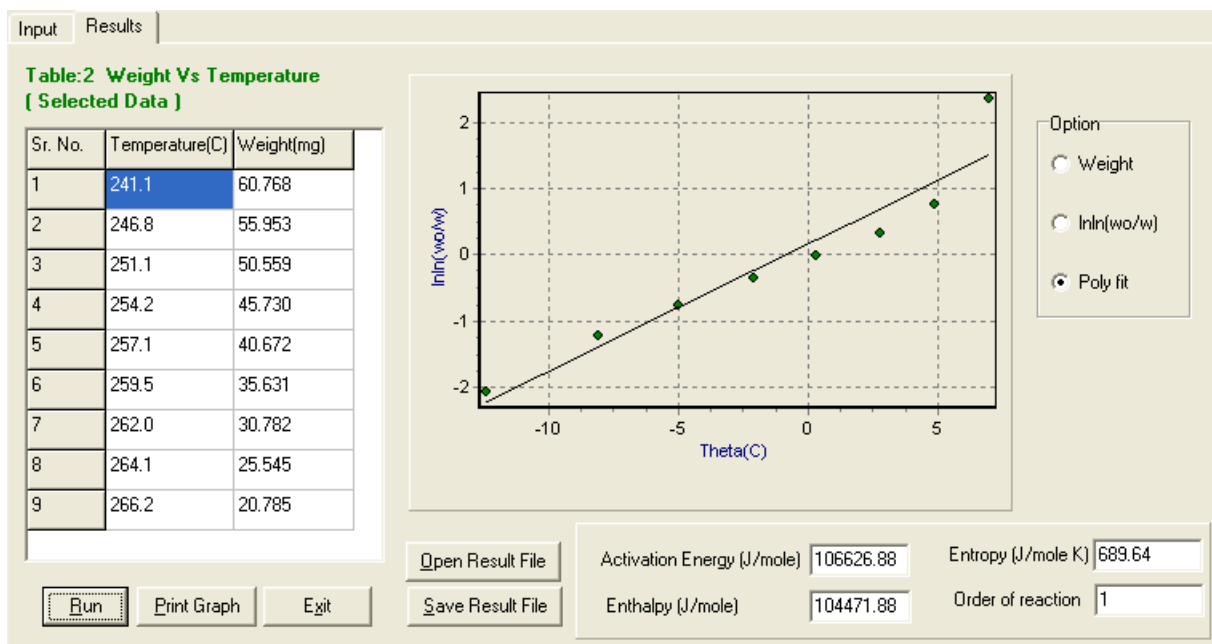


**Fig:37 DTA curve of amatol at 20<sup>0</sup> C/min Heating Rate**

### **KINETIC PARAMETERS**

The data obtained from the thermal analysis was used in the curve fitting program to find out the kinetics parameters. The graph shown below shows the kinetics parameters of amatol at the heating rate of 20<sup>0</sup> C/min. The order of reaction comes out to be 1 and activation energy value is calculated as 106 KJ/mole.





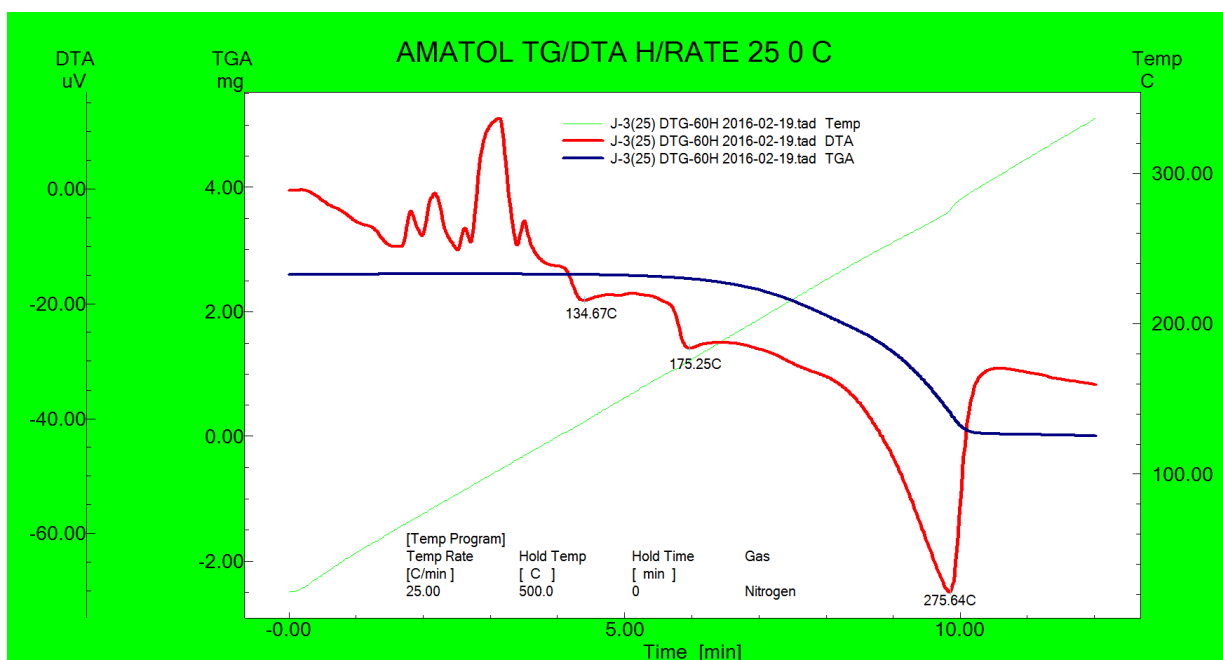
**Fig:38 Graph for calculation of kinetic parameters of amatol at 20 0 C/min Heating Rate**

## DISCUSSION

Thermal analysis of the amatol at the heating rate of 20 <sup>0</sup> C/min shows increase in the temperature at which three endothermic peaks occur when compare it to the previous experiment with the heating rate of 15 <sup>0</sup> C/min in the DTA profile. TGA profile shows the single stage decomposition of the sample with the increase in the temperature of decomposition which comes out to be 278 <sup>0</sup> C. The kinetic parameters of the experiment show that activation energy of amatol at the heating rate of 20 <sup>0</sup> C/min comes out to be 106 KJ/mole. When we compare this activation energy value with the previous experiment at 15 <sup>0</sup> C/min, decrease in the value of activation energy is noted.

#### 4.17 THERMAL ANALYSIS OF AMATOL AT HEATING RATE OF 25 °C

Thermal analysis of amatol was carried out by keeping heating rate at 20 °C/min with nitrogen atmosphere with flow rate of 20ml/min. Temperature range was set from ambient temperature to 400 °C. The analysis performed provided the simultaneous TG and DTA curve to reach to the results for which profile is shown below. DTA and TG curve will be discussed separately for analysis.



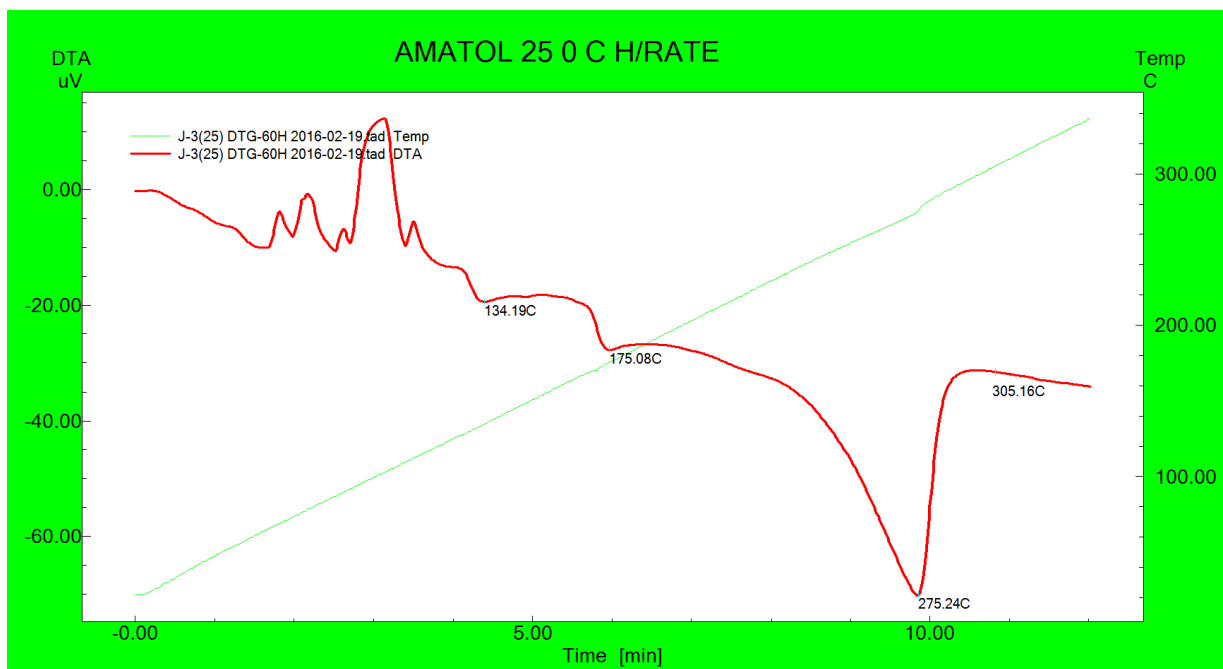
**Fig:39 TG/DTA curve of amatol with Heating Rate 25 °C/min**

Note: Approximately 3 % carbon is leftover in the form of soot

#### DTA CURVE

The DTA curve of the amatol at the heating rate of 25 °C/min is shown below. In the profile it was found that initial portion of the curve shows exothermic peaks with no change in the weight. After that three endothermic peaks as the temperature is increased are shown. First endothermic peak appears at 134 °C which depicts the solid state transformation. Second endothermic peak appears at about 175 °C which clearly shows the melting point transition. After that procedural decomposition temperature starts at about 175 °C reaches to a maximum endothermic peak at the temperature of 275 °C

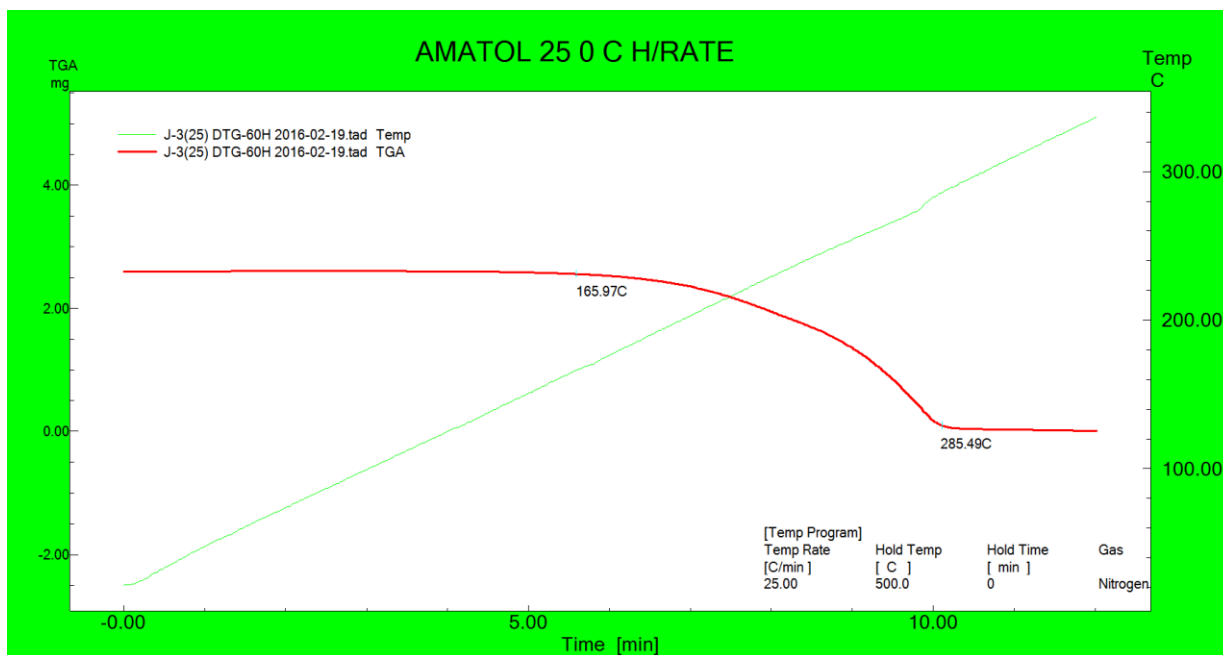
which is called as the decomposition peak where sample is decomposed.



**Fig:40 DTA curve of amatol with Heating Rate 25 °C/min**

### **TG CURVE**

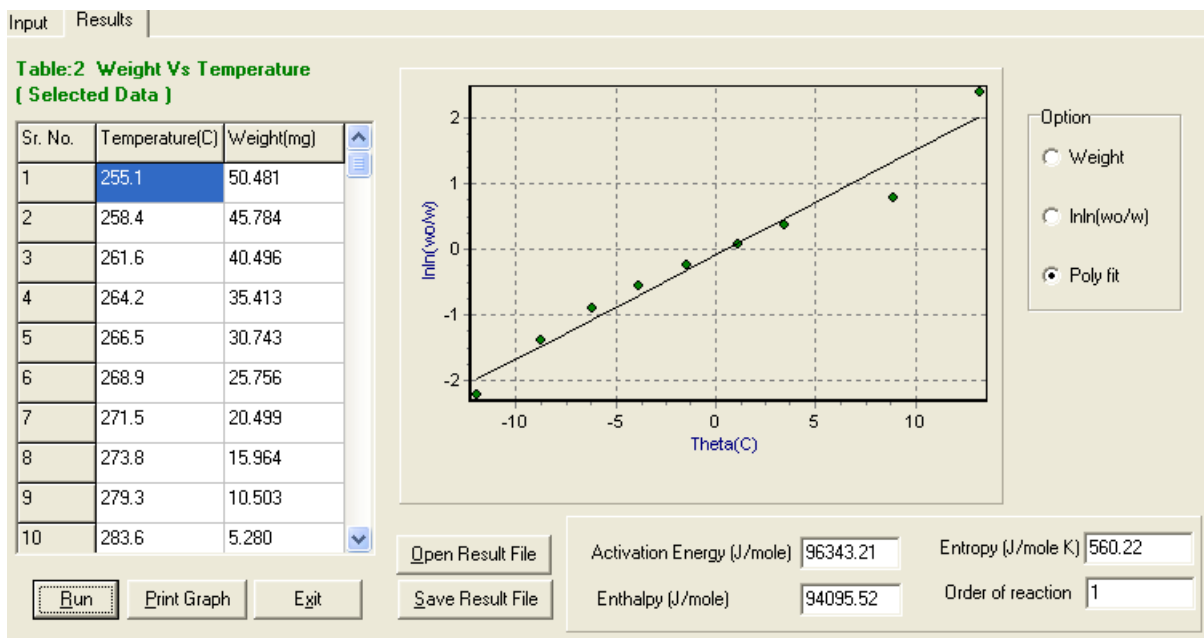
The TG curve of the amatol at heating rate of 25 °C/min is shown below. This profile shows the weight loss taking place during the experiment. The first portion of the profile is the plateau and it lasts till the temperature of about 175 °C where weight of the sample remains unchanged. After the 175 °C temperature is attained weight starts reducing. This reduction in weight is slow in start and increases at the later part. The complete sample is finished till it reaches to the temperature of about 285 °C.



**Fig:41 TG curve of amatol with Heating Rate 25<sup>0</sup> C/min**

## **KINETIC PARAMETERS**

The graph for evaluating the kinetic parameters by using the curve fitting program is shown below. The thermal experiment data is used by the Horowitz and Metzger method to obtain the values of kinetic parameters. Order of reaction comes out to be 1 and activation energy is calculated as 96 KJ/mole for the amatol at 25<sup>0</sup> C/min heating rate. This value of activation energy is less as compared to the value of the activation energy in the previous experiment at 20<sup>0</sup> C/min which was 106 KJ/mole.



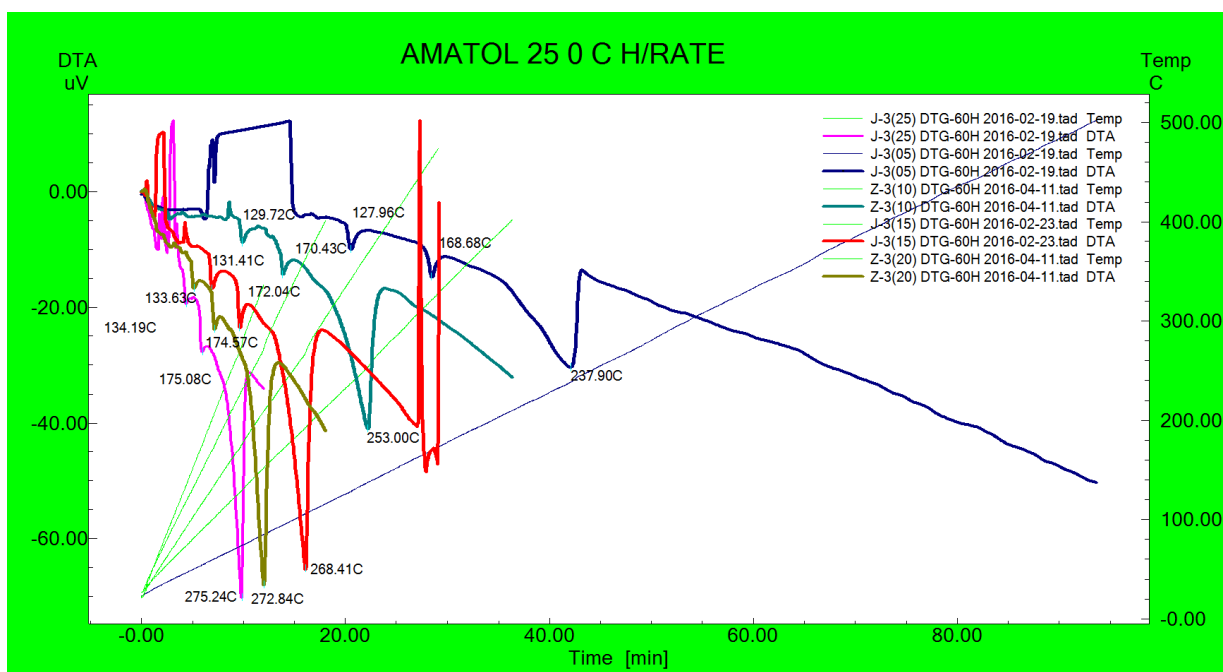
**Fig:42 Graph for calculation of kinetic parameters of amatol at heating rate of 25<sup>0</sup> C/min**

## DISCUSSION

The thermal and kinetic parameters have been analyzed for the amatol at the heating rate of 25<sup>0</sup> C/min. The thermal experiment shows that DTA profile has shown increase in the temperature at the peaks when compare it to the previous experiments at less heating rates. The procedural decomposition temperature for the DTA curve at the endothermic peak comes out as 275<sup>0</sup> C as compared to the 272<sup>0</sup> C at the heating rate of 20<sup>0</sup> C/min. When see the TGA curve it is found that single stage decomposition takes place similar to the previous experiments curve but it is found that decomposition temperature when weight of the sample becomes zero has increased and becomes 285<sup>0</sup> C as compared to the other temperatures at the low heating rates. The data of the thermal study when was used to extract the kinetic parameters we found that activation energy comes out to be 96 KJ/mole for the heating rate at 25<sup>0</sup> C/min which has reduced as compared to the other low heating rates which shows an inverse trend in the values of activation energy with relation to the heating rates.

#### 4.18 Comparison of Peak of DTA Temperature of Amadol at Different Heating Rate

The experiments were conducted on the 80/20 amatol with the varying rates of heating which were 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min respectively. Profiles of DTA of all the heating rates have been shown in the figure below.



**Fig:43 DTA curve of amatol at different heating rates**

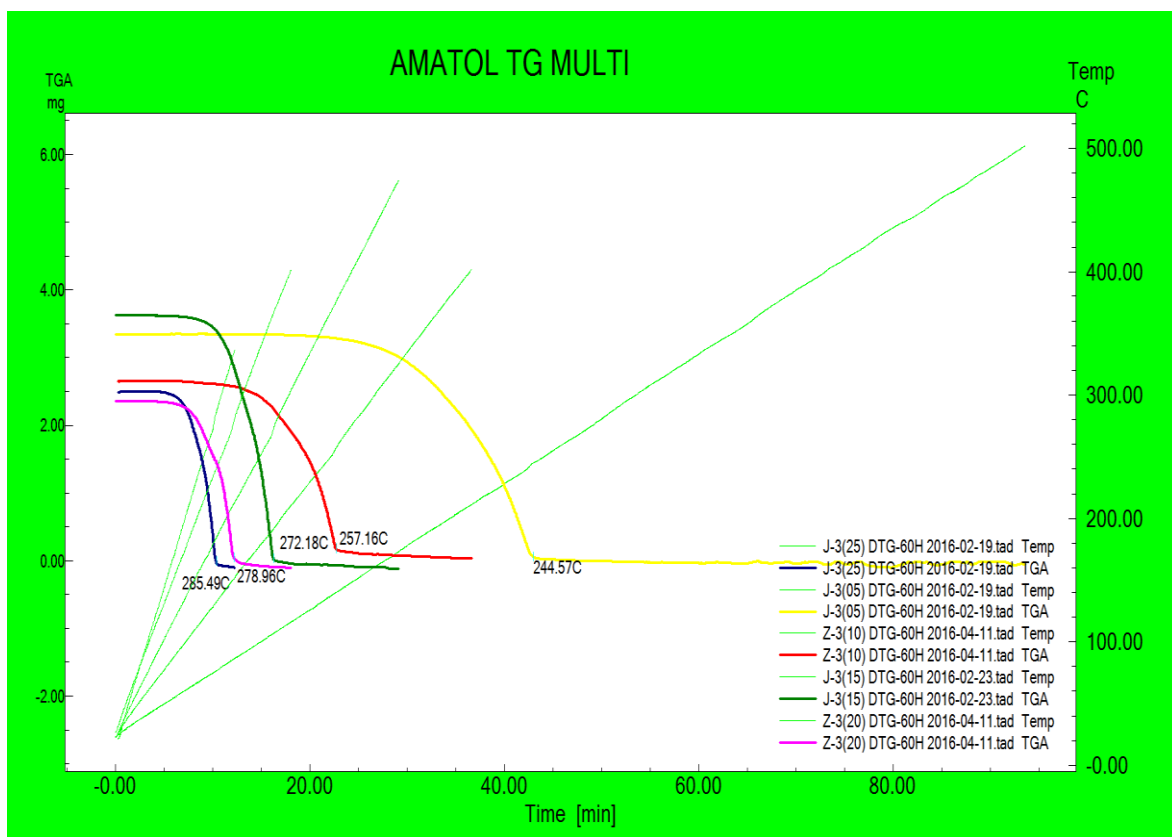
From the above graph we find that with the increase in the heating rate there is increase in the peak temperatures. In the table below we have shown the temperatures at the peaks at increasing heating rates. When compare the first endothermic at increasing heating rate it is found that all the peak temperatures increase for the solid phase transformation peak. When compare the second peak which represents the melting point it is found that with the increase in the heating rate the temperatures at all the peaks increase. When compare the third peak which represents the decomposition peak it is found that with the increase in the heating rates there is increase in the peak temperature.

#### **Comparison of Peak Temperature at Different Heating Rate**

Heating Rate	1st Endo Peak (± 1)	2 <sup>nd</sup> Endo Peak (± 1)	3 <sup>rd</sup> Decomposition Peak (± 1)
5	127.96	168.68	237.90
10	129.72	170.43	253.00
15	131.59	172.04	268.41
20	133.07	173.85	272.29
25	134.67	175.25	275.64

#### **4.19 Comparison of Amatol Decomposition Temperature of TG at Different Heating Rate**

The experiments were conducted on the 80/20 amatol with the varying rates of heating which were 5 °C/min, 10 °C/min, 15 °C/min, 20 °C/min and 25 °C/min respectively. Profiles of TGA of all the heating rates have been shown in the figure below.



#### **Fig:44 TGA curve of amatol at different heating rates**

From the graph it is found that with the increase in the heating rate there is increase in the decomposition temperature which has been shown below in the table. This trend clearly states that increase in the heating rate has great influence on the decomposition temperature.

#### **Comparison of Amatol Decomposition Temperature at Different Heating Rate**

<b>Heating Rate</b>	<b>Decomposition Temperature</b> ( $\pm .5$ )
5 $^{\circ}$ /min	244.57 $^{\circ}$ C
10 $^{\circ}$ /min	257.16 $^{\circ}$ C
15 $^{\circ}$ /min	272.18 $^{\circ}$ C
20 $^{\circ}$ /min	278.96 $^{\circ}$ C
25 $^{\circ}$ /min	285.49 $^{\circ}$ C

#### **4.20 Comparison of Activation Energy of Amatol at Different Heating Rate**

Calculation of the activation energy for the 80/20 amatol at different heating rates has been done which are shown in the table below. From the table we find that with the increase in the heating rate there is decrease in the activation energy. This brings us to the conclusion that activation energy is inversely proportional to the heating rate i.e. it is effected inversely with the increase in the heating rate.

<b>Heating Rate</b>	<b>Activation Energy (<math>\pm 2</math>)</b>
5 $^{\circ}$ /min	168.3 KJ/mole



10 °min	165.8 KJ/mole
15 °min	136.05 KJ/mole
20 °min	106.6 KJ/mole
25 °min	96.34 KJ/mole

## **4.21 COMPARISON OF RESULTS OF TNT AND AMATOL**

- **Comparison of DTA Decomposition curves of TNT and Amatol at Different Heating rates**

<b>Heating Rate</b>	<b>Decomposition Temperature TNT (<math>\pm 1</math>)</b>	<b>Decomposition Temperature Amatol (<math>\pm 1</math>)</b>
5 <sup>0</sup> /min	219.27 <sup>0</sup> C	237.9
10 <sup>0</sup> /min	242.89 <sup>0</sup> C	253.00
15 <sup>0</sup> /min	243.04 <sup>0</sup> C	268.41
20 <sup>0</sup> /min	260.62 <sup>0</sup> C	272.29
25 <sup>0</sup> /min	252.38 <sup>0</sup> C	275.64

- **Comparison of TG Decomposition curves of TNT and Amatol at Different Heating rates**

<b>Heating Rate</b>	<b>Decomposition Temperature TNT (<math>\pm 0.5</math>)</b>	<b>Decomposition Temperature Amatol (<math>\pm 0.5</math>)</b>
5 <sup>0</sup> /min	240	244.57 <sup>0</sup> C
10 <sup>0</sup> /min	255	257.16 <sup>0</sup> C
15 <sup>0</sup> /min	257	272.18 <sup>0</sup> C

20 °/min	275	278.96 °C
25 °/min	265	285.49 °C

- **Comparison of Activation Energy of TNT and Amatol at Different Heating Rates**

<b>Heating Rate</b>	<b>Activation Energy TNT (± 2)</b>	<b>Activation Energy Amatol (± 2)</b>
5 °C/min	78.6 KJ/mole	168.3 KJ/mole
10 °C/min	84.9 KJ/mole	165.8 KJ/mole
15 °C/min	86.5 KJ/mole	136.05 KJ/mole
20 °C/min	127.7 KJ/mole	106.6 KJ/mole
25 °C/min	125.7 KJ/mole	96.34 KJ/mole

## **DISCUSSION**

In the table shown above comparison of the results of the thermal studies along with the kinetic parameters has been carried out. In the first table comparison of the results of DTA curve of decomposition peak of the TNT and Amatol has been done. It is found that with the increase in the heating rate there is increase in the decomposition temperature of amatol but in case of TNT it is noted that there is increase in the decomposition temperature till the heating rate of 20 °C/min but at the heating rate of 25°C/min there is a decrease in the temperature i.e. temperature reduces.

In the second table comparison of the TG curve of amatol and TNT has been carried out. It is seen that same trend of increase in the temperature has been found out in the amatol with

the increase of the heating rate. In case of TNT it has been noted that there is increase in the temperature of decomposition till the heating rate of 20 °C/min and then after that at the heating rate of 25 °C/min there is decrease in the decomposition temperature.

From the TG curve it is also evident that amatol is safer in handling than the amatol as it has higher decomposition temperature making it more stable in use.

In the third table comparison of the activation energy of the TNT and Amatol has been carried out at different heating rates. It is seen from the results in case of TNT there is increase in the activation energy with the increase in the heating rate till the heating rate of 20 °C/min but at the heating rate of 25 °C/min there is decrease in the activation energy. This behavior somewhat resembles with the DDT phenomenon where in the start heat produced is less which increases with the confinement leading to the detonation. Likewise, in case of TNT, as the heating rate is increased to 25 °C/min heating rate is increased to the level after which activation energy starts decreasing. It shows that as the heating rate is increased then energy produced is so much more than the energy dissipated and it also overcomes the thermal lag due to which activation energy starts reducing at higher heating rate in TNT. In case of amatol it is seen from the results that there is inverse trend of the values of activation energy i.e. with the increase of the heating rate there is decrease in the value of the activation energy.

Some of the reasons of such trends in the thermal analysis are as under:

a. **Thermal lag phenomenon**

It occurs due to the non-uniform heating of the sample caused by the thermal lag. The sample is exposed for less time for the specific heating rate at higher heating rate [1]. Similar effects have been observed by other researches as well [2].

b. **Influence of the Furnace Atmosphere**

The mechanism of many chemical reactions is influenced by the atmosphere and in particular by the gas pressure. With increasing partial pressure reaction moves to the higher temperature. With the higher partial pressure DTA effects are more pronounced [3]. The hot humid gases formed by the decomposition reaction diffuse

slower into the furnace atmosphere than new gases are produced.

c. **Influence of the Heating Rate**

As the heating rate is increased, temperature rises quickly, causes less time for the substance transition from one state to the other, thus chemical reactions move to higher temperatures. In addition, there is local change in the furnace atmosphere and on the sample surface in contrast to the bulk of material, as reaction rate is linked with the temperature increase [4]. Higher the heating rate higher will be gases output, lower will be gases diffusion rate in the atmosphere which will increase the partial pressure thus increasing the decomposition temperature.

d. **Higher Heat Dissipation**

It may be explained that at a higher heating rate, heat is dissipated more conveniently so decomposition process starts at the higher temperatures and also has the higher heat of diffusion. [5]

e. **Increased Surface Area**

Amatol has Interconnection of gaps and evenly distributed porous structure. Its surface area is increased resulting in high oxidation. With increasing heating rate more heat is evolved and is utilized by high oxidizing potential causing reduction in activation energy.

f. **Similar to DDT Phenomenon**

Likewise, DDT phenomenon, deflagration leads to detonation due to confinement and atmospheric pressure. TNT has great explosion potential which when deals with increased heating rate then at higher heating rates it reaches to a baseline after which decrease in the activation energy occurs with increase in the heating rate.

## REFERENCES

- [1] A. Eslam S.M, Pourmountazavi, Hajimursadeghi, combustion flame 141(2005)322
- [2] C.G Hosseiri, A. Eslami, journal of thermal analysis and calorimetry ,101(2010),1111
- [3] R.F. Speyer, Thermal analysis of materials, Marcel Dekker, Inc., New York,1994
- [4] Christian-albrechts-universitat zu Kiel, Differential thermal analysis, M110 ,05/09/2011
- [5] Fouzia Rafat, Effect of different heating rate on the thermal decomposition of urea in an open reaction vessel, Scholar Research Library, 2014

## CONCLUSION

The efficiency of all the explosives is dependent upon many factors among them oxygen balance factor is considered as of great importance. TNT has been used extensively for the military purpose but it has negative oxygen balance of 74%, which has been addressed by using 80/20 amatol for different shades of operations which gives us the positive oxygen balance of 1.2%. Due to this positive oxygen balance of 80/20 amatol blast effects are increased to generate more practical effects.

Explosives are very dangerous material and warrant extreme caution for the safe handling which may be for the practical use or research. When using the explosive for the research purpose we need to use very safe techniques for the analysis for which reason thermal analysis methods are considered most appropriate.

For thermal study of TNT and 80/20 amatol, DTA/TGA techniques have been used in the form of simultaneous thermal method. In case of TNT thermal analysis, it is found that with the increase in the heating rate thermal decomposition temperature and activation energy increases till heating rate of 20<sup>0</sup>C/min after that decomposition temperature and activation energy reduces at heating rate of 25<sup>0</sup>C/min. This effect is similar to the DDT phenomenon which takes place due to increase in heat rate due to which heat generated is more than the heat liberated which results in the increase of internal temperature and reduction in the activation energy, here as well, as the heating rate is increased beyond 20<sup>0</sup>C/min more heat is generated resulting in the reduction of activation energy of TNT.

During the study several experiments were conducted with the increasing heating rates on the 80/20 amatol and it was found from the data that when we increase the heating rate for the 80/20 amatol thermal analysis, peak temperatures also increase for all the peaks which leads us to the conclusion that peak temperatures are dependent to the increase in the heating rate. This is due to the thermal lag, higher heat dissipation and furnace atmosphere. The data obtained from the thermal analysis of 80/20 amatol was further used to obtain the kinetic parameters i.e. activation energy, order of reaction, enthalpy etc. From the kinetic data we found that for the 80/20 amatol activation energy is effected by the heating rate.

From the data it is concluded that activation energy is inversely dependent upon the heating rate. When we increase the heating rate, activation energy reduces with some proportion. This phenomenon is due to the several factors effecting the thermal phenomenon which are thermal lag, effects of the furnace temperature, higher heat dissipation and higher heating rate.

From the data we have seen that decomposition temperature of the TNT is 240 °C while in case of the 80/20 amatol the decomposition temperature comes out to be about 245 °C making the 80/20 amatol more stable in handling.

The upshot of this study is that 80/20 amatol has more blasting capabilities than the TNT due to the positive oxygen balance resulting in the production of higher volume of gases. Also the decomposition temperature of TNT is lower than the decomposition temperature of the 80/20 amatol due to which 80/20 amatol is considered to be more safe in the handling. Thirdly when comparing the activation energy of the TNT with 80/20 amatol it is found that activation energy of the 80/20 amatol (168.3 KJ/mole) at the heating rate of 5 °C/min is higher than the TNT (78.6 KJ/mole) which makes it more safe in the handling.

## **FUTURE RECOMMENDATIONS**

1. Thermal and kinetic study may be conducted by using the 70/30 amatol with the varying rates of heating.
2. Thermal and kinetics study of PE3A military explosive be conducted and compared with the 80/20 amatol.