

CHAPTER 1

ENERGETIC MATERIALS

1.1 WHAT ARE ENERGETIC MATERIALS?

These are the materials which include combustible materials as well as high explosives. These materials are better defined by considering them as compounds or as mixtures of different compounds that generate energy by undergoing decomposition. The rate of decomposition can be slow in case of combustible materials and rapid in case of high explosives. Regardless of the type of energetic material it cannot undergo decomposition until sufficient energy has been added to get the process started. Until and unless a sufficient amount of energy is supplied to start the process the energetic material cannot be decomposed. The required energy can be in the form of shock, heat or friction or it can also be any combination of these sources of energy. As and when the energetic material undergoes decomposition it starts to change into different materials. For example when we burn wood it produces noncombustible ashes and smoke. Therefore the more stable type of stuff is produced as a result of burning. Energetic materials on decomposition produce gasses in large volume and some amount of residues with a tremendous amount of heat. Since the first production of explosives human beings have been captivated by its power and horror-struck by its destruction. The mining of the huge amounts of coal, metal ore, minerals and huge construction project excavations would have been nearly impossible without explosives. Without the positive use of energetic materials the pace of industrial revolution would have been very slow. Since the ancient times when Greek fire was first used in AD 673 the energetic materials have played the crucial role in enabling the military might in reshaping the world political structure.

According to Explosive Act 1875 the legal definition of explosive is given where an explosive is a substance used or manufactured with a view to produce a practical effect by explosion [1]. An explosive must have the ability to remain stable under almost all kinds of storage and use conditions and it must not react with the substance with which it's expected to come in contact. It must also be sensitive enough to be initiated easily by convenient means. Collectively all these properties constitute the two main properties for a useful explosive which are reliability and safety. For an explosive to be effective it must be able to perform some useful work on the surroundings. Therefore an explosive can be defined as a single substance or mixture of different substances which when suitably initiated has the capability to produce a very rapid intense pressure with release of gases at very high temperatures. Petrol releases approximately ten times as much energy per gram as the explosive TNT, but the explosive will release its energy far more quickly and so causes a much more severe effect. A combination of a fuel and an oxidizer is required in an explosive material. For a more efficient reaction which will allow the maximum amount of energy to be released to the environment, a balance between the two is necessary, represented by a quantity known as the oxygen balance. The fuel and oxidizer can be physically mixed to allow them to react (for example in the case of hydrogen gas reacting with air, a common school laboratory experiment). Alternatively, the two can both be present in the same molecule, as is the case with the most efficient military explosives today [2].

1.2 WHAT IS AN EXPLOSION?

Explosion is an abrupt and extremely quick release of gases out of a confined space along with thunderous noise, shock and very high temperatures. This phenomenon happens when all of a sudden a huge amount of energy is released. This outburst of energy can be the result of a rapid chemical reaction with in an energetic material or it may also come from a steam boiler which has been over pressurized as well as a result of nuclear fission reaction [2].To make this event happen there has to a buildup of a

huge amount of energy in a specific confined space from where it can escape or can be released suddenly. The creation and rapid release of gases is in fact the main characteristic of an explosion and is available in following three types of explosion.

1.2.1 PHYSICAL

The explosion which occurs without any nuclear or chemical reaction is known as physical or mechanical explosion. The bursting of a vessel containing any gas or liquid under high pressure in such a manner that its contents rapidly expand forming a shockwave is a very common example. If we consider a balloon which bursts open or bursting of a gas cylinder that would suggest that mere presence of a known explosive or heat is not the most important precondition for an explosion. Nevertheless these explosions result in air blast and propulsion of the fragments at very fast velocity which cause destruction and damage. The bursting of steam boiler and pressure cooker due to buildup of very high pressure are other common examples [2].

1.2.2 CHEMICAL

The explosion that occurs due to a very rapid chemical reaction producing extremely large amount of gas and large quantity of heat is known as a chemical reaction. These types of explosions are caused by energetic materials or explosive compositions which have been pressed but confinement is not necessarily a prerequisite always. In this type of explosion highly exothermic change occurs at an extremely rapid pace forming vapors and hot gases. Due to extremely fast reaction the gases instead of expanding right away stay in the vessel for a very small part of a second and eventually occupy the space which was occupied by explosive material just before the time of explosion. Now this space is very small and explosion produced a temperature which is about several thousands of degrees, consequently pressure rises to the extent where it results in a blast wave breaking the vessel walls and damaging everything all around it. Moderately the destruction due to an explosion depends upon the speed of the reaction. It must be

remembered that due to unstable nature of explosives the decomposition reaction once started usually cannot be stopped [2].

1.2.3 NUCLEAR

A nuclear or atomic explosion result from fusion or fission reactions and produces energy which is billions of times more than that of a chemical explosion. Shockwaves produced as a result of a nuclear explosion are same as that of a chemical explosion but these remain longer and pressure is higher. Neutrons would be deadly for anyone in the near vicinity and for those at farther distances would be seriously damaged by the gamma rays. Very strong ultra-violet and infra-red rays are also emitted [2].

1.3 TYPES OF REACTIONS IN AN EXPLOSIVE

There are three basic types of reactions which are as follows.

1.3.1 COMBUSTION

It's simply a chemical reaction taking place between a material and oxygen. It's a very exothermic and quick reaction and usually produces flame. During this process the temperature of the unreacted part of material is raised and consequently the reaction rate rises. For example when we strike the match head of match stick, energy is produced in the form of heat due to friction which will initiate the combustion reaction and match head gets ignited. In explosives and propellants this process is exothermic, rapidly oxidizing and self-sustaining reaction. During this reaction explosives and propellants release a large volume of very hot gases and do not require the availability of oxygen in the atmosphere. Explosives and propellants are classified as combustible as they contain oxidizer and fuel. Fundamentally the explosives and propellants have almost same composition and propellants produce gases by deflagration whereas explosives detonate.

In explosives the combustion reaction is supersonic whereas in propellants it's subsonic [3].

1.3.2 DEFLAGRATION

Deflagration (Lat: deflagrare, de + flagrare, "to burn down") [4] is a combustion reaction propagating at subsonic rate by thermal conductivity. It is purely a swift and rapid type of combustion whereas normal combustion is a sluggish or slow type of deflagration. Basically it's the burning speed which governs the difference among combustion, deflagration and detonation. When a little amount of a material exposed to flame, shock, spark, high temperature or friction ignites in an unconfined state, it's classified as deflagrating explosive. Deflagrating explosives produce a hissing sound and burn with sparks or flame violently as compared to other kinds of combustible materials. The process is self-propagating as it produces heat and energy which is enough to start decomposition of more and more exposed explosive surface. With an increase in confinement the rate of deflagration will increase. For example, explosive placed in large quantity will contain confined particles. As soon as the explosive deflagrates the gases are produced which are trapped inside the explosive material due to its large quantity and resultantly the internal pressure is increased. Consequently the temperature is raised resulting in higher rate of deflagration which is normally around 1 to 10 feet/second. During this process the product gases are at subsonic speed and move in the direction opposite to that of the flame. This is a surface phenomenon so the rate of deflagration or the rate at which the material is being consumed depends on surface area.

1.3.3 DETONATION

Detonation (Lat: detonare, de + tonare, "to expend thunder") [4] occurs as a result of a chemical reaction which is exceptionally fast along with a shock wave and very powerful change in pressure. The detonating energetic materials are those which

undergo decomposition by means of a shock wave instead of thermal means. In explosive material may it be solid or liquid the shock wave velocity or velocity of detonation ranges from 1500 to 9000 meters per second. The decomposition rate does not depend on the heat transfer rate but it entirely depends on the transmission of shock wave through the material. This creation and transmission of the shock wave through the explosive into the surroundings is the reason that gives detonation its very fierce destructive power. The detonation once started with a chemical reaction followed by the detonation wave stops only when the complete explosive gets decomposed. Outside the energetic material the detonation wave moves just like the wave created by an air craft breaking the sound barrier and its strength reduces gradually as it loses its energy. Explosive can be detonated by either initiating with the help of a shock wave or by deflagration. In burning or deflagration to detonation the explosive material is confined for example in a tube which is initiated from one end. The gases produced due to the decomposition of explosive are trapped in the tube resulting in a rapid rise in pressure at the burning surface which raises the burning rate. Due to increasing pressure the burning rate rises at an extremely fast pace that it finally exceeds the velocity of sound resulting in detonation. Shock to detonation is normally used to detonate the secondary explosives [5]. The shock wave is produced by initiating a primary explosive which initiates the main charge.

1.4 CLASSIFICATION OF EXPLOSIVES

Explosives can be classified by the uses, performance and sensitivity to initiation. Commonly these are classified into low and high explosives by velocity of detonation and primary and secondary explosives by sensitivity to initiation [2].

1.4.1 LOW EXPLOSIVES

Combustible materials that contain oxygen required for their burning within their composition and are designed not to explode but to function with the production of a large volume of gases are known as low explosives. Low explosives normally deflagrate

at rates ranging from some centimeters per second to four hundred meters per second. When initiated in a confined space these can also lead from deflagration to detonation. These are primarily propellants which contain a specific mixture of explosive compound in which the deflagration produces gases which produce a swift pushing effect in rockets rather than the shocking effect produced by high explosives. Low explosives are also used in pyrotechnique applications. These can be initiated by simple flame and unlike high explosives do not require shock of a detonator.

1.4.2 HIGH EXPLOSIVES

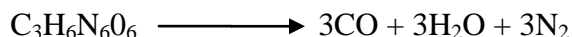
High explosives are manufactured to destroy, blow something apart by exploding. High explosives have a high detonation or shock rate which has to be above 999.7 meters per second. These are different from low explosives as these are initiated by a shock wave and detonate rather than deflagrate as in the case of low explosives. Confined or unconfined they apply a destructive shattering effect upon surrounding objects. High explosives are normally divided into two main types basing upon sensitivity to initiation.

1.4.2.1 PRIMARY EXPLOSIVES

Explosives which are the most sensitive and most powerful are known as primary explosives. Due to the power combined with very high sensitivity these are most dangerous to handle. Due to their sensitivity primary explosives can easily be initiated by applying heat, friction, flame and shock. Owing to their high velocity of detonation these are capable of producing strong detonation waves which can cause detonation of explosives which are less sensitive. Therefore these are employed as initiating step in explosive trains in shape of blasting caps and detonators. Commonly used are lead azide, mercury fulminate, lead styphnate and diazodinitrophenol.

1.4.2.2 SECONDARY EXPLOSIVES

Class of explosives which are more powerful than primary explosives and are not detonated by shock, friction or heat. Due to their less sensitive and more stable nature these can be initiated to detonation by detonation wave produced by primary explosives. When initiated, the explosive composition dissociates immediately into stable components. For example



When detonated with a primary explosive the molecule of RDX breaks down into disordered atoms for a very short time. These atoms recombine instantaneously to produce gases mainly with evolution of large quantity of heat. A shock wave is evolved due to high velocity of detonation which exerts a shattering effect on the surrounding objects. Some of these are so stable that even a rifle bullet can be fired through these explosive or even if set on fire these will burn completely but will not detonate. Due to their high stability and velocity of detonation these explosives detonate violently and exert larger force than the primary explosives. Velocity of detonation of these explosives range from 5500-9000 meters per second. Widely used secondary explosives for military applications include HMX, TNT, RDX, tetryl, nitrocellulose, nitro guanidine, nitroglycerine, picric acid and TATB.

1.5 PROPERTIES AND CHARACTERISTICS OF EXPLOSIVES

All types of explosives are chemical compounds or their mixtures each having different characteristics. For explosive engineer knowledge of the properties governing the performance and finally the blast design is very critical. Some of the important characteristics are given below [3].

1.5.1 STABILITY

Stability is the ability of an energetic material to be stored for a longer period without getting deteriorated. Stability in explosives commonly depends on the chemical contents, exposure to temperature changes, sunlight and electrical discharge. Explosive must be thermodynamically and kinetically stable. The decomposition of explosives gets accelerated at high temperature and military explosives mainly are unstable above 70°C. Nitrogen rich explosives decompose when exposed to sunlight for longer duration. There are some explosives which are highly sensitive to electrostatic discharge as well as electric sparks. Therefore due to decomposition the explosives are liable to become either more sensitive or insensitive.

1.5.2 DENSITY

Density means the explosive mass per unit volume. In dealing with explosives the density is given in gram per cubic centimeters [5]. According to the characteristics of explosive material there are a variety of loading methods which include cast loading, press loading and pellet loading. Depending upon the loading method 80 to 90 percent of loaded density of theoretical maximum density can be achieved. An increase in density will increase the velocity of detonation up to a maximum limit above which there will be a decrease in VOD. A higher loading density also means that more explosive can be packed in a warhead, thereby resulting in more power. Explosive engineer must also be beware of the fact that if loaded beyond a specific limit the explosive becomes insensitive [3]. It is very much true as the explosive mixture reaches a limit where it is too dense then the explosive will not help in hot spot formation and its known as dead pressed [5][3]. At dead pressed state the explosive cannot be initiated with reliability.

1.5.3 VELOCITY OF DETONATION

The velocity of the shock wave moving through the mass of explosive is called detonation velocity. . When rating any explosive this is main property which is considered and it's measured in feet per second or meters per second. There are mainly two parameters that influence the detonation velocity of any explosive one is density and the other one is diameter of explosive charge. Generally when the detonation velocity increases on increasing the diameter till the hydrodynamic velocity is achieved. In case the diameter of explosive charge is reduced, the velocity of detonation will keep on decreasing until a point is reached where no detonation will occur and it's known as the critical diameter.

1.5.4 BRISANCE

Shattering capability of an explosive is called its brisance. It is important property to determine the capability of an explosive to fragment the grenades, bomb walls or shells. The brisance of an explosive is measured by the sand crush test and plate dent test [1].

1.5.5 SENSITIVITY

The amount of shock, friction or heat necessary to initiate or detonate an explosive is referred to its sensitivity. In order to determine the suitability of any energetic material for specific munitions or application and its safety, knowledge of the effect of these stimuli is important. Impact sensitivity, shock sensitivity, electrostatic sensitivity and sensitivity to heat or thermal shocks are required to be calculated for safe application of any explosive. For example in amour-piercing anti-tank rounds the shock of impact would cause premature detonation of the main charge if it is not insensitive enough. In nuclear lenses the explosive charge is required to be insensitive in order to safeguard against unwanted explosion.

1.5.6 WATER RESISTANCE

The entrance of moisture and water in an explosive is highly detrimental as it results in reduction of its strength, detonation velocity and sensitivity. Water resistance is in fact the measure of ability of an explosive to withstand water and restrict its penetration into the ingredients [3]. Upon detonation the moisture evaporates reducing the heat of reaction. Since moisture accelerates the decomposition process hence stability of explosive is also reduced as well as it damages the metal body of shell by causing corrosion.

1.5.7 OXYGEN BALANCE

It is defined as the sum total of oxygen in weight percent, released on full conversion of explosive into products like carbon dioxide, sulfur oxide, water, aluminum oxide etc [2]. It is basically a way to indicate the extent of oxidation of an explosive when detonated. In case molecule of an explosive carries oxygen sufficient to oxidize all carbon and hydrogen to carbon dioxide and water as well as metal to metal oxides with no extra oxygen left then its oxygen balance is zero. If the molecule contains more than the required amount of oxygen then it has a positive value of oxygen balance and if it is less than the required amount it has a negative value. To some extent the strength, sensitivity and brisance of explosives are related to oxygen balance and are likely to reach at maximum values as oxygen balance gets closer to zero.

1.6 EFFECTS OF EXPLOSION

On detonating a block or a stick of an explosive material, it converts instantaneously into a fast increasing mass of different gases. This event produces mainly three primary special effects and many secondary related effects which cause the destruction of surrounding area. Primary effects include blast pressure, thermal or incendiary and fragmentation effects.

1.6.1 BLAST PRESSURE WAVE

On detonating an explosive material very fast expanding hot gases are formed in nearly 1/10,000 of a second. These product gases move away as fast as 7000 mph from detonation point and apply pressure close to 700 tons per inch square on the surrounding atmosphere. This tons of expanding mass of these gases move outward in circular rolling pattern shattering and smashing everything in the way. As this wave moves away from the detonation point its power reduces gradually and finally it attenuates or dies down. This pressure wave is known as blast pressure wave. This wave has two distinguished phases, the positive pressure phase and the suction or negative phase. These phases particularly apply distinct type of pressure on objects in surrounding area. Though less powerful but negative phase lasts about four minutes longer than positive phase. These distinct phases act like a one-two punch to the surrounding objects. The effect of blast pressure is the destructive and powerful most effect of the effects produced by a high explosive [6].

1.6.2 BLAST PRESSURE SECONDARY EFFECTS

Just like the light or sound waves the blast pressure wave on striking any surface will rebound off the surface and this reflection may cause the wave to focus or get scattered. When explosive detonates in open this wave will lose its velocity and power very rapidly. For example when we detonate an explosive block in open the blast pressure wave would get dissipated by the time it reaches at about 100 feet from the detonation point. If we detonate the same explosive block in a large pipe or hallway, the same wave could be measured even at 200 feet or more from the detonation point. Now all this is due to the reflection of the wave off the surrounding surfaces and the reflected part of the wave by overlapping strengthens the primary wave and it can also be focused on striking any surface. In case the wave hits an immovable strong object in its path, the object will create a hole in the wave and it results in shielding effect [6].

1.6.3 SECONDARY BLAST PRESSURE EFFECTS: EARTH AND WATER SHOCK

An explosive material when detonated under earth surface or under water same amount of heat, shock and loud noise due to rapid expansion of hot gases will occur. The energy released will be the same as it was in open air, however there will be different effects. Blast wave moves as shock wave through water or earth, which can be compared to a powerful, short and sharp earthquake. The shock wave moves under earth or water and when it hits any foundation of a building in its path; if strong enough it will hit the building as does an earthquake. Since as compared to earth, water is incompressible and therefore unable to absorb energy. If the explosive is detonated in water the shock wave will travel farther and faster damaging objects in a larger surrounding area [6].

1.6.4 FRAGMENTATION EFFECT

If we take the example of a hand grenade having strong metal walls, when an explosive charge is detonated in it the blast pressure is created as well as the fragments of the grenade body are thrown in all directions at an extremely fast velocity. These fragments would be moving at the velocity of a rifle bullet (2700 feet per second) in 10 to 15 feet distance all around the detonation point. These fragments will either hit an object or will fly outward until they fall to earth. When this encased charge such as grenade detonates, the hot gases expand and the grenade casing before breaking into small sharp fragments enlarge to nearly one and one-half times its original diameter [3]. About half of the total released energy is consumed in enlarging the case and fragments propulsion. High explosive filled bombs can also be equipped with shrapnels which are normally small size ball bearings and nails. These shrapnels not only have the same effect as fractured casing fragments but an added advantage is the amount of energy instead of expanding the casing would be utilized in shrapnel propulsion. Consequently, shrapnel placed inside or being attached on the outer surface of the bomb will cause increased blast damage through slicing, punching or cutting [6].

1.6.5 THERMAL INCENDIARY EFFECTS

This effect produced by explosive detonation varies with respect to the type of explosive. Low explosives produce this effect for longer time duration as compared to that produced by high explosives. It is measured in fraction of seconds and seen as a fireball or bright flash on detonation. For this thermal effect to play a damaging role the presence of combustible material is required. If the combustible material is available at the site of detonation and fire is started, the hot burning explosion debris will act as a fuel and aid in fire spreading. This effect however is the least damaging primary effect [6].

1.7 MILITARY APPLICATIONS OF HIGH EXPLOSIVES

Origin of offensive weapons was perhaps stones and development of motors originated throwing of stones or spherical balls on target. When the explosive materials were developed it was found very effective to design the hollow bomb or missile shells filled with explosive and these were made to explode in the center of enemy forces or the target. Explosives have varying detonation velocities which dictate the specific work to be performed by the explosive material. Propulsion effect or power of heaving is related to low explosives and due to the very fast expansion of hot gases the High Explosives produce shattering effect. Thus high or low explosives are selected according to the nature of work to be performed. The focusing of explosive energy with the research and development of cavity or shaped charges is a significant development in application of explosives for a specific work. It is a metal cone of concave shape known as liner which is backed by explosive with casing made of aluminum or steel. Shaped charges are specially used to punch or cut holes in concrete, steel and heavily armored vehicles. Since its first development after WW-I, military was the primary user. These were employed in High explosive Anti-tank warheads, unguided rockets, guided missiles and mines to destroy strong concrete bunkers and tanks mainly. Today the shaped charges are extensively used in oil exploration and gas industry where these are employed in

final completion of the wells [7]. These are also used in demolition of huge structures or buildings, quarrying and mining.

1.8 HIGH MELTING EXPLOSIVE

With the development of space exploration, deep oil well drilling etc, there was a need to develop thermally stable explosives. This resulted in new research which was then perused all over the world to develop explosive materials that are thermally stable, safe and reliable at high temperature. HMX is one such explosive which is thermally stable as it undergoes melting as well as decomposition at 280°C. HMX is also known as Octogen, Her Majesty's Explosive, High Melting Explosive, High Velocity Military Explosive or High-Molecular-Weight RDX. It is a less sensitive and powerful high explosive belonging to Nitramine class [8].

1.8.1 DEVELOPMENT AND PRODUCTION OF HMX

In 1940 Bachman when developing a more practical and easier method to produce RDX accidentally discovered HMX. Bachman used nitric acid, hexamine, acetic anhydride and ammonium nitrate to produce RDX. He discovered that there was always 8-12% of an impurity in the final product and he later realized that this byproduct was a more powerful with higher VOD, density, molecular weight, melting point and a stable high explosive as compared to RDX. He took another three years to study it and in 1943, he modified his method to produce HMX by nitrating hexamine with ammonium nitrate in presence of paraformaldehyde and acetic anhydride [8].

1.8.2 CHEMICAL PROPERTIES OF HMX

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, HMX is an energetic chemical compound with very high performance. It is found in four different solid phase polymorphs. HMX is produced in beta phase which is stable at normal operating temperature and has highest density. Some of the known properties of this high explosive are as given below:

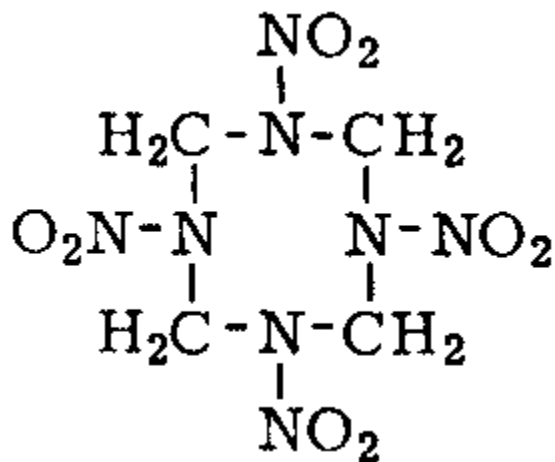


Table 1-0-1: Properties of HMX

Appearance	Colorless crystal
Empirical Formula	C ₄ H ₈ N ₈ O ₈
Molar Mass	296.1 g/mol
Oxygen Balance	-21.6 %
Melting Point	275°C
Density	1.96 g/cm ³
VOD	9100 m/s
Deflagration Point	285°C

1.8.3 APPLICATIONS OF HMX

HMX, due to its high density, high calorific value and smokeless combustion is applied in composite propellants, plastic bonded explosives and as nuclear weapon detonator. HMX based plastic-bonded explosives are additionally used in missile warheads and

anti-armor shaped charges. Civilian application of Octogen is almost restricted to oil and gas wells drilling where it is employed as a shaped charge that is used in wellbore to make a hole through casing creating a pathway and providing a passage for hydrocarbon fluids to reach to the outer surface. It is also used in demolition and mining but since it is not easily available and expensive explosive therefore, it is not used in bulk quantity. Due to its reliability and powerful performance, it is being used to manufacture detonators with better performance. HMX is also used in making powerful detonation cord which is used as a detonation wave carrier to initiate explosive in a large amount. Another significant application is on fighter jets and airplanes. Extremely precise actions like pilot seat ejection, dropping off of fuel tanks and bombs are performed with the help of explosive bolts and nuts which contain HMX. Today the role played by HMX in military applications could not be accomplished by any other explosive [7].

1.9 AIM OF PRESENT STUDY

An explosive must be powerful and destructive for military use, but it must be easy and safe to handle and it must also be safe in storage for longer periods in all kinds of climatic conditions. Another vital characteristic is that the sensitivity of explosive should remain in safety limits after long storage and it should only detonate in a programmed manner. The thermal and kinetic studies of HMX are very important not only for analyzing its reliability, application and safety but also the thermal and kinetic characterization data helps in future research. Techniques of thermal analysis for testing the explosive are very advantageous from the point of view that these techniques use very little amount of sample to give accurate desired measurements in a short time. HMX is a powerful explosive but it is expensive and difficult to manufacture as compared to other conventional explosives. Military uses this powerful explosive in very specific type of ammunition and the ammunition is sometimes stored for quite a long duration which is why two different HMX samples, a fresh pure HMX sample and a 12 years old HMX sample were studied to obtain thermal and kinetic parameters by thermal decomposition of HMX. The study was carried out with an objective to characterize the

samples by taking TGA and DTA measurements using a Differential Thermogravimetric Analyzer in non-isothermal condition for final comparison of the two sets of measurements. Kinetics is an important part of thermo chemistry and it helps us to understand the mechanisms involved in different type of chemical reactions. In the present study, kinetic parameters such as activation energy and order of reaction have been determined using the weight loss data obtained from Thermogravimetry.

REFERENCES

- [1] <http://en.wikipedia.org/wiki/Explosives>
- [2] J. Akhavan The Chemistry of Explosives 2nd Edition, Department of Environmental and Ordnance Systems Crenfield University.
- [3] Robert A. Sickler, Explosive principles: an essential guide understanding explosives and detonations, 1992.
- [4] Alexei M. Khokhlov, Elaine S. Oran and J. Craig Wheeler *Combustion Flame*, 1997, Vol. 108, pages 503-517.
- [5] Tenney Lombard Davis The Chemistry of Powder and Explosives, Angriff Press, 1972.
- [6] Guide to the Explosives Act. H.M.S.O., London, 4th ed. 1941.
- [7] Fordham, Stanley High Explosives and Propellants, 2nd edition, 1980.
- [8] Rudolf Meyer, Josef Kohler, Axel Homburg, *Explosives*, Wiley-VCH, 2007.

CHAPTER 2

2.1 LITERATURE REVIEW

HMX is a very powerful secondary high explosive used in specific military munitions due to its exceptional high velocity of detonation and stability at high temperatures. It is produced as a white crystalline solid and commonly used as polymer bonded explosives filler [1]. Research on thermal decomposition of Octogen has been under progress for quite many years. It has been very well known that this material is very complex and conditions such as heating rate, temperature, pressure and physical state play a very significant role [2][3]. The knowledge of its kinetics and thermal events taking place during its decomposition provides a valuable data that is helpful in studying its stability and reliability. Thermal analysis techniques as DSC, TG and DTA have been used in non-isothermal and iso-thermal conditions to evaluate its decomposition kinetics. We find a vast range of activation energy values ranging from 43 to 1070 kJ/mole just because of the reason that there are a number of different techniques that were used with different set of experimental conditions [4].

2.2 HMX THERMAL DECOMPOSITION: CHEMICAL AND MORPHOLOGICAL CHANGES INDUCED AT SLOW DECOMPOSITION RATES

The desire to know the explosive response to fire was the motivational factor to learn the thermal decomposition of HMX at low heating rates. This research was aimed at finding the chemical and physical processes controlling the thermal decomposition of HMX and evolution of different morphological structures occurring due to these changes. Therefore we used Simultaneous Thermogravimetric Modulated Beam Mass Spectrometry (STMBMS) experiments on HMX samples which provided us more detailed information as compared to the other thermal analysis methods. With these experiments we found that following are the physical processes that are involved in controlling decomposition and morphological changes.

- a) HMX sublimation at particle surface and its gas phase decomposition subsequently.
- b) Granular microscopic structure formation and cracks in particles during β - δ phase transformation.
- c) Earlier decomposition of explosive at inter-granular boundaries.
- d) During first 30% decomposition there is increase in reaction spots in the explosive grain producing gas product bubbles.
- e) Formation of a nonvolatile residue by reaction between several of the gaseous decomposition products.
- f) Gas products are released on grain boundary intersections.
- g) HMX in gaseous form and some of gaseous products flow in inter-granular region.
- h) HMX, gaseous decomposition products and the non-volatile residue (NVR) reactions.
- i) NVR are decomposed to form gaseous products.

The solid phase decomposition of this explosive is governed by a set of both the physical as well as chemical processes. These experiments were performed over a very wide range of different conditions and result obtained tells us that the process of decomposition is described by a reaction cycle. Hence there are a total of seven chemical and five physical processes governing the HMX decomposition [5].

2.3 THERMALDECOMPOSITION BEHAVIOUR OF HMX

In this research work thermal characterization of above mentioned explosive material was carried out by using DSC and TG. The kinetic parameters such as the activation energy and compatibility of explosives with the Silicon rubber were studied with non-isothermal DSC. Raw material including HMX and silicon rubber was used. The sample mass of 5mg was exposed to heating rates of 5,10,15 and 20°C /min. the HMX exhibits three peaks as the sample was run in DSC.

- a) Phase change from $\beta - \delta$ HMX at 190°C.
- b) Second endothermic peak showing melting of HMX
- c) A sharp and strong exothermic peak right after melting endothermic due to self-decomposition of HMX.

The kinetic parameters were calculated by Kissinger's method. Here by comparison among the melting point, phase changes, exothermic decomposition peaks and the activation energy between PBX formulations and the parent HMX, silicon appears to be compatible with the explosive under study [6].

2.4 HEATING RATE EFFECT IN THE HMX THERMAL DECOMPOSITION

The main aim of this work was to study the influence of heating rate of 1 to 25°C by DSC in non-isothermal environment. TGA was also employed and Ozawa method was used for obtaining kinetic parameters. The test conditions employed on DSC were as follows.

- a) Heating rates of 1 to 25°C/min.
- b) 2.5 mg of pure HMX in an aluminum pan.

We obtained endothermic peaks in the region of 185 to 200°C due to beta to delta phase change. At low heating rates from 1 to 5°C/min the peaks got shifted to lower temperatures and by employing higher heating rates these peaks occurred at higher temperature ranges. At higher rates the decomposition occurs after melting of the HMX. At slower rates of heating the decomposition is below the melting temperature 280°C [7].

2.5 HMX MIXED WITH CONTAMINANTS

In this investigation the effect of contaminants on HMX were studied. During the production of HMX the contaminants such as ferric chloride Hexahydrate, ferrous chloride tetrahydrate, acetone solutions, nitric acid and acetic acid come in contact with the explosive material. In this research DSC was used by employing heating rates of 1, 2, 4 and 10 °C/min to get the reaction heat, activation energy and thermal curves. The results gave following observations.

- a) Ferrous chloride tetrahydrate increased the release of initial exothermic heat by 75–90 °C and the endothermic phase change disappeared.
- b) In case of ferric chloride hexahydrate mixture initial exothermic heat release appeared at 172 to 182 °C and the endothermic phase transition was not observed.
- c) In case of Acetone solution exothermic heat release occurred at 15 to 43 °C. which meant that the acetone solution is safe for HMX storage.
- d) When mixed with acetic acid, production unit should be aware of the secondary heat release.
- e) When mixed with Nitric acid initial exothermic release of heat advanced by 50–60°C. HMX endothermic phase change disappeared.

Resultantly the investigation of HMX mixed with contaminant, energy of activation and frequency factors increased as compared to HMX. This means when mixed with different contaminants, reaction kinetics change causing instability and hazardous events can occur [8].

2.6 KINETICS OF HMX $\beta \rightarrow \delta$ SOLID-SOLID PHASE TRANSITION

High Melting Explosive has four different polymorphic forms which can be produced by exposing the reaction solution to certain specific cooling rates. HMX is produced and used in β -HMX form which is the most stable form of this material. HMX $\beta \rightarrow \delta$ transition of polymorphic phase is resisted by the electrostatic forces that are in the lattice of HMX. Therefore this process is endothermic as it requires energy.

DSC was used as an experimental technique to carry out this research work on HMX. To study this phase transition DSC data was recorded by taking 1 mg of sample and exposing it to heating rates of 1, 2, 5 and 10°C/min. The reaction process of $\beta \rightarrow \delta$ HMX phase transition was monitored with DSC and the obtained results were analyzed by three methods. The methods used were First Order Kinetics, the Isoconversional analysis and the Ozawa method. We analyzed the data and found activation energy of 500 kJ/mole which is a way higher than those values given in literature. The value is not physically reasonable and this may be because of the thermodynamics involved in this phase transition [9].

2.7 THERMOLYSIS OF HMX AND ITS PBX FORMULATIONS CONTAINING ESTANE

The explosive compositions in which a HE is used as filler or it is dispersed in a polymer acting as binder are known as Plastic Bonded Explosives. The reason for making these PBX compositions is to reduce the shock, impact and friction sensitivity of explosives. These are also meant to achieve integrity and mechanical strength in the explosive material which is important for shaped charges. During this research work HXE 9505 and HXE 9010 which are plastic bonded formulations of HMX and Estane (Polyurethane Binder) were studied by employing DSC, DTA and TGA techniques. For drawing a comparison the pure ingredients have also been studied.

Non-isothermal TGA study of samples was done by employing DuPont 2100 TG instrument. The sample mass of 2mg was heated at 10°C/min and nitrogen gas was used to provide an inert atmosphere at a flow rate of 60 ml/min. DSC analysis and the TGA

analysis results of HMX are same as that given in literature where the thermolysis was a very rapid single step process. The TG curve of Estane revealed that the loss of sample mass occurred at a very wide range of temperature ranging from 300–400 °C. In this study the decomposition of PBX formulations and the pure ingredients was examined and found that the peak, onset and inset temperatures for decomposition of HXE 9010 and HXE 9505 are quite lower than those found for pure HMX. It was further observed that this trend of lowering was directly proportion to the increases of Estane percentage in PBXs. The decomposition of HXE 9010 occurs faster than that of HXE 9505 and both the PBXs decompose faster than the pure HMX. This research work shows that the thermal stability of Octogen is at stake when Estane is used as a binder [10].

2.8 THERMAL DECOMPOSITION KINETICS OF HMX

The aim of this research work was to obtain kinetic models for loss of mass and generation of heat on thermal decomposition of HMX. The loss of mass and the kinetic parameters for the heat released are not the same, rather these are different processes. Now in this work the kinetic parameters based on loss of mass and thermal decomposition of HMX was studied by Simultaneous TGA/DTA instrument (STA) and the results were recorded. DSC was also used as an additional analysis technique. HMX sample of mass 0.5 mg was exposed to heating rate ranging from 0.1 to 1°C/min and nitrogen was used as purging gas at a flow rate of 100ml/min. The small sample mass and a lower heating rate was used because the higher heating rate may lead to thermal runaway on reaching decomposition temperature resulting into higher and incorrect values of activation energy.

The activation energies obtained in these set of thermal analysis data are smaller than those given in most of the literature where work was done at higher rates of heating with larger sample mass. They resulted from more careful attention to using conditions in which sample self-heating is minimized, meaning sample sizes less than 0.5 mg and pyrolysis temperatures lower than about 260°C. At higher temperatures, both thermal runaway and interference of the melting endotherm prevent getting accurate thermal

history. A broad range of experiments and kinetic analysis methods indicated that the global activation energy is in the vicinity of 150kJ/mol, depending on conditions, which is lower than determined by most workers. By compiling a greater number of experiments over a wider range of conditions and temperatures, these fluctuations can be put in their proper perspective. Finally it was conclude that the mean activation energy of HMX decomposition is in the 165 kJ/mole range [11].

REFERENCE

- [1] B. T. Fedoroff and O. E. Sheffield, Encyclopedia of Explosives and Related Items, Dover Picatinny Arsenal, 3 (1966) C605.
- [2] M. Schroeder, Proc. 18th JANNAF Combustion Meeting, 2 (1981) 395.
- [3] N. E. Ermolin and V. E. Zarko, Combustion, Explosion and Shock Waves, 33 (1997) 251.
- [4] J. Kimura and N. Kubota, Propellant and Explosives, 1980.
- [5] Richard Behrens Thermal Decomposition of HMX: Morphological and Chemical Changes Induced at Slow Heating Rates, Sandia National Laboratories, Combustion Research Facility, Livermore, California 94551-0969
- [6] Jinn Sigh Lee Studies on Thermal Decomposition Behavior of PETN, RDX and HMX, Thermochemica Acta 392-393 (2002) 173- 176.
- [7] G. F. M. Pinheiro, V. L. Lourenço² and K. Iha Influence of the Heating Rate in Thermal Decomposition of HMX, Journal of Thermal Analysis and Calorimetry, Vol. 67 (2002) 445-452.
- [8] Deng-Jr Penga, Cheng-Ming Chang^{a,*}, Miin Chiub Thermal reactive hazards of HMX with contaminants, Journal of Hazardous Materials A114 (2004) 1–13.
- [9] R.K. Weese, J.L. Maienschein, C.T. Perrino Kinetics of the $\beta \rightarrow \delta$ solid–solid phase transition of HMX, *Lawrence Livermore National Laboratory, Livermore, CA 94550, USA*, Thermochemica Acta 401 (2003) 1–7.
- [10] Felix and Pramod Soni Studies on energetic compounds part 28: thermolysis of HMX and its plastic bonded explosives containing Estane, *Department of Chemistry, DDU Gorakhpur University*.
- [11] A. K. Burnham, R. K. Weese Thermal Decomposition Kinetics of HMX, Lawrence Livermore National Laboratory, Livermore, CA 94550, USA, November 29, 2004.

CHAPTER 3

THERMAL ANALYTICAL TECHNIQUES

Thermal analytical techniques such as Differential Thermal Analysis DTA and TGA have been used in this research work for the study and analysis of HMX fresh and old samples. Weight loss data was primarily used to determine the kinetic parameters. In this chapter the thermal analysis techniques used for the present research work have been discussed.

3.1 THERMAL ANALYSIS

Since 1965 when ICTA (international confederation of thermal analysis) was established in Aberdeen and development in the thermal analysis equipment, thermal analysis has become an extremely powerful and active field worldwide [1]. This tech is used to study the effect of heat on any material and to detect the amount of changes in physical properties taking place when the material is exposed to some specific and preprogrammed temperature changes. These techniques not only observe the physical changes taking place in the sample but also measure the temperature difference between an inert material and a sample when both are exposed to temperature variations at the same time. Thermal events in solid mixtures and in solid pure samples can be studied by using these techniques. Phase transition temperatures, glass transition temperatures, melting points, boiling points and decomposition of a material can be easily studied and determined with these techniques. These are accurate instruments to observe the endothermic and exothermic events taking place in the sample as well as the measuring of very important kinetic parameters for chemical reactions in the material under study. Thermal analysis has become an extremely reliable and effective technique which is why the thermal and kinetic studies of HMX are being carried out by making use of this technique.

3.2 THERMO-ANALYTICAL TECHNIQUES CLASSIFICATION

There are several technique that have been assessed by the nomenclature committee of ICTA and the prominent techniques showing future prospect were classified according to interrelationship. Some of the thermal analytical methods are listed below [2].

- a) Thermogravimetry (TG): Measures mass as a function of temperature.
- b) Differential Thermal Analysis (DTA): Measures temperature difference.
- c) Differential Scanning Calorimetry (DSC): Measures Energy input into a sample and a reference material.
- d) Evolved Gas Analysis (EGA): Measures volatile gas products by sample material.
- e) Evolved Gas Detection (EGD): Detects gas evolution from a sample.
- f) Emanation Thermal Analysis (ETA): Measures evolution of radioactive gas.
- g) Thermoparticulate Analysis (TPA): Measures evolution of particles
- h) Thermomagnetometry (TM): Measures magnetic properties
- i) Thermoelectrometry (TE): Measures electrical characteristics of a sample.

All of the above mentioned techniques are being used as vital analytical research tools worldwide. Depending on the nature of HMX sample and information required for our present research scope we will use DTA and TGA which are discussed in detail.

3.3 THERMOGRAVIMETRIC ANALYSIS (TGA)

This is a thermo-analytical technique which measures the change in mass of a sample as the sample is subjected to programmed temperature variations. When subjected to a programmed temperature increase the substance can undergo weight loss either due to the evaporation of moisture or some chemical reaction resulting into the release of product gases. Likewise a sample may gain weight as well by coming in contact with the atmospheric gases in the laboratory environment. Therefore, both weight loss and gain

provide valuable information for sample under study. This change in mass is recorded as thermogravimetric curve which is a temperature vs weight curve which provides important information regarding thermal stability of the sample [3]. With the precise knowledge of thermal stability of a sample we can assess the hazards of explosive storage as well as shelf life of some samples. The precision and accuracy of the sensors detecting changes in temperature and weight govern the accuracy and reliability of the measurements obtained from the TG instrument.

3.3.1 TGA MEASUREMENT PRINCIPLE

Two different driving coils support the sample and reference beams. Change in the weight of sample causes beam displacement which is precisely detected by the optical position sensors with respect to a slit. The optical position sensor sends a signal to the balance circuit which supplies a proportionate feedback current to the driving coil so that the slit returns to its original position. The change in weight of the sample is measured in comparison to the reference by measuring the amount of current supplied to the coils as it is equal to the weight change. TG mechanism has been shown below in Figure 2.1.

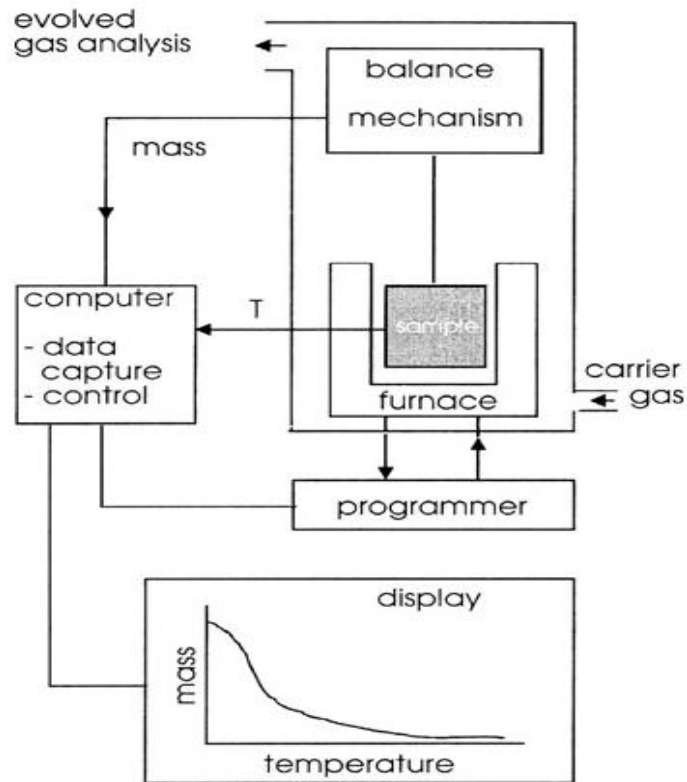


Figure 3-1: Block Diagram showing main components of TGA equipment

3.3.2 FACTORS EFFECTING TG CURVE

There are many factors that can affect the TGA curve. Mainly these factors are related to the instrument and nature of the sample. Some of the factors affecting precision, shape and accuracy of thermogravimetric curves include:

Instrumental factors

- a) Furnace heating rate.
- b) Furnace environment.
- c) Speed of recording.
- d) Sensitivity of recording sensors.

Sample Characteristics:

- a) Amount
- b) Particle size
- c) Heat of reaction

- d) Nature of sample

3.3.3 APPLICATIONS OF THERMOGRAVIMETRIC ANALYSIS

TGA despite just giving the understanding of decomposition chemistry of a particular sample also gives the information about the range of temperature over which the sample is stable. There are many other applications, for example TGA is used to determine:

- a) Thermal stability.
- b) Purity.
- c) Mixture composition.
- d) Reaction kinetics.
- e) Moisture and volatile content.
- f) Inorganic and organic compound decomposition.

3.4 DIFFERENTIAL THERMAL ANALYSIS (DTA)

Differential thermal analysis (DTA) is another thermal analytical technique which is being used worldwide. In DTA the sample under study and an inert reference is placed in different pans and these are exposed to a programmed temperature change. A pair of thermocouples is used, one is attached to the sample container and the other one with the reference container. The temperature difference between the reference and the sample is accurately recorded with the help of thermocouples. When this temperature difference is plotted against temperature or time a curve is obtained which is called a thermogram [4]. If the sample undergoes some chemical reaction or some physical change occurs, its temperature will keep on changing while the reference material will remain at the same temperature. This is due to the reason that the chemical reactions involving changes in enthalpy or net heat content of the sample material and the physical changes such as phase changes. The resultant curve or thermogram shows the endothermic or exothermic changes in the sample. This thermogram gives a variety of useful information. DTA phenomena causing changes in temperature or heat.

Physical

- a) Adsorption (exothermic)
- b) Desorption (endothermic)
- c) A change in crystal structure (endo – or exothermic)
- d) Crystallization (exothermic)
- e) Melting (endothermic)
- f) Vaporization (endothermic)

Chemical

- a) Oxidation (exothermic)
- b) Reduction (endothermic)
- c) Break down reactions (endo – or exothermic)
- d) Chemisorption (exothermic)
- e) Solid state reactions (endo – or exothermic)

3.4.1 REFERENCE MATERIAL

The reference material has a direct influence on the DTA measurements therefore; it should possess the following characteristics:

- a) It must not undergo any thermal change.
- b) It should not react with the holding pan or thermocouple.
- c) Heat capacity and thermal conductivity should be same as that of the sample.
- d) The thermal conductivity and heat capacity of reference should be similar to the sample under investigation.

3.4.2 (DTA) MEASUREMENT PRINCIPLE

As discussed earlier the pair of thermo couples is attached on one end to the holding pans and on the other end to the balance beams as shown in figure 2.2. The thermocouples record or measure the temperatures of the sample and the inert reference

and the temperature difference is detected. Temperature difference when plotted against time or temperature gives a thermogram. This thermogram gives different peaks which can be endothermic or exothermic depending upon the different thermal events taking place according to the nature of the sample material [5]. The Block diagram as is shown below.

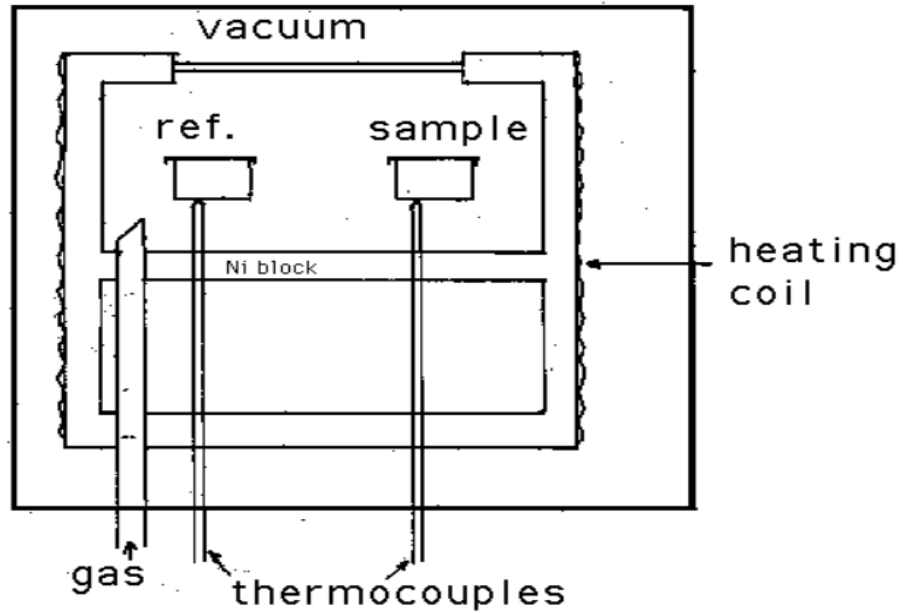


Figure 3-2: Block Diagram showing main components of DTA equipment

3.4.3 FACTORS AFFECTING DTA CURVE

Two types of factors which affect the DTA thermogram [2] are:

Factors Related to Sample

- a) Particles size
- b) Amount
- c) Heat capacity and Thermal conductivity
- d) Packing density

- e) Degree of Crystallinity

Factors Related to Instrument

- a) Atmosphere of the furnace
- b) Heating rate of the furnace
- c) Size and shape of the furnace
- d) Material of the sample holder
- e) Recording speed of instrument.

3.5 SIMULTANEOUS THERMAL ANALYSIS

Application of TGA and DTA in single equipment grouped together for thermal analysis of a single sample is called as Simultaneous Thermal Analysis (STA) [4]. All other testing conditions for sample and the reference are the same including the controlled temperature program. This technique is very useful as we obtain TGA curve as well as DTA curve at the same time. The combination of these two curves provides more information which is very useful for the analysis of the sample. These results obtained can be used separately or can be complimentary as well. STA records weight changes as well as heat flow in a material as a function of temperature and these simultaneous measurements of the sample if found complementary can simplify interpretation and increases the reliability of the results. The simultaneous TG/DTA curves can show clearly that which endothermic or exothermic events do not occur with a weight loss and which events involve weight loss of the sample under investigation. In our present study we have effectively applied Simultaneous Thermal Analysis technique to study the endothermic events like phase changing and melting as well as the exothermic decomposition of HMX samples. A typical simultaneous TGA/DTA curve is given below in Figure 2.3.

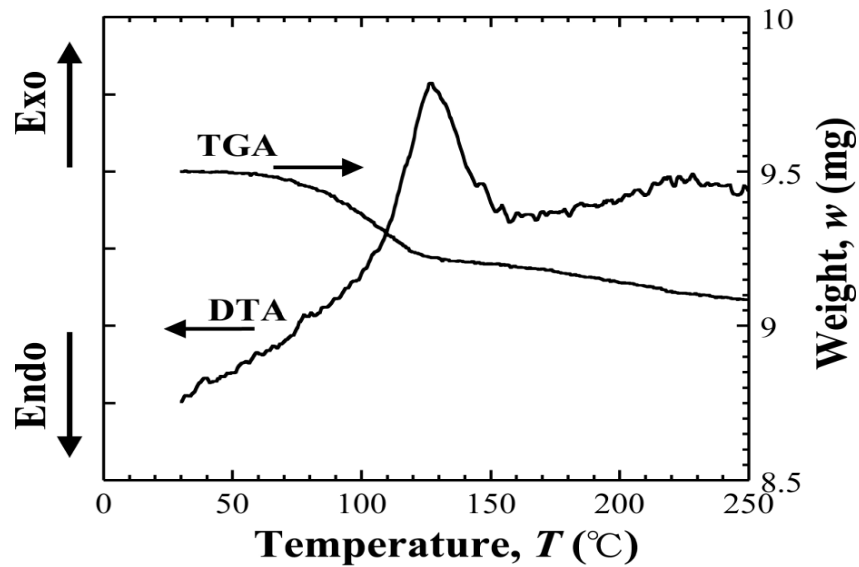


Figure 3-3: Typical TG/DTA Curve

3.6 CALCULATION OF KINETIC PARAMETERS

Different kinetic parameters such as activation energy, order of reaction and enthalpy etc have been calculated using the TG/DTA data with the help of a curve fitting program.

3.6.1 CALCULATION OF ACTIVATION ENERGY

There are different methods for calculating the activation energy of a material and some of them are as follows [6]:

- a) Doyle Method.
- b) Coats and Red fern Method.
- c) Horowitz and Metzger Method.
- d) Free man and Carroll Method.
- e) Newkirt Method.

Curve Fitting Program used in this study utilizes Horowitz and Metzger Method for calculating the activation energy of the sample. The method for calculation of activation energy has been discussed here briefly.

First of all a reference temperature is determined and called as T_s . This is that temperature where the rate of decomposition is the maximum and hence the weight loss is also the maximum. It is determined by the relationship given below

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

Here

T_s = Reference temperature.

W_t = Weight of the sample at given temperature T .

W_o = Total initial weight of the sample.

e = exponential.

In the next step θ (theta) is calculated from the reference temperature.

$$\theta = T - T_s$$

Where T is the sample temperature at weight W_t . Now the plot of θ against $\ln \ln W_o / W_t$ gives a straight line. The gradient or the slope of the straight line obtained in the above mentioned manner is given by

$$\text{Slop} = E_a / RT_s^2$$

Where

E_a = Activation Energy

R = Universal Gas Constant (1.987 Cal/mole^{°C}).

From the above relationship we can get the value of the activation energy.

W = weight remained at some given temperature.

REFERENCES

- [1] Michael E Brown 1988, Introduction to Thermal Analysis techniques and applications, Page 3.
- [2] Wisley WM Wendlandt 1964, Thermal Methods of Analysis, Page 139,140.
- [3] C.Duval, *Inorganic Thermogravimetric Analysis*, Elsevier Amsterdam, 1962.
- [4] P. Gabbott, Ed., *Principles and Applications of Thermal Analysis*, Blackwell, 2008.
- [5] D. A. Skoog, F. J. Holler, and T. A. Nieman, *Principles of instrumental analysis*, 5/e, Harcourt Publishers, 2001.
- [6] YasmeenJamil 1999, M. Phil thesis on synthesis, characterization and thermal degradation of some vinyl polymers, Department of chemistry Quid-e-Azam University Islamabad, Pakistan.

CHAPTER 4

EXPERIMENTAL SET UP

4.1 DIAMOND TG/DTA ANALYZER

In order to carry out the thermal and kinetic studies of two different HMX samples the Diamond Thermo Gravimetric/Differential Thermal Analysis (TG/DTA) module has been used. This instrument has been so designed that it precisely records the thermo gravimetric as well as the differential thermal analytic measurements of a single sample simultaneously and it produces TG curve along with DTA curve at the same time. It is mainly used for inorganic materials like ceramics and metals and it can also be used for high polymer organic materials. This thermal analyzer operates from room temperature to the temperature as high as 1600°C. The Diamond TG/DTA is an instrument which is controlled and commanded by specific software named as the Pyris software installed on a computer directly connected to the analyzer. The equipment has been shown below in figure 4-1.



Figure 4-1: Diamond TG/DTA instrument by Perkin Elmer

4.1.1 BASIC MODULES

The Perkin Elmer Diamond TG/DTA module is mainly a combination of two modules.

- a) Base Unit
- b) Measurement Unit

These two basic modules namely basic and measurement unit are directly connected to one another by nuts, bolts, data cables and power cables. Both these units operate as one instrument but these can be separate as well. These two parts have been shown below in figure 4-2.

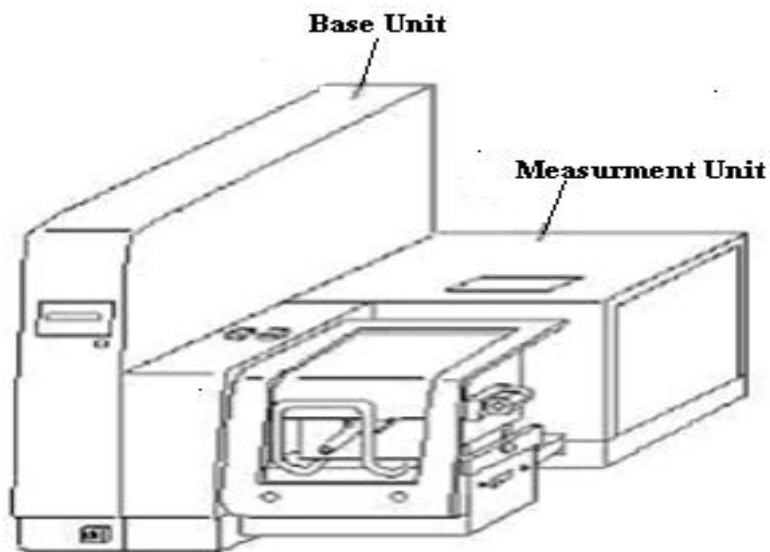


Figure 4-2: TG/DTA instrument base and measurement units

Base unit maintains and controls the programmed temperature and carries out the signal processing provided by the measurement unit. The measurement unit controls the sample measurements and it is used for setting different parameters.

4.1.2 TG/DTA INSTRUMENT CONFIGURATION

The standard configuration of Diamond TG/DTA module set up for thermal analysis is given below.

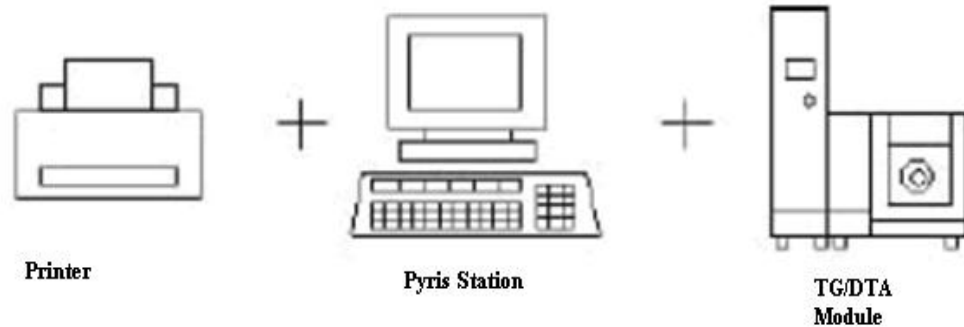


Figure 4-3: Configuration of TG/DTA module set up

It consists of

- a) TG/DTA module
- b) Pyris Station
- c) Printer

This Diamond TG/DTA module has been used for the thermal analysis of HMX samples. The measurement unit is equipped with two pans for sample and the reference and these pans are connected to thermocouples for sensing the temperature. The measurement unit also contains the heating furnace for heating the sample at programmed heating rate as well as the gas flow or cooling unit which has been used to maintain an inert environment by providing an inert gas flow through the furnace. This unit supported by the base unit is connected to a computer. Pyris software has been installed on the computer to command and run the TG/DTA module and display the readings in a graphical form. The results including graphs and the complete data can then be printed by using the attached printer.

4.2 DIAMOND TGA MEASUREMENT PRINCIPLE

A TG differential balance mechanism is used to take measurements. The sample and reference balance beams are supported by their respective driving coils. The optical position sensors are sensitive enough to detect the change in sample weight with respect to a slit. The optical position sensor sends a signal to the balance circuit which supplies a proportionate feedback current to the driving coil so that the slit returns to its original position. The current supplied is equal to the weight changes so the sample weight change is detected in comparison with the reference. Operating mechanism of the TG system has been illustrated below in figure 4-4:-

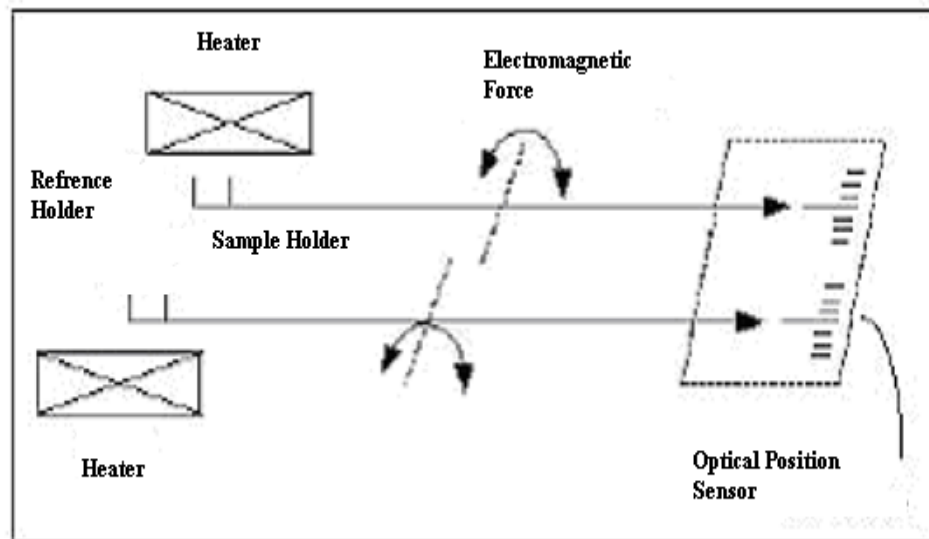


Figure 4-4: Diamond TGA Measurement principle

4.3 DIAMOND DTA MEASUREMENT PRINCIPLE

The sample and the reference pans are required to be of the same material which will ensure the precision of the readings. These pans are connected to balance beams which are further connected to thermocouples. In order to find the temperature difference

between the sample and the reference the thermocouples initially record the temperature of both sides separately and then the difference is detected. This temperature difference is then plotted against the temperature or time to get the DTA thermo gram which gives exothermic as well as endothermic peaks depending upon the chemical composition and nature of the sample under investigation.

4.4 SPECIFICATIONS OF THE SYSTEM

The above mentioned system is the best available and one of the most accurate thermal analytical technique. This instrument has been accurately used for carrying out thermal analysis of HMX samples. The specifications of this system have been tabulated below:

Table 4-1: Specification of TGA/DTA instrument

	TG/DTA System
Weight Measurement Sample weight	Horizontal Differential Balance Method Max 200mg
Temperature Range	RoomTemp-1550°C Nominal 1330°C
Heating Rate TG Measurement Range DTA Measurement Range	0.01°C/min—200.00°C/min + 200mg (0.2µg) + 1000µV (0.06µV) 0.5mg/min—1g/min
Gas Flow	Max 1000ml /min

4.5 AIM OF THE PRESENT STUDY

The aim of the present work was to study the thermal behavior and kinetics of a HMX sample manufactured in May 2012 and a sample manufactured in 1998. The HMX

initially was produced at POF for filling of some shaped charged anti armor and anti bunker light weight rocket propelled projectiles. Since there was no research work available where the thermal and kinetic parameters of an actual old sample were studied to draw a comparison with the standard fresh sample in order to evaluate the worthiness and serviceability of the explosive within the safety limits after a long storage period. Therefore, this attempt was made to study the thermal behavior including phase transformation, melting point and decomposition temperatures to analyze the thermal stability of HMX and the kinetic parameters including activation energy and order of reaction to predict the reliability and safety of HMX after 14 years of long storage period.

4.6 ANALYSIS METHOD

With an aim to achieve above mentioned objectives Simultaneous Thermal Analysis of HMX samples was carried out using the Diamond TG/DTA by Perkin Elmer. The samples were subjected to simultaneous TG and DTA analysis and experiments were carried out at different sample masses and heating rates under inert atmosphere. The weight loss patterns of both the samples were observed on TG curves as well as the exothermic and endothermic events including phase transformations, melting and decomposition were observed with the help of DTA curves. The data obtained from TG curve was then utilized in Curve Fitting software to calculate the kinetic parameters.

4.7 MATERIAL USED FOR INVESTIGATION

The materials used in this study are two different HMX samples. Old HMX sample was obtained from Inspection Depot Armaments Havelian and the fresh sample was manufactured and provided by Wah Nobles POF on the instructions of Chairman POF. The two samples are listed below:-

- a) HMX sample (fresh pure sample)
- b) HMX sample (14 years old pure sample)

4.8 EXPERIMENTAL CONDITIONS

The experimental conditions to obtain TG curve and DTA curve were kept different in order to get the desired measurements. It helped in comparing the obtained results for the two samples and also comparison with values given in literature could be made. The experimental conditions have been described below:

Table 4-2: Experimental conditions

Conditions	TG	DTA
Sample Mass	3 mg	1 mg
Temperature Range	25°C to 350°C	25°C to 400°C
Heating Rate	1°C/min	10°C/min
Atmosphere	Argon	Argon
Flow Rate	100 ml/min	100 ml/min
Pan Material	Alumina Crucibles	Alumina Crucibles

4.9 EXPERIMENTAL PROCEDURE

TG/DTA equipment was checked for calibration accuracy by running alumina standards. Both alumina pans for sample and the reference are automatically balanced in empty state with the help of Pyris Software command. Then the sample was very carefully placed in the sample pan while its weight could be monitored on the pyris software for keeping it to the required experimental condition. When the desired weight was in the sample pan the furnace was closed onto the pans and the sample percentage was taken to be hundred percent with the help of the software. Finally the complete method to be followed including the heating rate, maximum temperature limit, sample size and sample name was loaded into the Pyris system Then the argon gas cylinder was attached to the

cooling unit, the instrument was run and the purging gas automatically started flowing through the furnace to provide an inert atmosphere to the sample. Both the weight loss and the heat flow curves were obtained by using Diamond TG/DTA equipment. The data provided by DTA curve was analyzed for comparison with the standards given in literature and the data obtained from TG curve was processed in curve fitting software and the kinetic parameters were determined. Same procedure was repeated for all the experiments.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 CHARACTERIZATION OF HMX SAMPLES BY FT-IR

Instrument Specifications:

- a) FT-IR model: Perkin-Elmer Spectrum series 100
- b) IR Detector: Lithium Tantalate, LiTaO₃
- c) Response Measured: Transmittance %
- d) Resolution: 4 cm⁻¹
- e) Spectral Region: 4000-400 cm⁻¹

For FTIR analysis the fresh pure HMX sample was taken as standard and its FT-IR spectrum was recorded by preparing the HMX sample on KBr pellet or KBr disc. This disc was then placed on sample compartment and the FT-IR analysis was made. The FT-IR spectrum is consisting of fingerprint region and functional group region. Fingerprint region describes the region that absorbs the wavelength due to all manners of bending vibrations occurring within the molecule. It ranges from 1500 – 500 cm⁻¹. This region is complicated one and is at the right-hand side of the spectrum. The region towards the left of spectrum is called the functional group region and describes the type of functional groups present within the molecule. It ranges from 4000-1500 cm⁻¹. FT-IR spectrum of the pure HMX sample was taken first so that the standard result can be obtained in order to compare with that of the old sample. There is one precaution that must be taken into consideration while interpreting the spectra obtained from analysis, there is a band at ~ 3400 cm⁻¹ which is mostly due to the moisture in KBr.

FT-IR analysis of standard HMX sample:

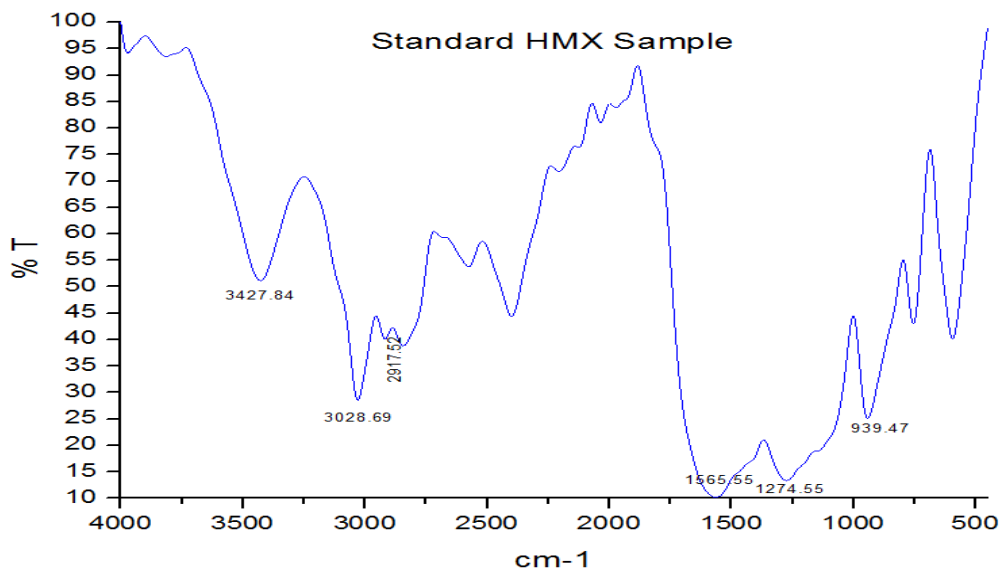


Figure 5-1: FT_IR Spectra of Standard/ fresh HMX sample

FT-IR analysis of old HMX sample:

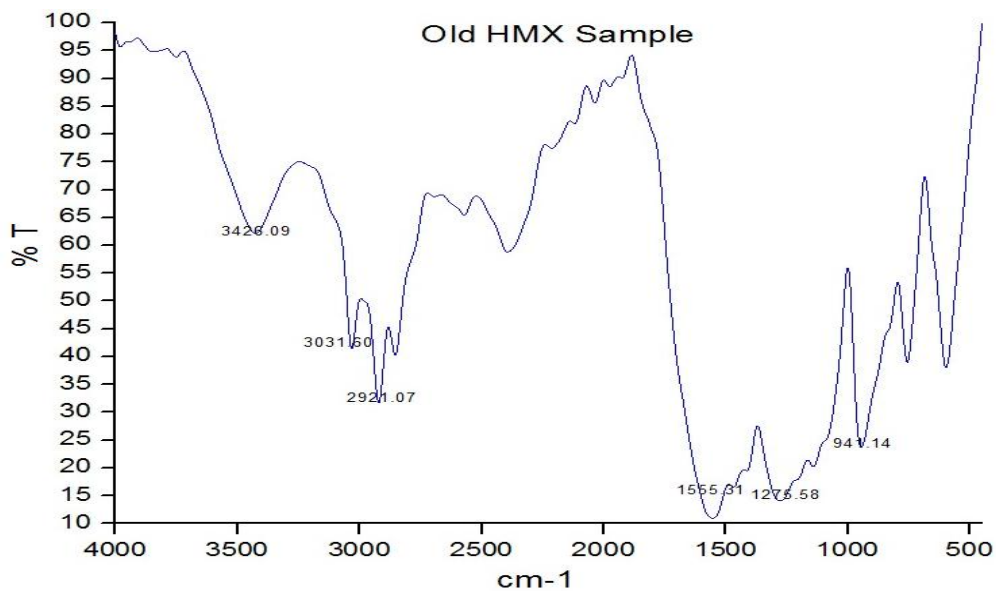


Figure 5-2: FT_IR Spectra of Old HMX sample

Table 5-1: Table showing absorption frequencies

Standard β -HMX cm^{-1}	Old β -HMX cm^{-1}	Functional Group
3427	3426	OH(moisture)
3028	3031	CH ₂ Vibrations
1565	1555	NO ₂ Asymmetric vibrations
1274	1275	NO ₂ Symmetric vibrations + N-N vibrations
939	941	CN vibrations

A comparison has been drawn between the standard or reference sample and the second or old sample. The spectra obtained provide us with the frequencies that clearly show that there has not been any significant change in the band characteristics of the older sample under study.

5.2 THERMAL STUDIES OF HMX

Thermal studies of HMX were carried out by using thermal analysis. The Diamond TG/DTA instrument of Perkin Elmer was used for the Simultaneous Thermal Analysis. For DTA 1 mg sample of HMX was heated in an alumina crucible from 25-400°C at a constant heating rate of 10°C/min in order to obtain DTA data comparable with the standards given in literature. Then HMX sample mass of 3 mg was heated in an alumina crucible from 25-350°C at a constant heating rate of 1°C/min for obtaining best possible TG data that could be utilized to calculate and compare the kinetic parameters of the explosive. In order to maintain an inert atmosphere in the furnace Argon gas flow rate of 100ml/min was maintained during all experiments. This standard experiment procedure was employed for thermal and kinetic investigation of both the samples separately.

5.3 THERMAL STUDIES OF STANDARD HMX SAMPLE

The thermal investigation of fresh HMX sample by using TGA/DTA instrument has been described below.

5.3.1 THERMAL ANALYSIS RESULTS

The results of the thermal studies of HMX with DTA and TGA have been described separately under different set of conditions.

5.3.2 DTA ANALYSIS

The thermal behavior of two different HMX samples has been observed from room temperature to approximately 400°C. The aim of investigating the samples by obtaining the DTA thermogram is to observe different thermal events taking place within the samples and determining stability of the sample which has been in storage for a long duration. These thermal events then are compared to those obtained from the standard sample.

5.3.3 STANDARD HMX DTA CURVE

At first DTA analysis of the standard samples were carried out. In the experiment a sample mass of 1 mg was heated from room temperature to approximately 400°C at a programmed heating rate of 10°C /min. In order to provide an inert atmosphere Argon gas was made to flow through the furnace with the help of cooling unit at a rate of 100 ml/min. Another sample was run as a confirmatory test by applying same set of conditions. The results in the form of DTA thermo grams are gives below in figure 5-3 and 5-4.

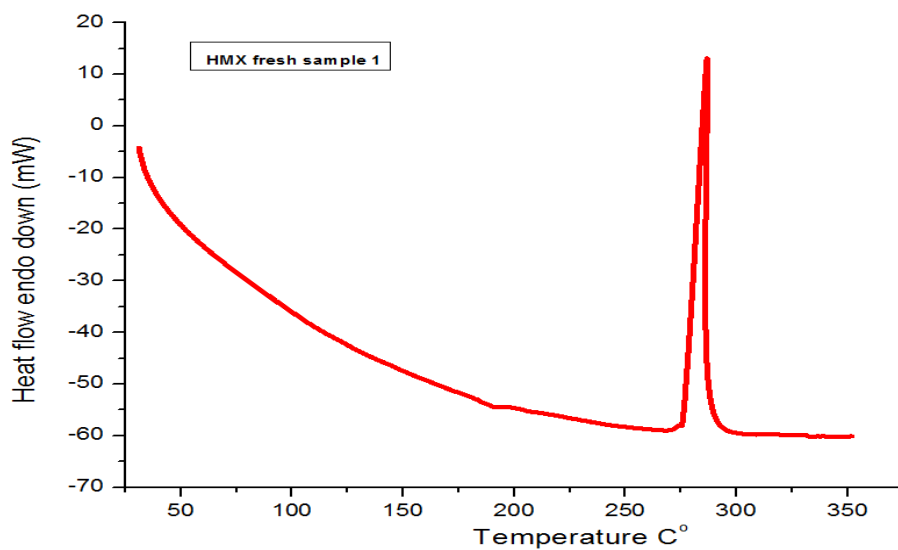


Figure 5-3: DTA curve of Standard/ fresh HMX sample 1

Second Confirmatory sample analysis:

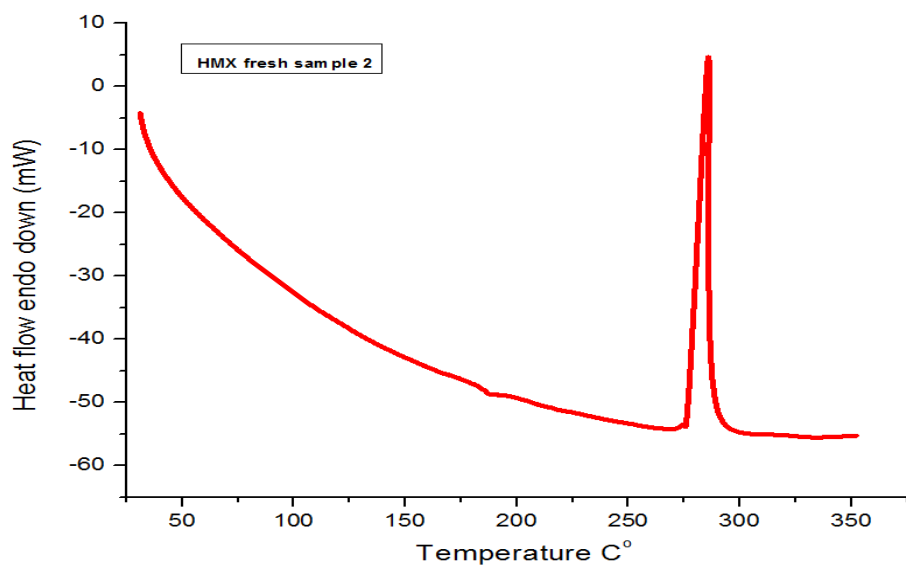


Figure 5-4: DTA curve of Standard/ fresh HMX sample

DTA curves of HMX sample 1 and sample 2 exhibit distinct endothermic and exothermic peaks at different temperatures within the programmed temperature range as shown in figures. The first peak is an endothermic peak which appears at a temperature of about 185°C to 190°C and corresponds to a phase transformation of HMX from one morphological form that is β -HMX to δ -HMX. This phase transformation of HMX falls within the thermal stability limits and has been given in literature. The next endothermic peak near 275°C also corresponds to the melting of the sample and signifies the melting point of HMX. Then immediately after the melting final third most noticeable, strong and sharp exothermic peak is due to the self decomposition of HMX which appears at a temperature of about 280°C. This peak signifies the thermal decomposition point of HMX. The peak reaches its maximum value near 285°C corresponding to the maximum rate of decomposition of the HMX. The decomposition is complete before 295°C.

5.3.4 TGA CURVE OF STANSARD HMX SAMPLE

Non-isothermal TGA analysis of the standard samples were carried out by taking a sample mass of 3 mg and exposing it to heat from room temperature that is 25°C to approximately 350°C at a programmed heating rate of 1°C /min. In order to provide an inert atmosphere Argon gas was made to flow through the furnace with the help of cooling unit at a rate of 100 ml/min. Following the pattern for DTA analysis another sample was run as a confirmatory test by applying same set of conditions. The results in the form of TGA thermograms are gives below in figures 5-5 and 5-6.

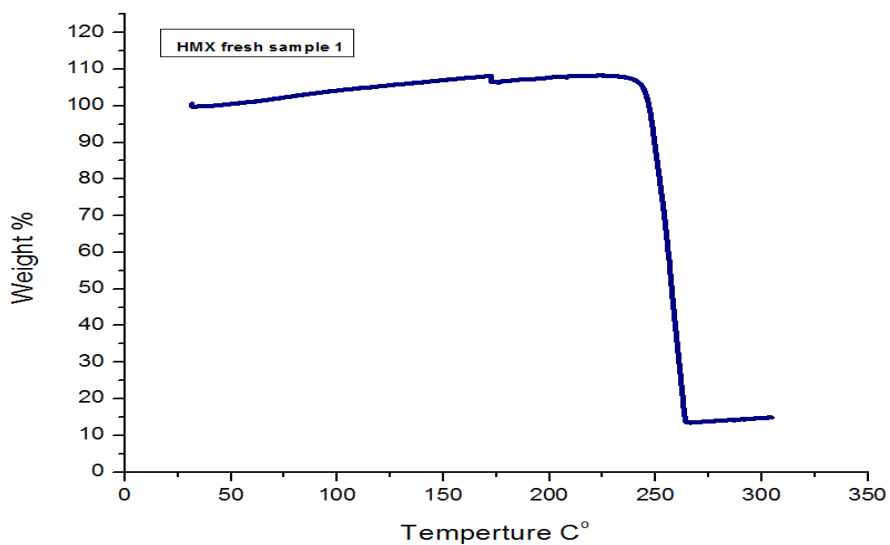


Figure 5-5: TGA curve of Standard/ fresh HMX sample 1

Second Confirmatory sample analysis:

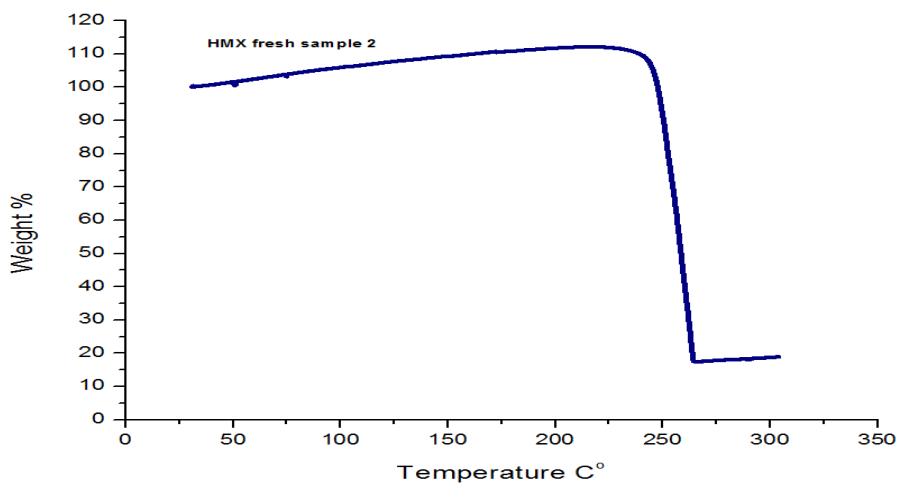


Figure 5-6: TGA curve of Standard/ fresh HMX sample 2

Non-isothermal TGA curves for HMX samples shown above signify that the decomposition of HMX takes place in a single stage. The curve confirms that the decomposition starts near 240°C. We observed that there was no loss of mass before the start of decomposition and all weight loss of HMX is due to its thermal decomposition. The thermogram clearly shows that the explosive material remains stable from room temperature to nearly 235°C and then starts to decompose. The powerful and volatile nature of explosive causes it to decompose rapidly as the temperature increases beyond 240°C. This results into significant and rapid weight loss of explosive. The decomposition completes near 265°C.

5.3.5 KINETIC PARAMETERS OF STANDARD HMX

The kinetic parameters of the decomposition of HMX have been calculated by using TG data obtained through experiments with the help of curve fitting software based on Horowitz and Metzger Method. Figures 5-7 and 5-8 show the graphs obtained with the help of Curve Fitting software and are used for determination of activation energy and the order of reaction.

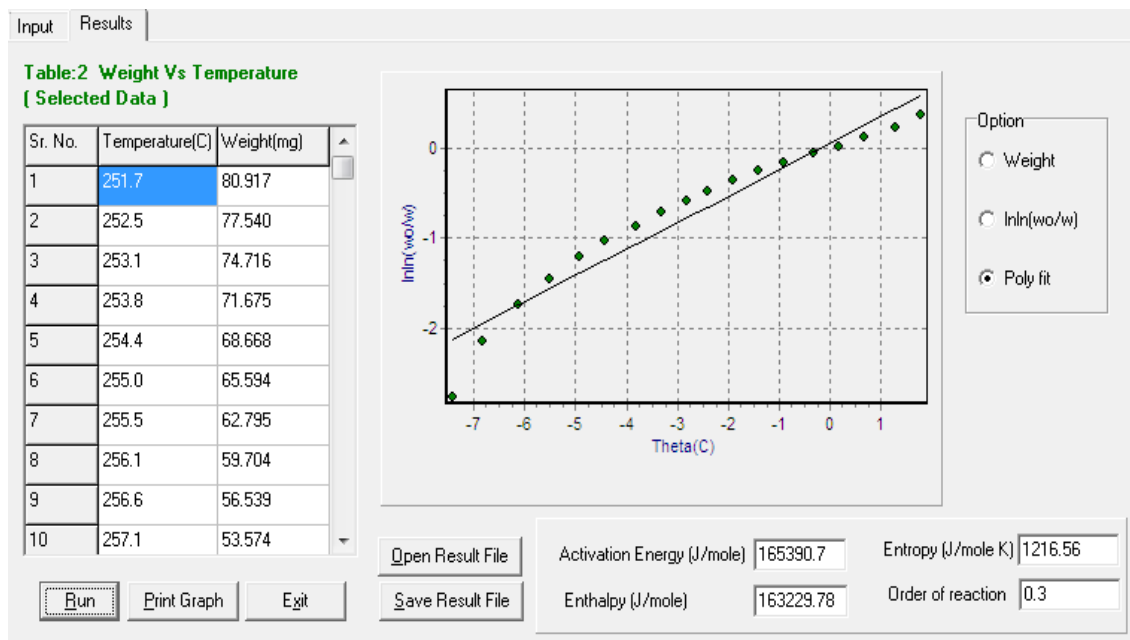


Figure 5-7: Graph for kinetic Parameters of HMX Sample 1

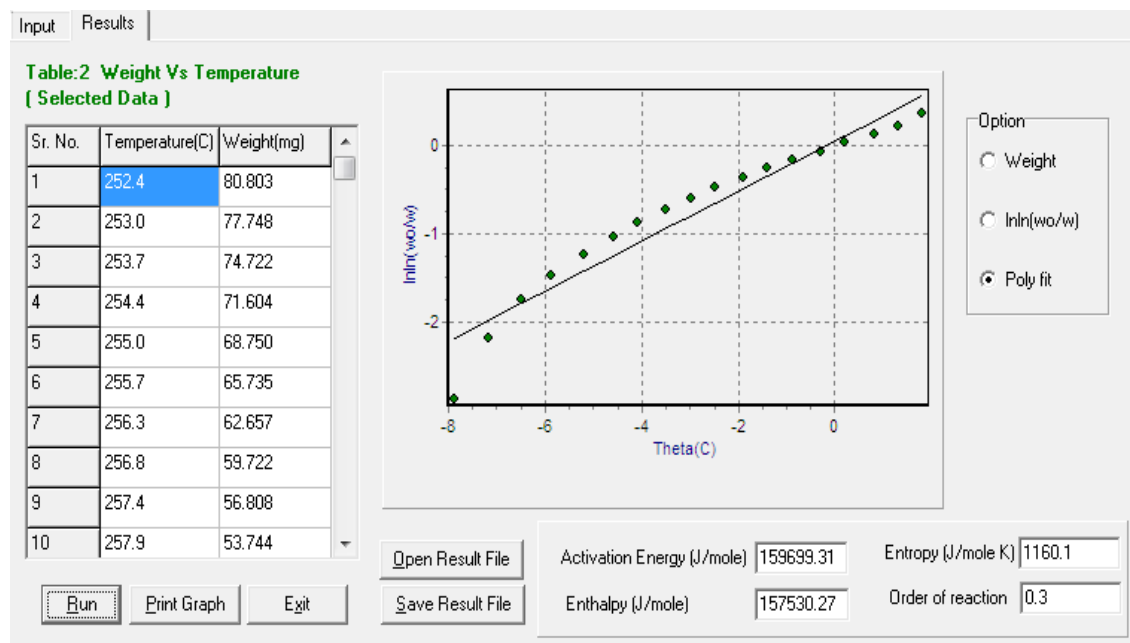


Figure 5-8: Graph for kinetic Parameters of HMX Sample 2

The curve fitting software was given specific data points from the TGA decomposition curves and under the specified experimental conditions the calculated value of activation energy is 165 kJ/mole for sample 1 and 160 kJ/mole for sample 2. The order of reaction for decomposition of HMX means that the decomposition of HMX obeys first order kinetics.

5.3.6 DISCUSSION

The thermal stability criterion for explosives requires that they should be thermally stable between the temperature ranges of -40°C to $+70^{\circ}\text{C}$. By carrying out sample investigation with the help of DTA curves as given in Fig 5-3 and 5-4, there is one phase transformation near 185°C and the melting followed by rapid thermal decomposition occurs at 275°C which falls very much within thermal stability limits. After studying the sample with DTA the experiments were carried out to obtain the TGA curve data by applying different set of conditions. More attention was paid in DTA analysis to avoid sample self-heating which means a sample weight of 1 mg was used. At high heating rates the melting endotherm and the thermal runaway of the sample was interfering with the correct weight loss history of the sample with the change in temperature, therefore heating rate of $1^{\circ}\text{C}/\text{min}$ was used in TGA analysis. The resultant TGA curve data points occurring within the region where the decomposition reaction took place were used to calculate the activation energy. Consequently the standard activation energy was found to be in the range of 165kJ/mole for fresh HMS sample which corresponds to the value given in literature very precisely.

5.4 THERMAL STUDIES OF OLD HMX SAMPLE

After studying the thermal and kinetic behavior of standard or fresh HMX, thermal studies of an approximately 15 years old HMX sample were carried out using Diamond TG/DTA instrument. All the conditions for the experiments were kept the same as in case of the fresh or standard HMX sample.

5.4.1 RESULTS

The results of the thermal studies of the old HMX with DTA and TGA have been discussed below.

5.4.2 DTA CURVE

DTA analysis of the old samples were carried out by using sample mass of 1 mg which was heated from room temperature to approximately 400°C at a programmed heating rate of 10°C/min. Inert atmosphere was provided by using Argon as purging gas at a rate of 100 ml/min. As previously done a second sample was run by applying same set of conditions. The results in the form of DTA thermograms are gives below in figures 5-9 and 5-10.

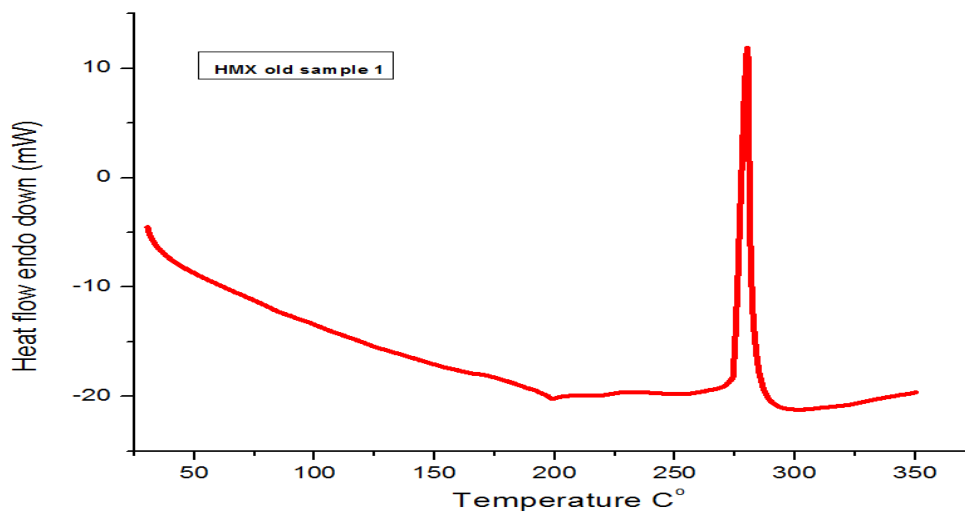


Figure 5-9: DTA curve of Old HMX sample 1

Second Confirmatory sample analysis:

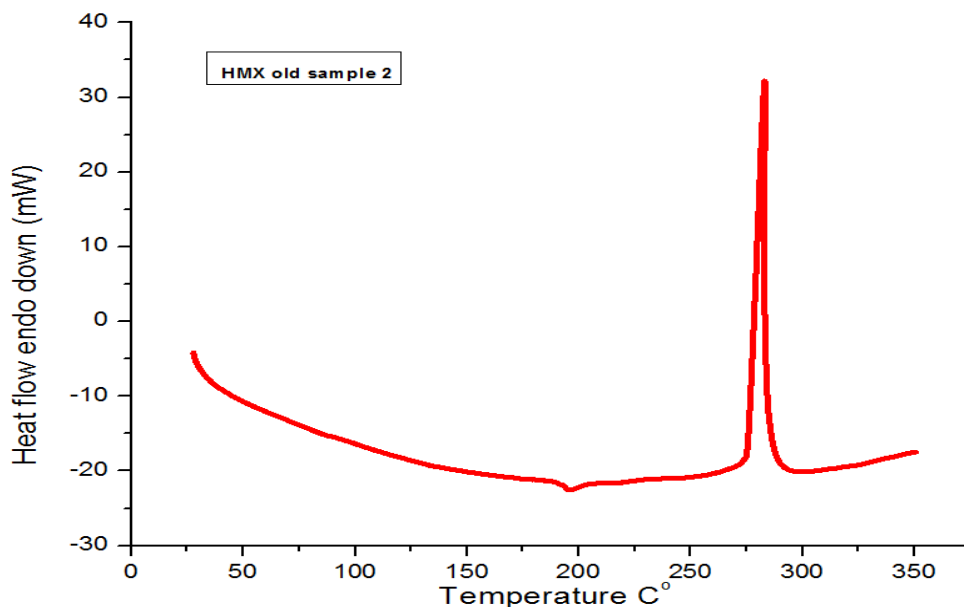


Figure 5-10: DTA curve of Old HMX sample 2

Now in case of old HMX samples the significant endothermic and exothermic peaks at different temperatures within the programmed temperature range are shown in Figures. The first one is an endothermic peak which appears at a temperature of about 195°C to 200°C and corresponds to a phase transformation of HMX from β -HMX crystalline form to δ -HMX crystalline form. This phase transformation of old HMX also falls within the thermal stability limits. The next endothermic peak representing the melting of the sample and signifying its melting point is not clearly visible. The most significant strong and sharp exothermic peak is appearing at 275°C due to the self decomposition of HMX. This peak signifies the thermal decomposition point of HMX. The peak reaches its maximum value at 285°C corresponding to the maximum rate of decomposition of the HMX. The decomposition is completed before 290°C.

5.4.3 TGA CURVE

Non-isothermal TGA analysis of the two old HMX samples were carried out by taking a sample mass of 3 mg and applying the exact same set of conditions as were applied for the standard sample. The results in the form of TGA thermograms are gives below in figures 5-11 and 5-12.

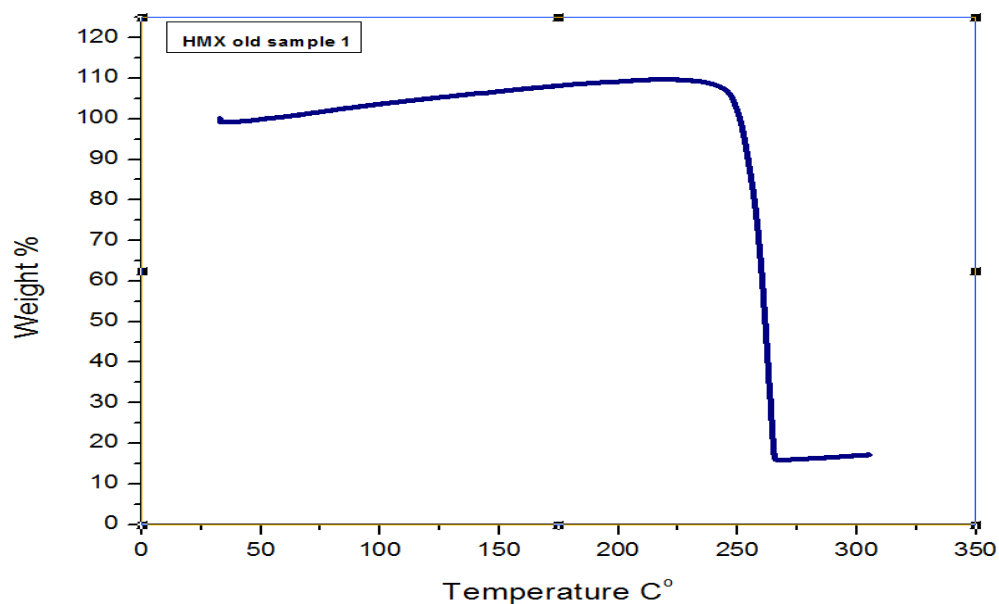


Figure 5-11: TGA curve of Old HMX sample 1

Second Confirmatory sample analysis:

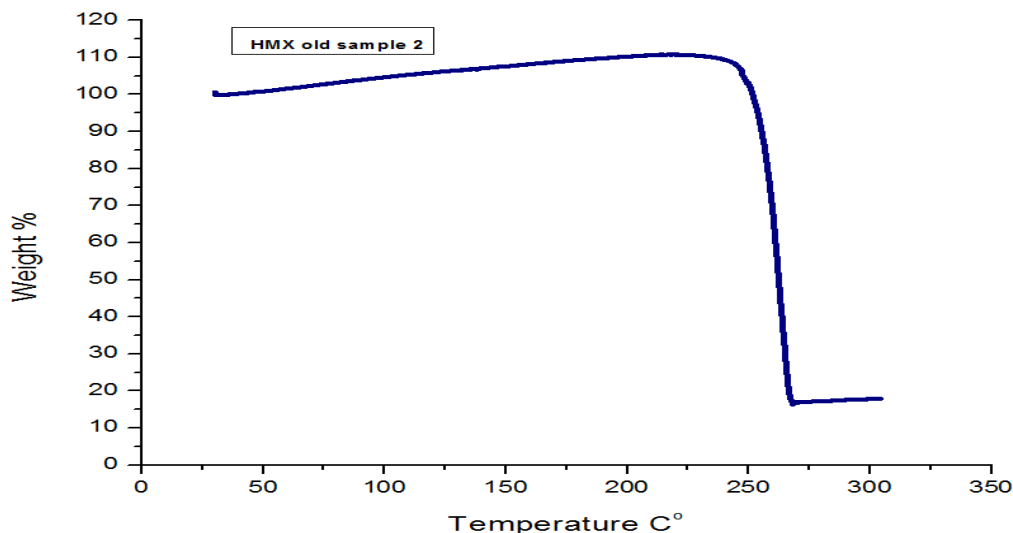


Figure 5-12: TGA curve of Old HMX sample

The weight loss curve also shows that there is no significant variation in the weight loss pattern. Non-isothermal TGA curves for HMX samples are shown above signify that the decomposition of HMX takes place in a single stage. It was again observed that there was no loss of mass before the start of decomposition and all weight loss of HMX is due to its decomposition. The decomposition starts near 245°C as in case of standard sample and completes before 270°C and the sample almost gets decomposed. The slope of the decomposition curves seems to be quite similar to the one shown in figure 5-5 and 5-6 for decomposition of the standard sample.

5.4.4 KINETIC PARAMETERS

The graph for calculating the kinetic parameters with the help of weight loss data is given below.

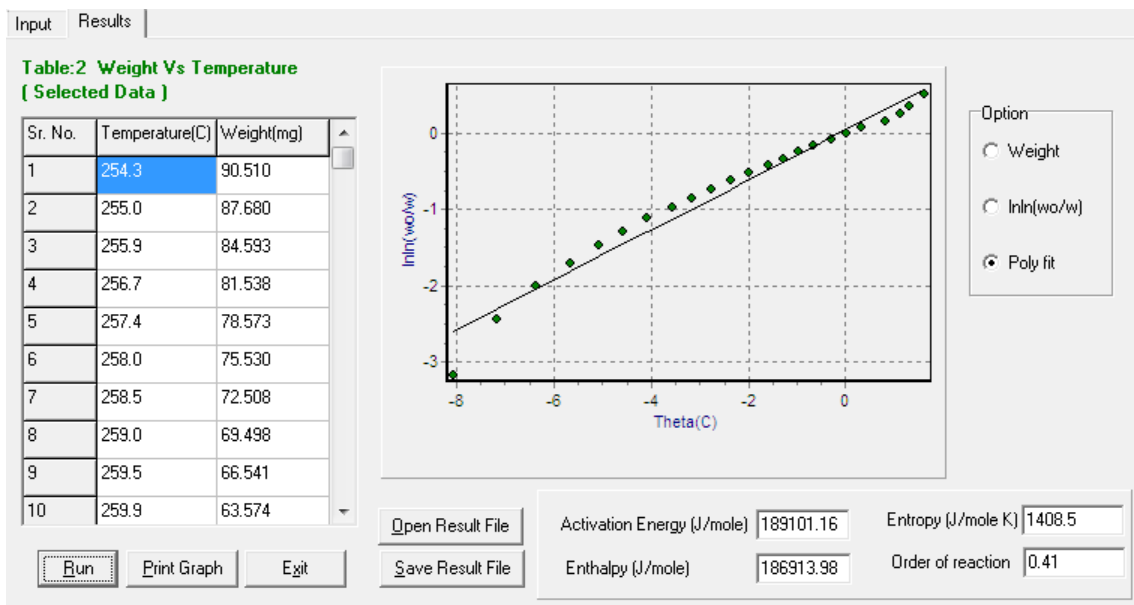


Figure 5-13: Graph for Calculation of Kinetic Parameters of Old HMX Sample 1

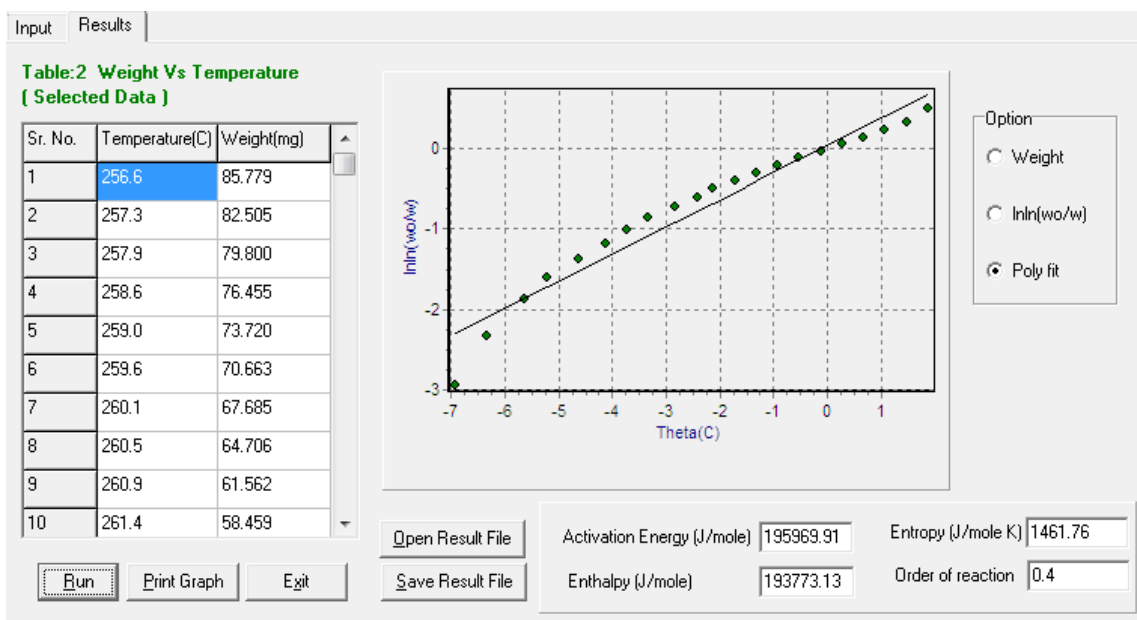


Figure 5-14: Graph for Calculation of Kinetic Parameters of Old HMX Sample 2

From the TGA decomposition curves obtained under the specified experimental conditions the calculated value of activation energy with the help of Curve Fitting software comes out to be 189 kJ/mole for sample 1 and 195 kJ/mole for sample 2. The order of reaction also shows that the decomposition of HMX obeys first order kinetics.

5.4.5 DISCUSSION

From the thermal and kinetic analysis of the old HMX sample it is seen that at temperature of about 198°C to 200°C the β -HMX crystalline form transforms to δ -HMX crystalline form which appears in the form of an endothermic peak. Right after this peak another strong and sharp exothermic peak is appearing at 275°C due to the self-decomposition of HMX and the decomposition reaction completes around 280°C. This shows that the despite exposure to long storage conditions the explosive is very much stable. For calculating activation energy the TGA curve data points were processed in Curve Fitting software. The calculated value of activation came out to be 189 kJ/mole and 195 kJ/mole for sample 1 and sample 2 respectively. These values signify that there was a very minute reduction in the sensitivity of the explosive, therefore the explosive is safe and reliable. The 15 years long storage conditions did not alter the characteristics of this explosive and it is still very safe, thermally stable and reliable to produce desired results.

5.5 COMPARISON OF SAMPLE INVESTIGATION BY DTA

The DTA curves for different experiments conducted for both new as well as the old samples have been shown in figure 5-15 for comparison.

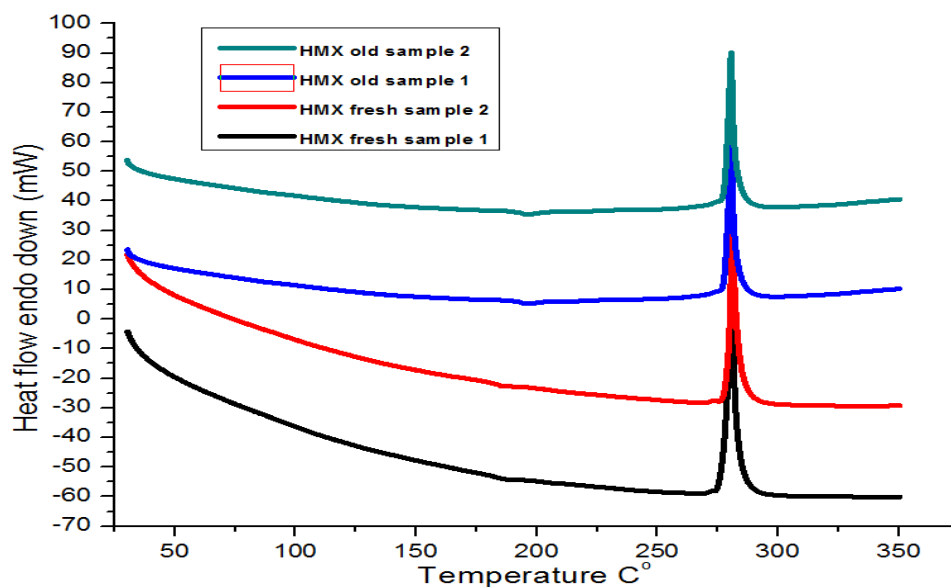


Figure 5-15: DTA curves of HMX Samples

From the above figure, four distinct endothermic peaks can be identified in all the cases which represent transformation of β -HMX to δ -HMX. Similarly in all the study cases four distinct exothermic strong and sharp peaks are visible which represent the decomposition of HMX. These all DTA curves suggest that all the four samples are thermally stable.

5.6 COMPARISON OF TGA CURVES

The TGA curves for different experiments conducted with four HMX samples separately have been shown in figure 5-16 below.

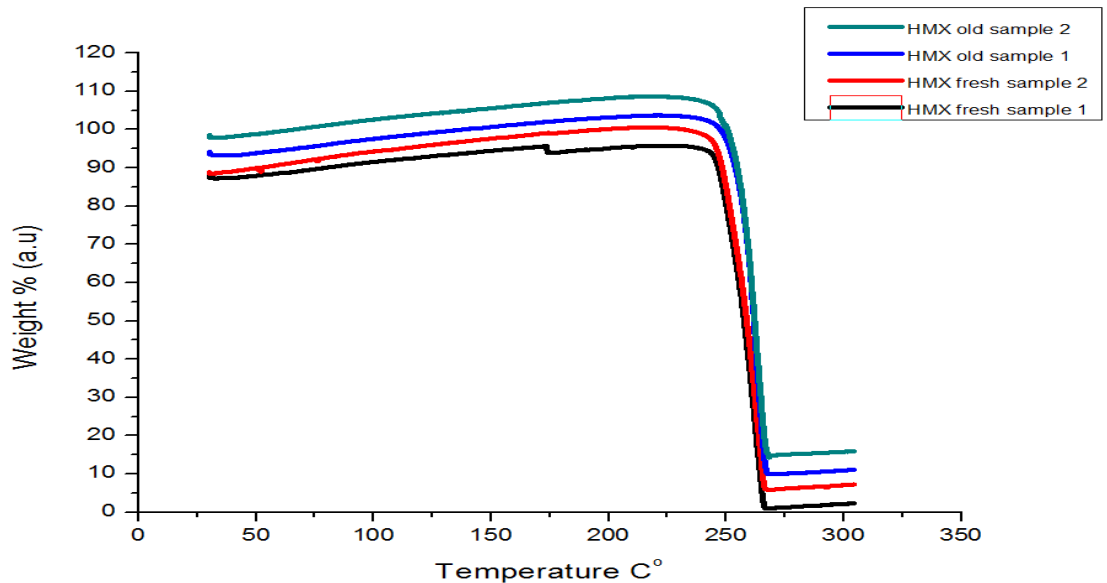


Figure 5-16: TGA curves of HMX Samples

It is clearly evident from figure 5-16 that there is no significant effect on the weight loss pattern of HMX. It is observed from TGA graph that all the curves are quite similar to each other. In all the TGA analysis the decomposition of the explosive starts near 245°C. Decomposition is very rapid and it completes around 270°C. The TGA curve data points from the point where rapid HMX self-decomposition took place were used to calculate kinetic parameters. The activation energy values for standard sample were found to be well within the range given in literature. Whereas the activation energy values for old sample were slightly higher but were having no significant effect on the reliability of the explosive.

Table 5-2: Activation energies

Sample	Activation Energy (kJ/mole)
HMX Standard Sample 1	165.39 kJ/mole
HMX Standard Sample 2	159.69 kJ/mole
HMX Old Sample 1	189.1 kJ/mole
HMX Old Sample 2	195.9 kJ/mole

CONCLUSION

Thermal Characterization of HMX was done in order to investigate the handling safety and reliability of the explosive material. It is somewhat mandatory for all the munitions of war that the energetic material must be studied thoroughly for its safety, reliability and performance. The energetic materials undergo decomposition with the passage of time and it grows faster when explosives are exposed to storage conditions with higher temperatures. Hence to understand the thermal stability of HMX, Simultaneous thermal analysis of two different samples of HMX was carried out in this work.

The thermal events taking place within the samples when exposed to non-isothermal DTA analysis were observed carefully. The distinct endothermic and exothermic peaks showing the phase changes, melting as well as thermal decomposition of the samples were observed. The thermal events included mainly the endothermic phase changes which were observed to occur in 185 to 200°C range for both the samples which was followed by the main strong and rapid exothermic decomposition occurring within the 270 to 290°C temperature range. We concluded from the DTA curves that the old sample was not affected by the long storage and it is very stable over a long period of time.

On the other hand a different sample mass was exposed to different temperature program due to the reason that at heating rates of 10°C /min and above the HMX decomposition took place after melting of the sample. In this case the decomposition is exceptionally fast and it has the potential to interfere with the thermal history record of our instrument. With the help of final values of activation energies obtained we conclude that the explosive is reliable and will serve its purpose efficiently after a 15 years storage period. HMX is an excellent, thermally stable, highly powerful and reliable explosive.