Kinetics Reactions of Ammonium Nitrate-Sodium Nitrite Reaction and Ammonium Nitrate Emulsion Explosives

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BY

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Declaration

I, Pumeza Melane, declare that **Kinetics Reactions of Ammonium Nitrate-Sodium Nitrite Reaction and Ammonium Nitrate Emulsion Explosives** is my own unaided work, and that all sources that I have used and quoted have been indicated and acknowledged by means of complete and clear references. This thesis is submitted for the Master of Science (MSc) degree, to the Department of Chemistry, Faculty of Science, University of Cape Town, it has not been submitted before for any degree or any examination at the University of Cape Town or any other university.

Pumeza Melane Signed by candidate

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Abstract

The aim of this study was to understand and control the gasification rates in ammonium nitrate emulsion explosive using ammonium nitrate-sodium nitrite reaction. This reaction produces N_2 gas which is the sensitizer in emulsion explosives.

The NH_4NO_3-$NaNO_2$ gassing reaction produces N_2 gas and so the reaction could be followed by the pressure increase in a closed reaction vessel. The reaction is pH sensitive, so the role of pH was investigated in the pH range 2 to 5. Gasification reactions for unbuffered NH_4NO_3-$NaNO_2$ reaction were found to be rapid below pH = 3 and maximum pressure was attained within 2 hours of starting the reaction. At pH = 4.5 and 5 the reaction failed to attain maximum pressure. Initial rate of reaction showed sensitivity to pH, the rate of reaction decreasing with increasing pH. The reaction was found to be second order with respect to nitrite species.

The effects of three different buffers (potassium hydrogen phthalate, sodium formate and sodium citrate) were also investigated. At pH = 3 pressure traces for the buffered reactions had attained maximum pressure while at pH = 3.5 only sodium citrate buffer had reached a pressure stable state. The presence of the buffers resulted in a lower overall pressure change and absolute pH change and higher rate constants and initial rate of reaction than in their absence.

A Lewis acid (Zinc Nitrate) was added to the buffered and unbuffered NH_4NO_3-$NaNO_2$ reactions to investigate a patent claim that addition of a Lewis acid would increase the rate of reaction. The presence of zinc nitrate in the buffered reactions resulted in rapid pressure increase; higher initial rate of reactions than the unbuffered with zinc nitrate.

Ammonium nitrate solution was emulsified resulting in an ammonium nitrate emulsion explosive and kinetics of gasification was investigated. The gasification reactions were found to be rapid at pH 3.2, slowing significantly with increased pH as indicated by initial rates of reaction and as predicted by the gasification reaction rate law. Maximum pressure increase was attained within three hours at pH 3.2, whereas reactions conducted at pH 4.0 and 4.5 failed to reach maximum pressure even after 24 hours as evidenced by plots of pressure versus time.

The effect of buffers in the ammonium nitrate emulsions was also investigated.

List of abbreviations

o/w:	Oil-in-Water Emulsions
w/o:	Water-in-Oil Emulsions
o/o:	Oil-in-Oil Emulsions
w/w:	Water-in-Water Emulsions
w/o/w:	Water-in-Oil-in-Water Emulsions
w/w:	Weight by Weight
AA/NA:	Acetic Acid/Sodium Acetate
CA/NC:	Citric Acid/Sodium Acetate

List of symbols

k:	Rate Constant
K:	Equilibrium constant
K_a:	Acid dissociation constant
K_b:	Base dissociation constant
$K_{w:}$	Dissociation constant of water
pH:	-Log $[H^+]$ of the activity of the hydrogen ion
P_{inf}.	Infinite pressure
P_{eq}	Measured initial pressure
P_t	Measured total pressure

Types of emulsions

Emulsion A: Acetic Acid/Sodium Acetate Emulsion pH = 3.20

Emulsion B: Acetic Acid/Sodium Acetate Emulsion pH = 4.01

Emulsion C: Acetic Acid/Sodium Acetate Emulsion pH = 4.50

Emulsion D: Citric Acid/Sodium Citrate Emulsion pH = 3.20

Emulsion E: Citric Acid/Sodium Citrate Emulsion pH = 4.50

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Chapter 1

Introduction

1.1 Explosives

Explosive devices may be mechanical, chemical or atomic. Mechanical explosions occur when a closed system is heated – a violent pressure rupture can occur. However, this does not make a heated can of soup an explosive. An explosive substance is one which reacts chemically to produce heat and gas with rapid expansion of matter. A detonation is a special type of explosion. It is a rapid chemical reaction, initiated by the heat accompanying a shock compression, which releases sufficient energy before any expansion occurs to sustain the shock wave [1, 2, 3].

Probably the oldest known explosive is black gunpowder, a mixture of charcoal (carbon), sulphur and saltpeter (potassium nitrate). When these three chemicals are ignited, a chemical reaction takes place very quickly. The products of that reaction are carbon dioxide, carbon monoxide, sulphur dioxide and nitrite oxide (they are all gases) as well as potassium carbonate and potassium sulphide (solids). The four gases formed in the reaction are heated to very high temperatures and expand very rapidly. They form shock waves that have the ability to knock down trees, buildings, people and other objects in their way. The shock wave also carries with it very hot gases that can burn objects and initiate fires. The combination of shock wave and high temperature is a characteristic of most kinds of explosives.

1.2 History of explosives

Gunpowder was first invented in China in approximately 1000 years ago [1, 2, 4]. For hundred of years it was used mainly to create fireworks. The Chinese did not use gun powder as a weapon of war; it was the Europeans who first adapted explosives for use in weapons. By the fourteenth century, Europeans were widely using the explosive as a military device to project stones and metal balls from cannons and guns. Gunpowder remained the only explosives for 300 years until 1628 when another explosive called fulminating gold was discovered.

There are other chemical explosives that have been discovered since the invention of gunpowder and fulminating gold. The most common of these are chemical compounds that contain nitrogen such as azide, nitrates and other nitro compounds. In 1846 Italian chemist Ascanio Sobrero invented the first modern explosive, nitroglycerin by treating glycerine with nitric and sulphuric acids [1, 4]. Sobrero's discovery was unfortunately for many early users too unstable to be used safely. Nitroglycerin readily explodes if bumped or shocked. This inspired Swedish inventor Alfred Nobel in 1862 to seek a safe way to package nitroglycerin. In the mid-1960s, he succeeded in mixing it with an inert absorbent material. His invention was called dynamite.

Dynamite replaced gunpowder as the most widely used explosive (aside from military uses of gunpowder). Nobel continued experimenting with explosives and in 1875, invented a gelatinous, an explosive jelly [4]. It was more powerful and even a little safer than the dynamite he invented nine years earlier. The addition of ammonium nitrate to dynamite further decreased the chances of accidental explosions. It also made it cheaper to manufacture.

1.3 Types and uses of explosives

They all fit into one of the following main groups: primary, low, high, nuclear and blasting explosives [5].

1.3.1 Primary explosives

Primary explosives are generally used to set off other explosives. They are very sensitive to shock, heat and electricity and therefore they must be handled with great care. Two common examples of primary explosives are mercury fulminate and lead azide. Primary explosives are also known as initiating explosives, blasting caps, detonators or primers.

1.3.2 Low Explosives

Low explosives are characterised by the fact that they burn only at their surface. For example, when a cylinder of black gunpowder is ignited it begins burning at one end of the cylinder and then continues to the other end. This process takes place very rapidly, however, and is complete in just a few thousandths of seconds. This property of slowed combustion is preferred in guns and artillery because too rapid an explosion could cause the weapon itself to blow up. A slower explosive has effects of building up pressure to force a bullet or shell smoothly out of the weapon. Fireworks (figure 1) are also low explosives. Low explosives are not used to blow things up but they are used as propellants instead.

Figure 1.1: *Fireworks as example of low explosives [55]*

1.3.3 High Explosives

High explosives are much more powerful than primary explosives. When they are detonated, all parts of the explosive blow up within few seconds. Some are less likely than primary explosives to explode by accident. Examples of high explosives include ANFO (ammonium nitrate-fuel oil mixture), dynamite, nitroglycerin, PETN (pentaerythritol tetranitrate), picric acid and TNT (trinitrotoluene). They provide the explosive force delivered by hand grenades, bombs and artillery shells.

Figure 1.1: *Dynamite as an example of high explosives [56]*

High explosives that are set off by heat are called primary explosives. High explosives that can be set off by a detonator are called secondary explosives.

1.3.4 Nuclear Explosives

Nuclear explosives were discovered during the World War II. Nuclear explosives produce their explosive power not by chemical reactions as with traditional explosives, but through nuclear reactions. In some types of nuclear reactions, large atomic nuclei are split into two pieces with the release of huge amounts of energy and in other types; small atomic nuclei are combined to make a single large nucleus to release a large amount of energy.

1.3.5 Blasting agents

Blasting agents are used for peaceful purposes, because they are not used in military weapons, yet they are very powerful and are used in mining and excavating. They are inexpensive and safe to use. Dynamites are the most well known blasting agents, as well as ANFO (ammonium nitrate-fuel oil mixture) which is used for excavating.

Another example of blasting agents is emulsion explosives. Emulsion explosives were developed in the early 1960s [6, 7] and have become quite important blasting means because of their comparatively high detonation parameters and exceptionally good safety characteristics [8 – 11]. These commercial explosives are used primarily for mining, tunnel construction and other specialized applications.

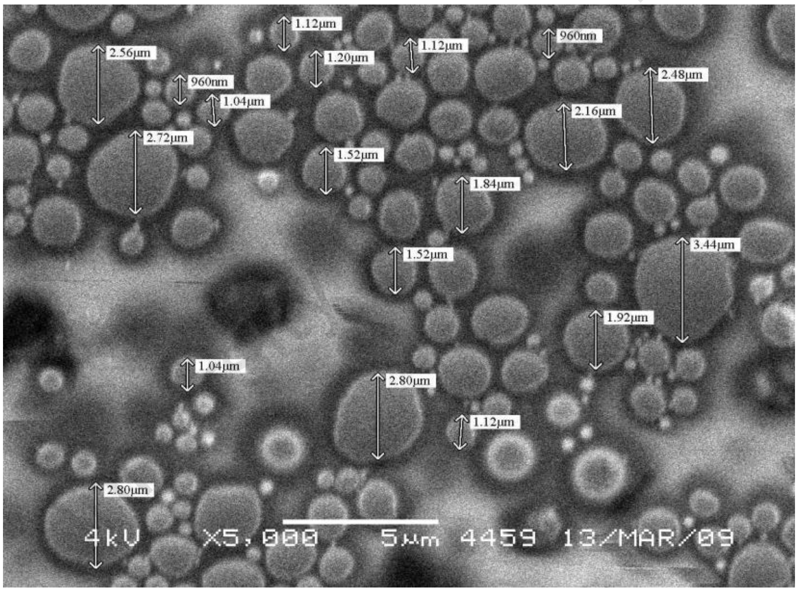

Figure 1.2: *A picture of microscopic emulsion explosives [57]*

Emulsion explosives are concentrated water-in-oil emulsions, composed of an aqueous phase finely dispersed within a continuous oil phase. The aqueous phase acts as an oxidiser, the basic oxidiser that is normally used in emulsion explosives is a supersaturated ammonium nitrate solution and/or other nitrate salts. The continuous oil phase comprises of hydrocarbon based fuel such as fuel oil or paraffin wax.

Emulsion explosives have the consistency of common emulsions such as mayonnaise and may be prepared in cartridges or in a bulk, pump able form. The emulsion matrix has no components that are explosive and requires the addition of sensitizers, such as hollow glass microballoons, fine particulates or gas-forming chemical ingredients to form a detonable mixture. Owing to their inherent insensitivity to detonation, emulsion explosives are among the safest commercial explosives to handle and have good water resistance. Emulsion explosives often contain solid particles additives, such as aluminium powder to increase the energy density of the mixture.

In order for an emulsion explosive to detonate, it must first be sensitized. Emulsion explosives will not detonate before they are sensitized. Sensitization involves introducing small low density voids into the emulsion matrix, which provide hot spots at which explosion may nucleate [12 - 15]. Sensitization requires distributing material of a hollow or porous nature throughout the emulsion, or by generating gas bubbles *in situ* via chemical reaction [16, 17]. The use of chemical reaction to produce voids within emulsion explosives is often referred to a chemical gassing, and this process has emerged as one of the most efficient and cost effective means of explosives sensitization [18].

Chemical gassing of an emulsion explosive proceeds via the addition of a concentrated nitrite salt solution to an emulsion, where it reacts with ammonia (present due to ammonium nitrate), yielding nitrogen gas via nitrosation mechanism. [19, 20]. Gas bubbles produced by chemical gassing range from around 80 to 400 μm in size [16, 21] compared to dispersed phase droplets of about 10 μm. These gas bubbles are stabilized by surface active molecules present in the oil phase of the emulsion [16].

The major disadvantage of chemical gassing is that it is very slow and long mine-site delays are often encountered before an explosive is ready to detonate. As such, certain reagents are added to accelerate the gassing process. One means of catalysing nitrosation reactions is by the addition of strong nucleophilic species such as thiocyanate, which will accelerate the gassing reaction through increased equilibrium concentration of the effective nitrosating agent [22]. Even in the presence of powerful catalyst (thiocyanate) chemical gassing still proceeds relatively slowly and this may cause costly delays. An alternate gassing process has been developed utilising the accelerant thiourea [23], though this process does not sufficiently increase the rate of the ammonia gassing process.

1.4 General Aspects of Emulsions

Traditionally, emulsions have been defined as dispersions of macroscopic droplets of one liquid in another liquid, with a droplet diameter approximately in the range of 0.5 – 100 µm [24 - 26]. A large number of emulsions do in fact consist of only two liquids. The stability of such simple systems is easy to understand from a theoretical point of view. However one must realize that most emulsion formulations used in practice are more complicated [27 - 29]. This fact made the International Union of Pure and Applied Chemistry (IUPAC) formulate the following definition of an emulsion: “In an emulsion liquid droplets and/or liquid crystals are dispersed in a liquid.”[30] Also many emulsion formulations contain solid particles or even three liquids.

An emulsion is formed when two immiscible liquids (oil and water) are mechanically agitated. During agitation, both liquids tend to form droplets, but when the agitation ceases, the droplets separate into two phases. Emulsion droplets exhibit all classical behaviours of colloids: Brownian motion, the reversible phase transitions as a result of droplet interactions and irreversible transitions that are generally involve in the destruction of the emulsion. If a stabilizing compound that is an emulsifier is added to the two immiscible liquids, one phase usually becomes continuous and the other remains in droplet form for a prolonged time. Droplets are formed by both phases during agitation and the continuous phase is actually obtained because its droplets are unstable.

Emulsions can be found in two forms that is diluted or simple emulsions and highly concentrated emulsions. These emulsions have different internal dynamics and mechanical properties. Simple emulsions are composed of oil droplets dispersed in water (O/W) (**Figure 1.4a**), while highly concentrated emulsions are made of water droplets dispersed in an oil continuous phase (W/O). Water in oil emulsions are the main focus of this study. These emulsions (W/O) consist of droplets of the water-containing phase dispersed in an organic liquid, which comprises of the continuous external phase (**Figure 1.4b**). This system can only be stable if the water droplets are covered with surfactant or emulsifier.

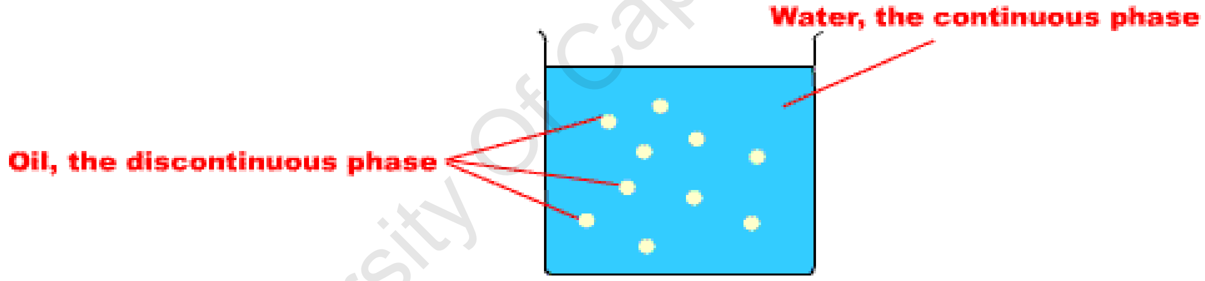

Figure 1a: O/W emulsion

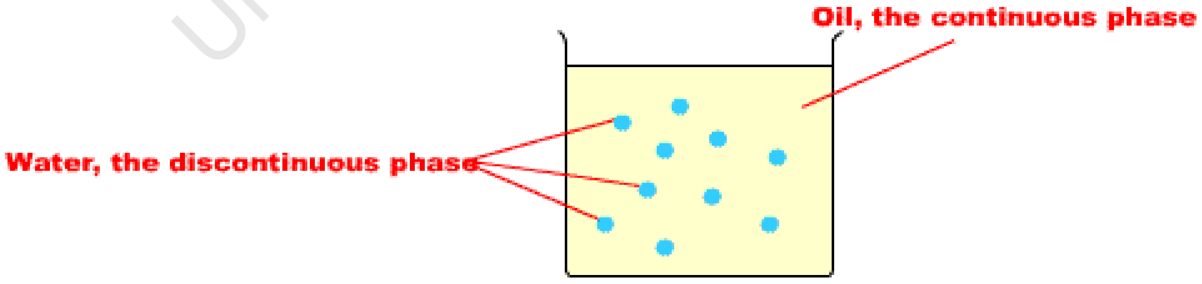

Figure 1b: W/O emulsion

Figure 1.3 a&b: *Examples of emulsions [58]*

It is also possible to have more complicated systems such as water- in- oil- in water (w/o/w) emulsions where the droplets themselves are comprised of a w/o emulsion dispersed in a n aqueous continuous phase. Such systems are called double emulsions or multiple emulsions [31]. They (emulsions) may also contain solid dispersion within each droplet as a possible route to produce magnetic colloids. In principle, it is possible to form oil – in- oil (o/o) emulsions, but in practise the two organic liquids are often too miscible and it is difficult to identify an effective emulsifier [32]. There is also a rare type of emulsions such as water- in - water emulsions [33]. Emulsions are generally made up of two immiscible phases for which the surface tension is non zero and may in principle involve other hydrophilic-like or lipophilic-like fluids in the presence of suitable surface-active species, each phase being possibly composed of numerous components.

Few studies have been conducted on the gassing of emulsions using different methods [34 - 36]; however structures and properties of emulsions have been studied in many papers from different points of view.

Pioneering works published by Princen [37, 38] and Princen and Kiss [39, 40] demonstrated the role of the concentration of the disperse phase and showed that the rheological properties are characterized by elasticity at low shear stresses and the existence of yielding behaviour. Palierne [41] proposed a model for predicting the linear viscoelastic behaviour of emulsions based on the properties of the individual phases. A study in water- in – water emulsions (mixtures of solutions of two different biopolymers, which are thermodynamically incompatible) performed by Capron *et al*. [33] showed that the linear viscoelastic behaviour of such emulsions corresponds with the Palierne model. The viscoelastic properties of oil – in – water emulsions were studied by Guerrero *et al*. [42], who found that their results in the linear viscoelastic domain corresponds to the empirical model of Madiedo and Gallegos [43]. Concentration dependence of viscosity for emulsions of two immiscible liquids was successfully described by a new model [44]. Later, theory was developed for calculating the shear moduli of such emulsions [45].

1.4.1 Stability of emulsions

Emulsions are metastable colloids and it is a question of when, not if, they will lose stability. Therefore the preparation of emulsions is the challenge of formulating a system that is at least stable enough to meet the demands of a particular application for the required timescale. In practise, some emulsions can be stable for years, whereas others exist for a very short time. For example, a simple salad dressing of vinegar and vegetable oil often barely exists as an emulsion for long enough, after shaking to pour it onto a salad. In contrast, mayonnaise is stable for months. The stability and physical characteristics of emulsions depend on many variables including the nature of liquids, temperature, additive types and amounts and the type and amount of mechanical or chemical energy used to form an emulsion [46 - 49].

There are three causes of emulsion instability, namely flocculation, where particles form lumps; creaming where the particles concentrate towards the surface of the mixture while staying separated; and breaking and coalescence where the particles coalesce and form a layer of liquid [46 - 49]. Instability of emulsions can be prevented and emulsifiers are one of the key to producing stable emulsions [46]. Emulsifier is a general term that refers to chemical species that occupy the interfacial region between the droplet and the continuous phase. Emulsifiers have two main functions: lowering the interfacial tension, which makes droplet formation less energy intensive and providing colloidal stability (i.e. stability against coalescence) to the droplet.

There are three main types of stabilizers for emulsions:

i) Monomeric surfactants: These are low molecular weight amphilipic molecules that can diffuse to the interface quickly to provide stability during emulsion formation. They are mobile and move in and out of the interface in a dynamic way.

ii) Polymers: These species are higher molecular weight than surfactants, have some affinity for both phases, they are slower to adsorb than surfactants, but provide significant steric stabilization. They have multiple attachment points to the droplet surface, so they tend to adsorb very strongly and remain at the interface.

iii) Particles: These are usually much smaller droplets and provide a hard, protective coating on the droplet.

To attain the stability, emulsifiers need to cover the surface of the droplets completely and remain firmly adsorbed. The amount of emulsifier needed for a given emulsion is highly dependent on the droplet size, the emulsifier efficiency and the composition of the two phases.

1.4.2 Applications of emulsions

Emulsions are encountered in a very wide range of applications in our daily lives. Some emulsions such as milk and latex from the rubber tree have been around for millions of years, whereas many emulsions were developed during the technology revolution of the 19th and 20th centuries.

Many functional chemical ingredients (such as drugs) are not water soluble and require alcohol or other organic solvents to form solutions. Emulsions are useful because they allow ways to deliver active materials in water which is inexpensive and safe. A related advantage of emulsions is they allow dilution of these active ingredients to an optimal concentration. For an example, in hair conditioning products the oils and other conditioning agents employed would leave hair floppy and sticky if they were directly applied. Through emulsification, these materials can be diluted to an appropriate level which deposits on hair without negative side effects. The major areas where emulsions find use are discussed below:

1.4.2.1 Food industry

A number of common food products are emulsions [50 - 52]. The most familiar food emulsions are dairy products. These include the o/w emulsions milk and cream and the w/o emulsions butter and margarine. When milk is homogenized, usually in a two stage process involving a high pressure homogenizer, the fat droplets are reduced to a very small size and stabilized by natural milk proteins. The internal phase ratio is low for milk and butter, and medium for cream. An example of a food emulsion with a high internal phase ratio is mayonnaise and it is an o/w emulsion. Creamy salad dressings are w/o emulsions, they are thickened with xanthan gum. Other relatively simple food emulsions include creamy soups and sauces, both of which are thickened to provide better stability. The types of stabilizers that are most often used include proteins, lecithin, starches and gelatine. Some food products start as emulsions, but end up as a more complex system. Examples include whipped cream, ice cream and baked goods. Clearly the range of emulsions in the food product area is quite broad.

1.4.2.2 Personal Care and Household Products

Emulsions are very common in personal care products [53]. Cold cream, vanishing cream, hand lotion and deodorant cream are among the emulsions found in the cosmetic and personal care product line. Some of the advantages of emulsions include efficient cleansing action, ease of application and the ability to apply both water and oil soluble ingredients at the same time. Cosmetic emulsions tend to have many ingredients such as fragrances, pigments, moisturizers, thickeners, preservatives and pH adjusters, in addition to the usual oils, waxes, emulsifiers and water. Sensory properties such as coolness, softness, spreadability and creaminess are important to the success of personal care products.

Emulsions can also be found in the area of household cleaning and maintenance products. Many furniture, floor and automobile polishes are oil wax emulsions in water. Although the wax droplets in these products are often solidified at room temperature, they were liquid at the processing temperatures used to manufacture them. This process is called emulsification and it can be used to emulsify many types of low melting solids.

1.4.2.3 Pharmaceutical industry

Emulsions are being used increasingly as delivery systems for pharmaceutical treatments. Lipid emulsions have been used to treat malnutrition by intravenous injection [54]. These o/w emulsions consist of a vegetable oil emulsified with the naturally occurring emulsifier lecithin. Emulsifier fluorocarbons can be used as artificial blood substitutes due to their ability to carry significant amounts of dissolved oxygen and carbon dioxide. Lotions, creams and ointments similar to cosmetics formulations are being used to deliver active pharmaceutical ingredients.

Emulsions have a wide range of applications, other applications are in the petroleum industry, agriculture (agricultural chemicals) and asphalt emulsions (roof coatings, insulating coatings and as a water resistant treatment for paper and fabric).

1.5 Aim and Objectives of this study

The aim of this study is to understand and control the gasification rates in ammonium nitrate solution and ammonium nitrate emulsion explosives.

In order to achieve this aim, the following objectives were carried out:

i) To devise and build apparatus for measuring the gasification rates of ammonium nitrate solution and ammonium nitrate based emulsions

ii) To study the effects of pH on the reaction of NH_4NO_3 with $NaNO_2$.

iii) Determine the effect of various buffers on the reaction of NH_4NO_3 with $NaNO_2$

iv) To study the role of a Lewis Acid (Zinc Nitrate) in the reaction of buffered and unbuffered NH_4NO_3 with $NaNO_2$

v) Determine the role of pH on the gasification reaction of emulsified Ammonium Nitrate with aqueous Sodium Nitrite.

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Chapter 2

Gasification Reaction Rates of Buffered and Unbuffered Ammonium Nitrate-Sodium Nitrite Reaction

2.1 Introduction

The reaction kinetics of NH_4NO_3 and $NaNO_2$ has been studied previously [1]. Despite the complexity of the reaction pathway, the reaction can be simplified into the scheme below.

$$NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \longrightarrow N_{2\,(g)} + 2\,H_2O_{\,(l)}$$

This reaction is important historically because of its role in the discovery of the element argon [2]. The kinetics of the reaction however, requires a detailed accounting of the various reactive species within the reaction mechanism and is described in detail below. It is also important to note that several of the reactive species within the reaction mechanism are pH sensitive, notably NH_3 and HNO_2.

2.1.1 Reaction Mechanism*:*

The reaction mechanism described by Rubin *et.al* [3] is a complex pathway which shows dependence on a number of equilibrium processes.

1. $NaNO_2 \rightleftharpoons Na^+ + NO_2^-$

2. $NH_4NO_3 \rightleftharpoons NH_4^+ + NO_3^-$

3. $2\,HNO_2 \rightleftharpoons N_2O_3 + H_2O$ **or** $2HNO_2 \rightleftharpoons NO + NO_2 + H_2O$

4. $N_2O_3 \rightleftharpoons NO + NO_2$

5. $NH_3 + N_2O_3 \rightleftharpoons H_3NNO^+ + NO_2^-$

6. $H_3NNO^+ + NO_2^- \rightleftharpoons H_2NNO + HNO_2$

7. $H_2NNO \rightleftharpoons N_2 + H_2O$

2.1.2 Rate Law:

From reaction **7**, the rate of formation of N_2 can be described by:

Rate $N_2 = k_1$ [H_2NNO], where k_1 is the rate constant

From reaction **6**, the rate of formation of H_2NNO can be described by:

Rate $H_2NNO = k_2$ [H_3NNO^+][NO_2^-] - k_1[H_2NNO], k_1 and k_2 are rate constants

As H_2NNO is an unstable species, a steady state approximation may be made, yielding

k_2 [H_3NNO^+][NO_2^-] = k_1[H_2NNO]

and

Rate $N_2 = k_2$ [H_3NNO^+][NO_2^-]

From reaction **5** the change in concentration of [H_3NNO^+] can be described by:

Rate $H_3NNO^+ = k_3$[NH_3][N_2O_3] - k_2[H_3NNO^+][NO_2^-], k_3 and k_2 are rate constants

Again, a steady state approximation may be made yielding another new term for N_2 formation:

Rate $N_2 = k_3[NH_3][N_2O_3]$, where k_3 is a rate constant

From the equilibrium reaction in equation **4** we can derive $[N_2O_3]$:

$[N_2O_3] = K_1 [NO] [NO_2]$, where K_1 is an equilibrium constant

The rate of formation N_2 can be rearranged to give:

Rate $N_2 = k_3K_1[NH_3][NO][NO_2]$

From the equilibrium reaction in equation **3**, [NO] and $[NO_2]$ can be related to $[HNO_2]$ as follows:

$[HNO_2]^2 = K_2 [NO] [NO_2]$, where K_2 is an equilibrium constant

Thus the rate of N_2 formation can be revised to give:

Rate $N_2 = k_3K_1K_2 [NH_3] [HNO_2]^2$

The rate law can be further simplified by adapting it to reflect the ionic species in solution:

$[NH_3] = K_b[NH_4^+][OH^-]$, K_b is a base dissociation constant

$[HNO_2] = K_a[H^+][NO_2^-]$, K_a is an acid dissociation constant

Substituting these into the rate law yields:

$$\text{Rate } N_2 = k_3K_1K_2K_w/K_aK_b\ [NH_4^+]\ [NO_2^-]^2[H^+]$$

where K_w is a dissociation constant of water;

K_a is an acid dissociation constant and

K_b is a base dissociation constant.

The concentration of NH_4^+ below pH 7.0 in a supersaturated solution can be considered constant, resulting in a further simplification of the rate law to:

$$\text{Rate } N_2 = \text{Rate constant } [H^+][NO_2^-]^2$$

This means that the rate of reaction is pH dependent. For this reason the reaction is normally buffered. Ammonium nitrate and sodium nitrite reaction can be buffered with different pH buffers. Citrate, lactate and acetate are commonly used acidic buffers.

Industrially, buffers are specifically used to:

- Reduce flavour variation from two pH effects; that is changes in flavour intensity of flavour chemicals with pH and changes in sourness, sweet/sour balance with pH;
- Decrease variation in colour shade of natural colours;
- Control gelling in pectin-based products.

The sodium nitrite - ammonium nitrate gassing reaction suffers from a drawback that limits its use. The problem is difficulty in controlling the rate of the reaction, the size of gas bubbles generated in the column and slowing down of the reaction at ambient and low temperature. Factors that might affect this are pH, presence of buffers and addition of accelerators.

As nitrogen gas is a product of the reaction, the rate of reaction can be determined by measuring the pressure increase (in a closed vessel) over time until a steady state condition is reached. A plot of the pressure versus time should give a characteristic convex growth curve. The inverse of the pressure difference versus time should result in a straight line graph whose slope represents the rate constant for the reaction under the experimental conditions.

Firstly, a system and apparatus for the ammonium nitrate-sodium nitrite reaction will be designed. In this system the reaction vessel/boiling tube for safety should be able to withstand high pressure and temperature should be kept in a certain temperature that is 25 ºC. Then the effects of varying pH and the presence of different buffers upon the reaction of ammonium nitrate and sodium nitrite will be investigated using the above mentioned methodology. A patent has been filled in respect of this emulsion explosive sensitization reaction in which a Lewis acid such as zinc nitrate is added to the formulation. The effect of this will also be investigated. By understanding the underlying physical chemistry of this process it is hoped that it may be possible to better control the reaction in situ.

2.2 Experimental Methods

The apparatus shown below was designed for the ammonium nitrate-sodium nitrite reaction (shown in **Figure 2.1**). The apparatus consists of a reaction vessel which is attached to a pressure sensor and reaction vessel was evacuated. The pressure sensor is connected to a computer which captures the data as a function of time. By connecting the reaction vessel to a gas bottle, the ambient pressure of the system can also be controlled. This allows the simulation of the conditions at the bottom of a large column of emulsion or in an underground blast hole.

Figure 2.1: Illustration of the apparatus/experimental set up for the ammonium nitrate-sodium nitrite reaction

All experiments (buffered and unbuffered with or without zinc nitrate) were conducted in a ≈ 250 ml metallic reaction vessel fitted with a pressure sensor. The apparatus was, in turn, mounted upon a stirrer assembly in a temperature controlled, insulated cupboard at 25 °C. Shown below are the system and the apparatus that were used.

40.0 ml of saturated, pH adjusted NH_4NO_3 was placed into the reaction vessel along with a small stirrer bar and the reaction initiated by the addition of 4.00 µL of 1M $NaNO_2$ solution. The vessel was quickly sealed, pressure and time readings were recorded. Experiments were typically run for between 10 and 15 hours. The material safety information is outlined in **Appendix A**. Microsoft Excel was used to process and analyse the experimental data. Rate constants were determined by linear regression of plots of $1/(P_{eq} - P_t)$ versus time. Initial rates of reaction were calculated using the known concentrations and the determined rate constants.

2.2.1 Measuring the rate constant and rate of reaction as a function of pH for the unbuffered reaction

Between three and four experiments were conducted for each of the pH values 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0 and 7.0. The pH of the $NaNO_2$ and NH_4NO_3 solutions was adjusted by the addition of either 0.1 M NaOH or 0.1 M HNO_3. The pH of the reaction mixtures was recorded after the reaction was complete. Other data recorded were, pressure, time and pressure change.

2.2.2 Measuring the effect of selected buffers upon the rate constant and rate of reaction.

Three different buffers were evaluated for their ability to affect the gasification reaction. These were potassium hydrogen phthalate ($KHC_8O_4H_4$), sodium citrate ($NaC_6O_7H_5$) and sodium formate ($NaCO_2H$). As the effective buffer range is defined as the pKa ± 1, a number of buffer solutions were prepared. Three experiments were performed for each of the pH ranges described below. Data recorded were initial pH, final pH, pressure change, pressure and time.

2.2.2.1 Potassium Hydrogen Phthalate ($pKa_1 = 2.94$):

A *ca* 0.1 M solution of the $KHC_8O_4H_4$ was made by dissolving 2.04 g in water and diluting to 100.00 ml in a standard volumetric flask. Aliquots of this solution were then adjusted to pH 3.0, 3.5 or 4 using 0.1 M HCl and then used to dissolve NH_4NO_3 until saturated.

2.2.2.2 Sodium Citrate/ Citric Acid ($pKa_1 = 4.07$):

A *ca* 0.1 M solution of $Na_3C_6O_7H_5$ was made by dissolving 2.94 g in distilled water and diluting to 100.00 ml in a standard volumetric flask. Another *ca* 0.1 M solution of $C_6O_7H_8$ was made by dissolving 2.10 g in 100.00 ml of distilled water. Aliquots of the $Na_3C_6O_7H_5$ solution were adjusted to pH 3.0, 3.5 or 4 using the 0.1 M $C_6O_7H_8$ solution. The resultant citrate buffer solution was then used to dissolve NH_4NO_3 until saturated.

2.2.2.3 Sodium Formate/ Formic Acid (pKa = 3.75):

A *ca* 0.1 M solution of $NaCO_2H$ was made by dissolving 0.45 g in a 100.00 ml volumetric flask. The pH of the solution was adjusted by adding CO_2H_2 until at the desired range of 3.0, 3.5 or 4.0. These solutions were then used to dissolve NH_4NO_3 until saturated.

2.2.3 Determining the effect of zinc nitrate on the buffered and unbuffered ammonium nitrate-sodium nitrite reactions

15 % (w/w) zinc nitrate and 7.9% (w/w) sodium nitrite solutions were prepared. The above mentioned methods were followed to prepare the buffered and unbuffered solutions with zinc nitrate. Instead of using 1M solution of $NaNO_2$, 7.9 % (w/w) $NaNO_2$ solution was used and 15 % (w/w) zinc nitrate was added as a last step in the solutions and data were captured.

2.3 Results

Some of the parameters that are known to limit the usage of ammonium nitrate-sodium nitrite reaction gassing reaction were investigated and their results are depicted below: This gassing reaction is known to be sensitive to pH so pH was measured before and after the reaction to see what effect the reaction had on it. Pressure was also measured so that rate of reaction could be calculated or determined. Furthermore zinc nitrate was used on the ammonium nitrate-sodium nitrite reaction gassing reaction as a pH lowering agent.

When conducting these experiments reproducibility was a problem. For an example (**Figure 2.2**), three experiments would be conducted for one reaction at the same pH and same temperature (25 °C) and it would be difficult to obtain the same or similar results for all three experiments. For this reason each reaction had to be repeated several times.

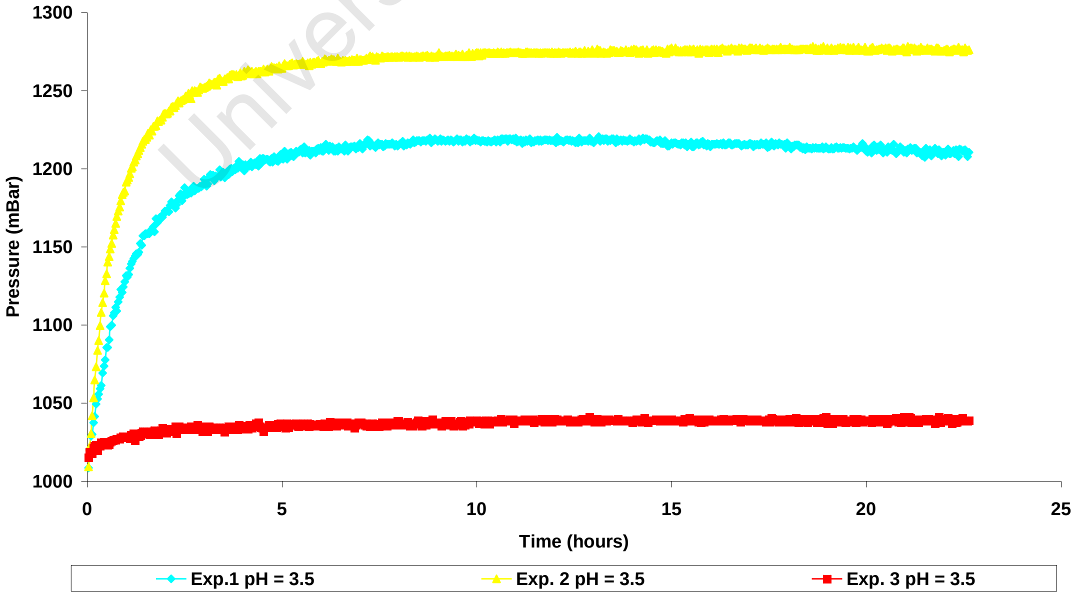

Figure 2.2: A plot of pressure versus time for unbuffered reactions at pH = 3.5

2.3.1 Pressure variation of unbuffered ammonium nitrate-sodium nitrite reaction

Nitrogen gas is one of the products for the ammonium nitrate-sodium nitrite reaction and rate of reaction can be measured using nitrogen gas, so pressure can be used as a parameter to measure the rate constants and rate of the reaction. This will be done by measuring pressure over time. From the pressure results rate constants and rate of the reaction can be calculated.

Typical pressure traces of the different pHs for the unbuffered reaction are depicted in **Figure 2.3**. At pH 2, 2.5 and 3 maximum pressure was reached within 2 hours of starting the reaction, while at pH 3.5 and 4 maximum pressure was reached within 3 and 5 hours (respectively) of starting the reaction. At pH =4.5 and 5 maximum pressure was not reached even after 16 hours of conducting the reaction and this shows that as pH increases it is difficult to attain a stable pressure state.

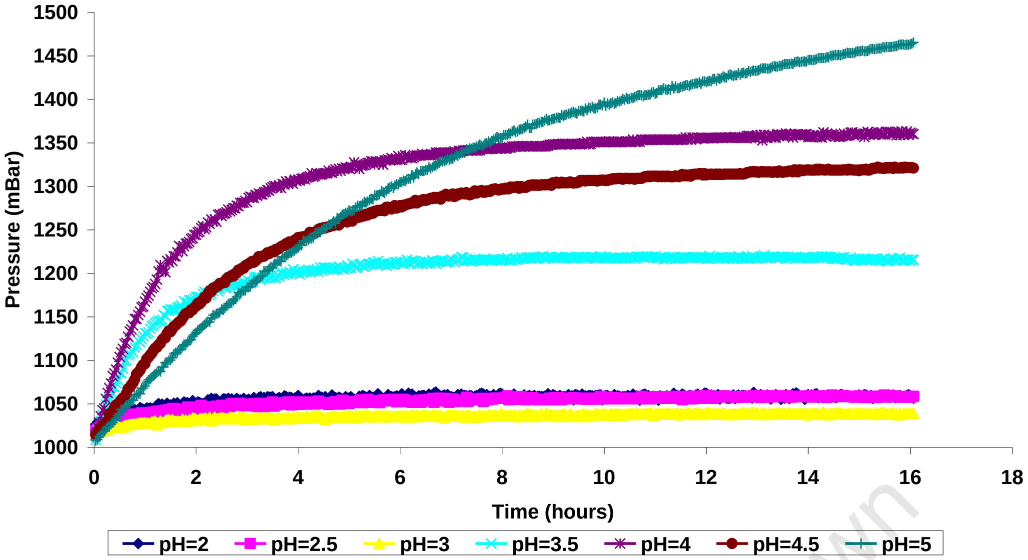

Figure 2.3: *Plot of pressure versus time for unbuffered ammonium nitrate-sodium nitrite reaction*

In Figure 2.4, a plot of the overall pressure change (initial pressure – final pressure) versus pH illustrates that as the pH increases the pressure change (or extent of the reaction) increases as indicated by the red trend line. This was not expected to happen, because at a higher pH there is less H_3O^+ upon which the reaction is dependent therefore at higher pH the pressure change was expected to decrease. There was no significant scatter in the pressure change performed at the same pH.

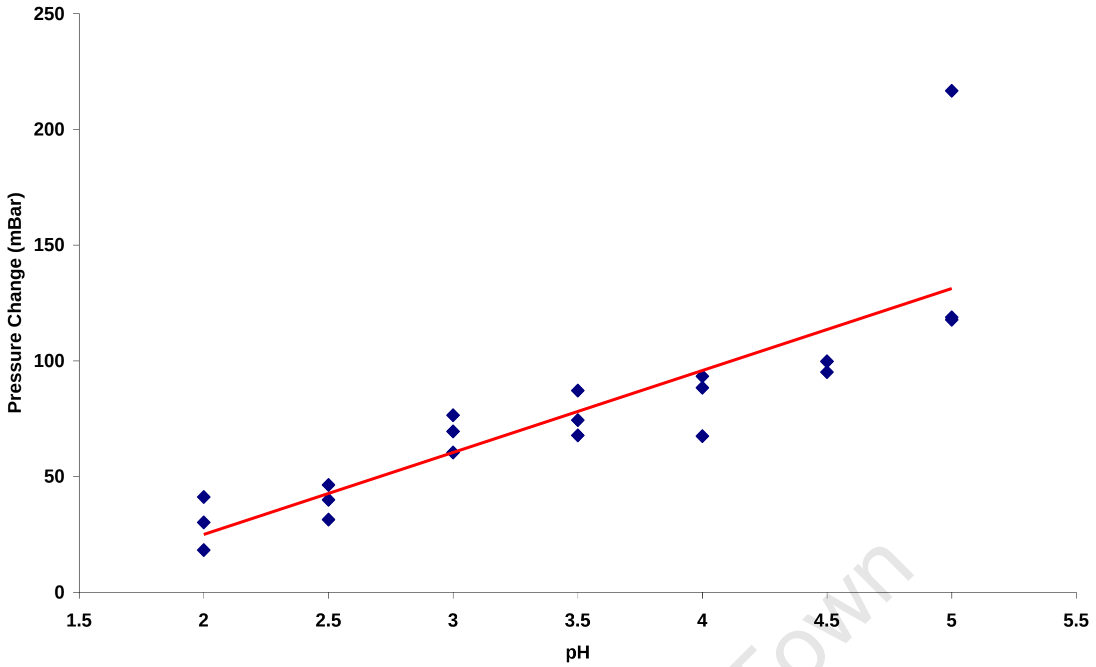

Figure 2.4: *Plot of final pressure – initial pressure (pressure change) versus pH for unbuffered ammonium nitrate-sodium nitrite reaction:*

2.3.2 The effect of unbuffered reactions upon pH

A plot of absolute pH change (difference between initial and final pH) against initial pH (**Figure 2.5**) shows that as the initial pH increases the absolute pH change decreases. This is outcome might be due to the fact that at a higher pH the concentration of H_3O^+ is smaller. Also there is not much absolute pH change variation experienced at the same pH. Although there is much scatter in the results what it does indicate is that, in order to study the reaction the pH has to be buffered.

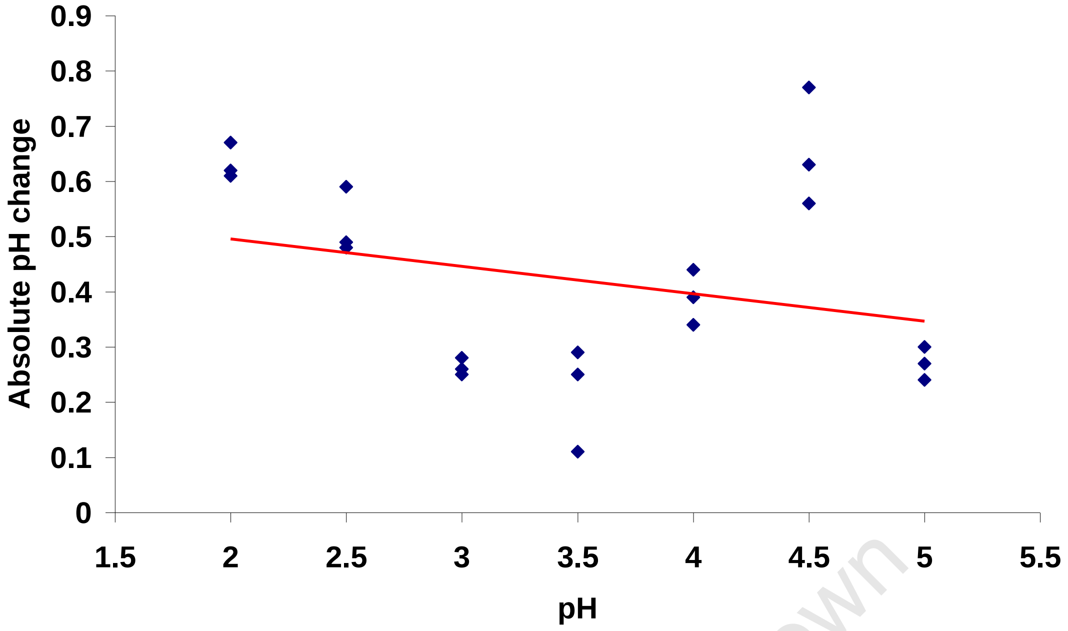

Figure 2.5: *Plot of absolute pH change versus pH for unbuffered ammonium nitrate-sodium nitrite reaction*

2.3.3 Rate Constants of the unbuffered ammonium nitrate-sodium nitrite reaction

Rate constants were calculated by plotting 1/ (P_{inf} – P_t) against time, with the slope of the straight line, obtained by linear regression, equal to the rate constant. A typical plot of 1/ (P_{inf} – P_t) against time is illustrated in **Figure 2.6** where pressure is increasing with time. The straight line means that the reaction is second order with respect to nitrite in agreement with the proposed mechanism.

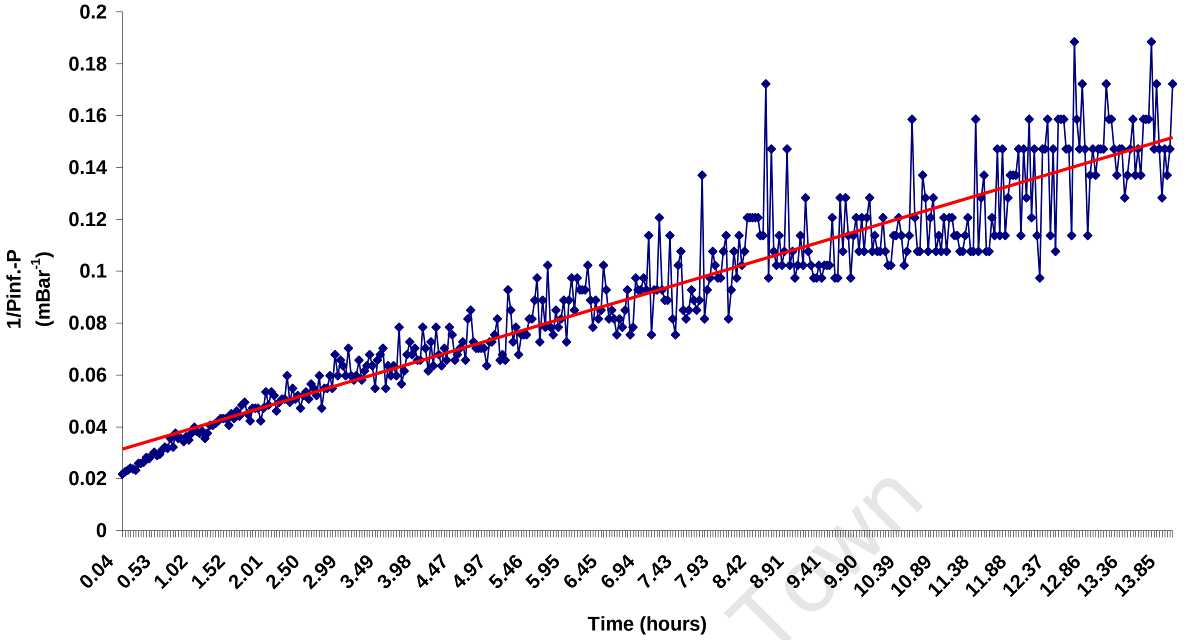

***Figure 2.6:** Typical plot of 1/P_{inf}-P versus time for unbuffered ammonium nitrate-sodium nitrite reaction*

The plot of rate constant versus pH (**Figure 2.7**) shows the run between experimental variation as well as the between pH variation. The rate constant and associated errors are reported in **Appendix B.** As the pH increases, there is no significant change in the rate constant. The regression line of rate constant had a slope of 2.01 E-07 $mBar^{-1}s^{-1}$, an order of magnitude smaller than the range of values determined for the rate constants. Furthermore, the R^2 factor for the regression line was 0.062 indicating that there is no correlation between the pH and the rate constant.

These results support the theoretical treatment of the reaction as outlined by the rate law, which states that the rate constant is independent of pH. With these findings, it can be concluded that there is no correlation between pH and rate constant. The average rate constant was found to be $(4.24 \pm 1.68) \times 10^{-06}$ mBar^{-1}s^{-1}.

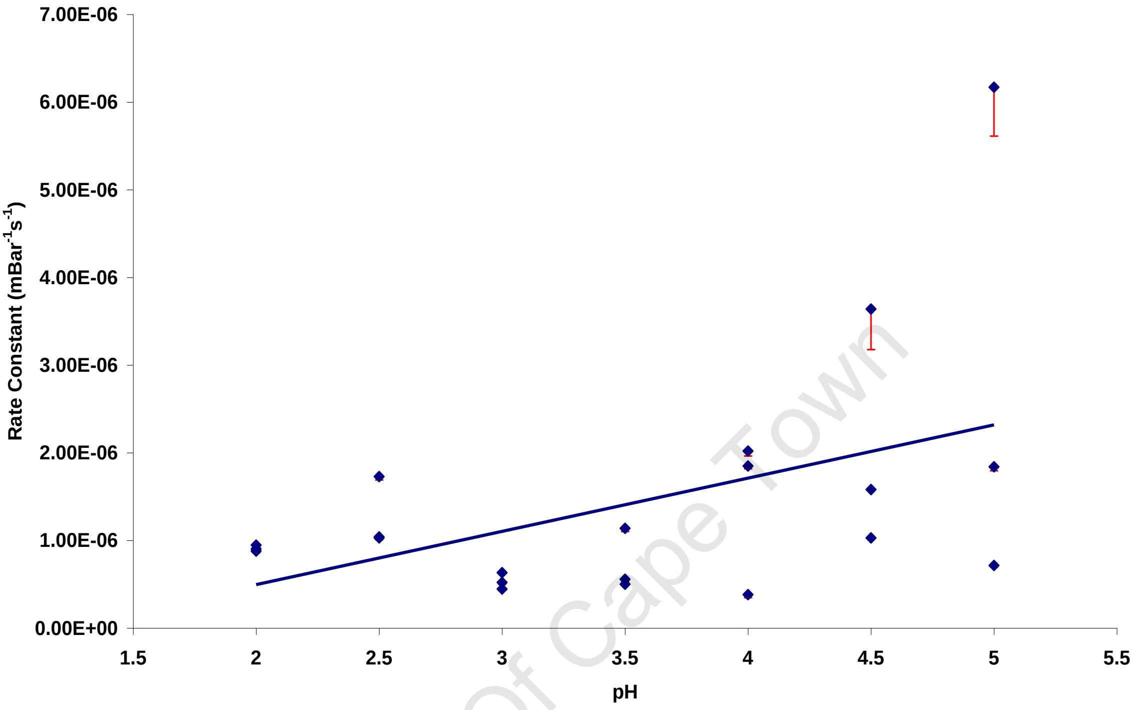

Figure 2.7: *Plot of rate constant and errors bars versus pH for unbuffered ammonium nitrate-sodium nitrite reaction:*

2.3.4 Initial rates of reaction for the unbuffered ammonium nitrate-sodium nitrite reactions

The Rate Law stated below was followed to calculate the rate of the reaction. The initial rates of the reaction were calculated from the rate constants determined in section 3.3 and the known initial concentrations of H^+ and NO_2^-.

$$\text{Rate } N_2 = \text{Rate constant } [H^+][NO_2^-]^2$$

Figure 2.8 illustrates an exponential relationship between initial rate of reaction and pH, with the initial rate of reaction decreasing as the pH increases. Below pH 3.0 the reaction was fast while at pH above 3.5 the reaction was slow. The red trend line shows the plot of the theoretical rate of reaction versus pH calculated using the average rate constant. These two exponential trend lines are very similar and are clearly showing that it is possible to use the rate constant to predict the outcome of reactions under specific conditions.

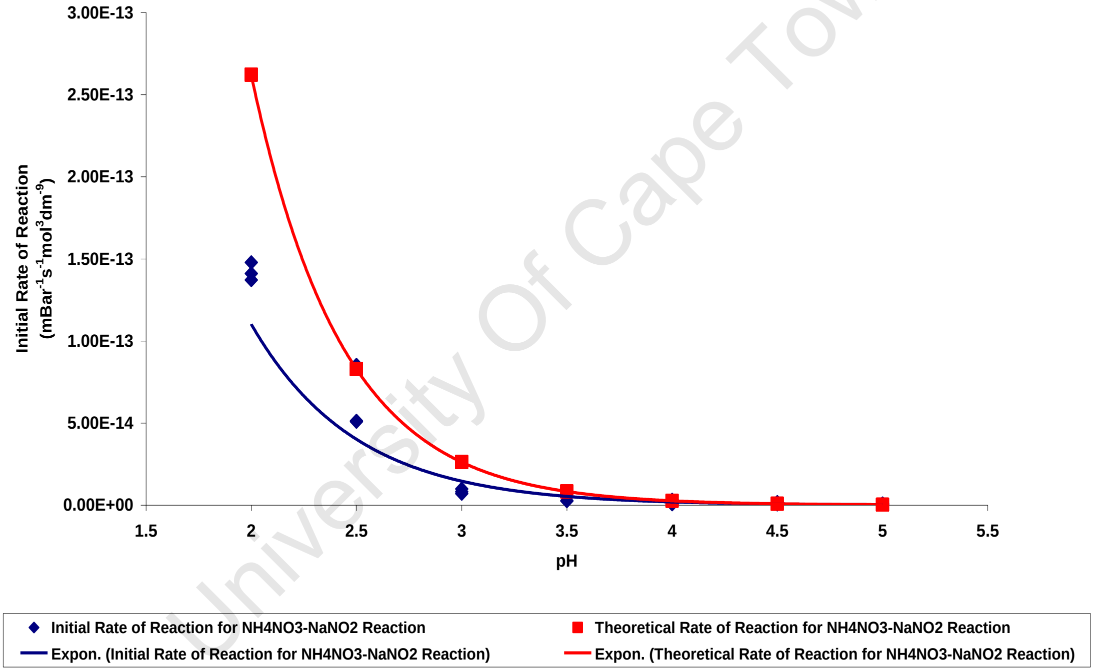

Figure 2.8: *Plot of initial rates of reaction versus pH for unbuffered ammonium nitrate-sodium nitrite reaction*

2.3.5 Gasification rates for buffered ammonium nitrate-sodium nitrite reactions

The rate of the ammonium nitrate sodium nitrite reaction is pH dependent and for this reason the reaction should be buffered. Ammonium nitrate-sodium nitrite reaction was buffered using three different buffers (potassium hydrogen phthalate, sodium formate and sodium citrate). These buffered reactions were investigated and their results are depicted in the following figures:

2.3.5.1 Effect of buffered ammonium nitrate- sodium nitrite reactions on pressure

Pressure was measured over time at three different pHs (3, 3,5 and 4) for the three different buffers; a diagram of the pressure findings is shown below (**Figure 2.9**, **Figure 2.10** and **Figure 2.11**). At pH = 3 it was found that all three buffered reactions had reached maximum pressure within 3 hours of starting the reaction and in all three reactions pressure had reached a steady state, that is a plateau was reached. Even though phthalate buffer had reached the maximum pressure, it showed a noticeably slower rate of pressure increase and formate buffer had the fastest rate pressure increase.

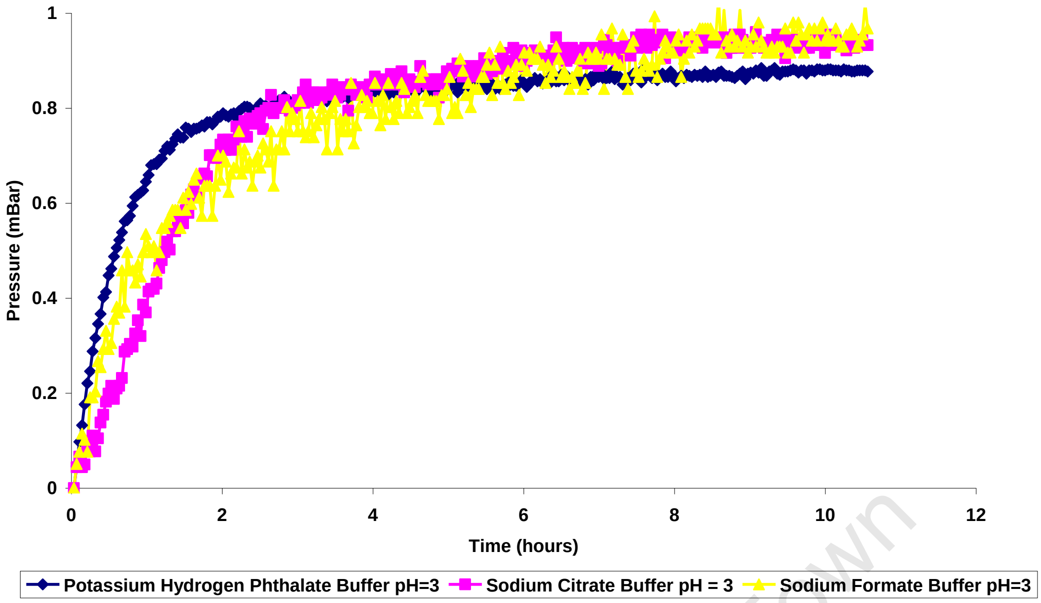

Figure 2.9: *A plot of pressure versus time for buffered ammonium nitrate-sodium nitrite reaction at pH =3.*

Three gasification reaction experiments were conducted for the buffered ammonium nitrate-sodium nitrite at pH=3.5. The pressure traces for these reactions are depicted in **Figure 2.10**, and are characterised by a slower increase in pressure until reaching a plateau for the citrate buffer. With regards to phthalate and formate buffers the pressure had not reached a steady state and this leads to a maximum pressure not being reached even after 10 hours of conducting the reaction.

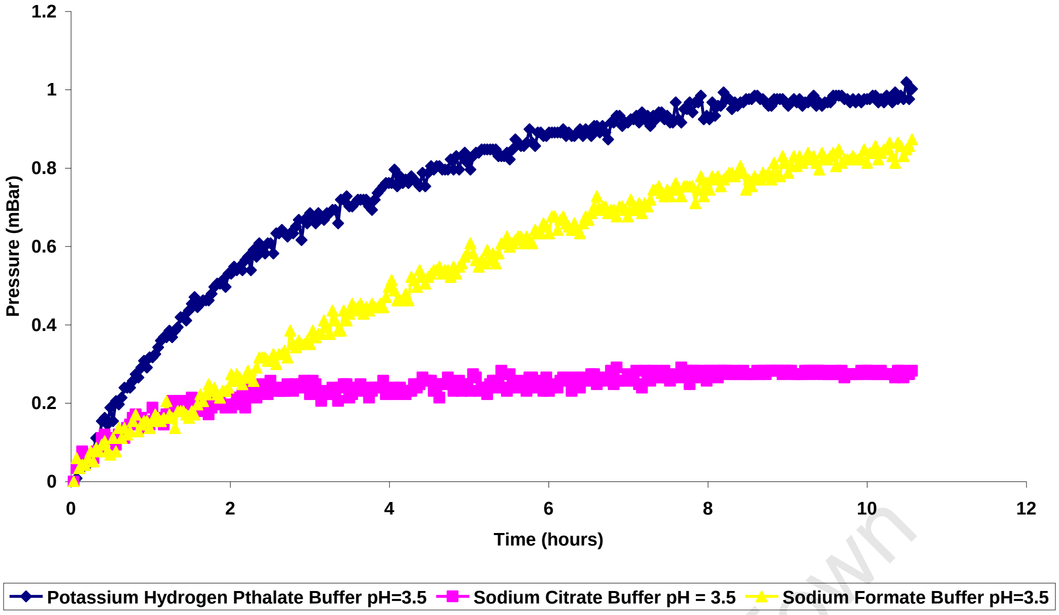

Figure 2.10: *A plot of Pressure versus Time for buffered ammonium nitrate-sodium nitrite reaction at pH =3.5*

Pressure traces for the buffered ammonium nitrate-sodium nitrite at pH = 4 are shown below (**Figure 2.11**). Formate buffer had not reached a maximum pressure and the reaction was continuing even after 10 hours, while citrate buffer had reached a steady state and maximum pressure. The pressure increase for phthalate buffer took place very slowly and after 5 hours a maximum pressure was attained and stable pressure was reached. This demonstrates that at a higher pH the reaction becomes slow or it takes a while to attain a maximum pressure or even to reach the plateau.

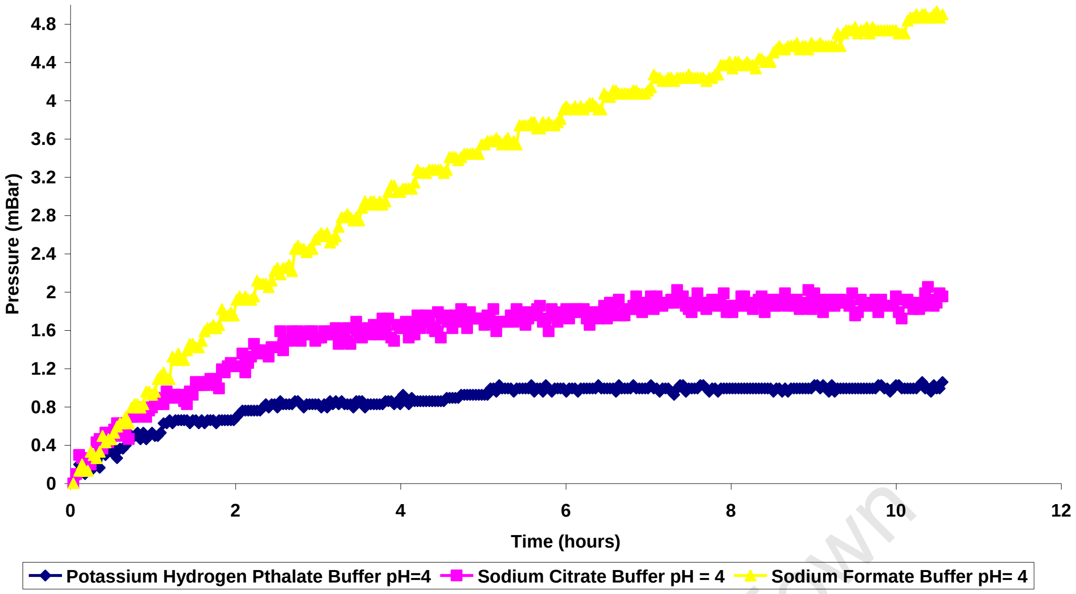

Figure 2.11: *A plot of Pressure versus Time for buffered ammonium nitrate-sodium nitrite reaction at pH =4.*

2.3.5.2 Effect of buffered ammonium nitrate-sodium nitrite reactions on the pressure changes

Since the same amount of reactant was used in each experiment, the final pressure increase can be used as an indication of the extent of the reaction. It is not absolute because the time taken to seal the reaction vessel may differ between experiments. A plot of pressure change against pH demonstrated that the overall pressure change decreased with an increasing pH for phthalate and citrate buffers. Citrate buffer had the least pressure increase at pH = 3.5 while on average formate and phthalate buffers had the same pressure increase. At pH = 4 formate buffer had a slightly larger average pressure increase compared to the citrate and phthalate buffers as shown in **Figure 2.12**. In this case the higher the pressure change is, the slower the reaction and vice versa. The buffers had a linear relationship with the pH and by looking at the scatter plot for the buffered reactions the change in pressure is inversely proportional to the pH.

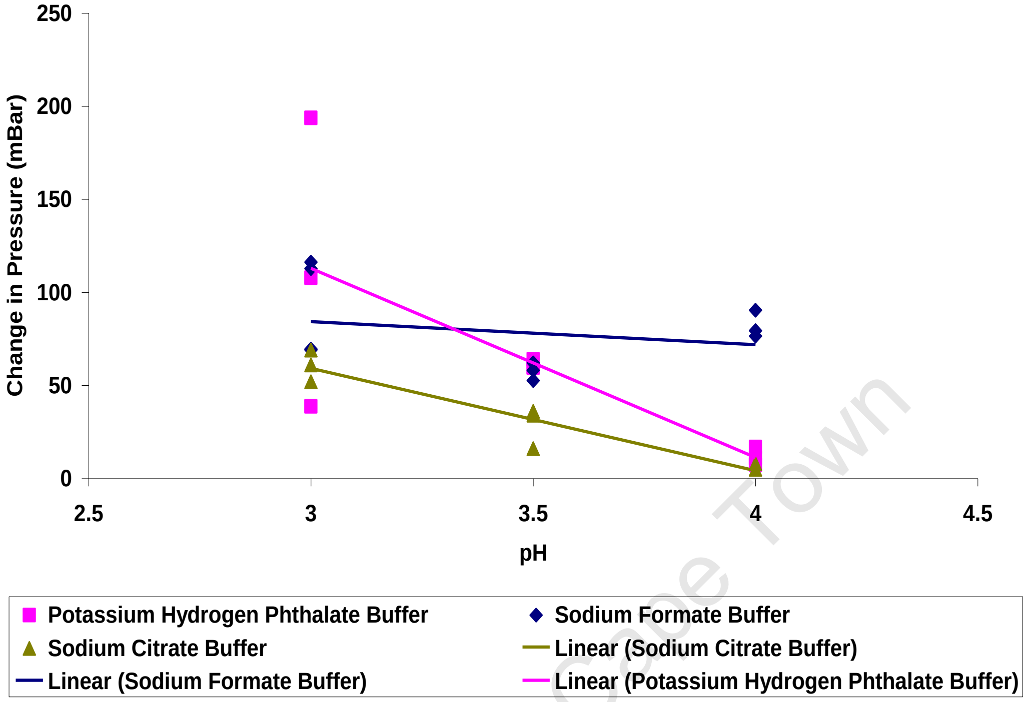

Figure 2.12: *Plot of pressure change versus pH for buffered ammonium nitrate solutions reacting with sodium nitrite:*

2.3.5.3 Effect of buffered ammonium nitrate-sodium nitrite reactions upon pH

Since pH is critical to the rate of reaction, the ability of the different buffers to control the pH was investigated. The pH was measured before and after the reaction. The pH change was determined by subtracting initial pH from final pH and this was done to see how much does the pH changes during the reaction. The pH change versus initial pH results are depicted in **Figure 2.13**. The formate buffer (pKa = 3.75) was best able to buffer the pH at 3.5 rather than 3.0 and 4.0. In the case of the citrate buffer (pKa = 4.07) the pH changes were found to be smaller at pH = 3 and larger at pH = 3.5. At pH = 3 and 3.5 the phthalate buffer had larger pH changes and this was unexpected since it has a pKa value of 2.94 and as pH increases the change in pH decreases. These results indicate that, at the concentrations of buffer used, which is typically higher than industrial concentrations, the pH still changed.

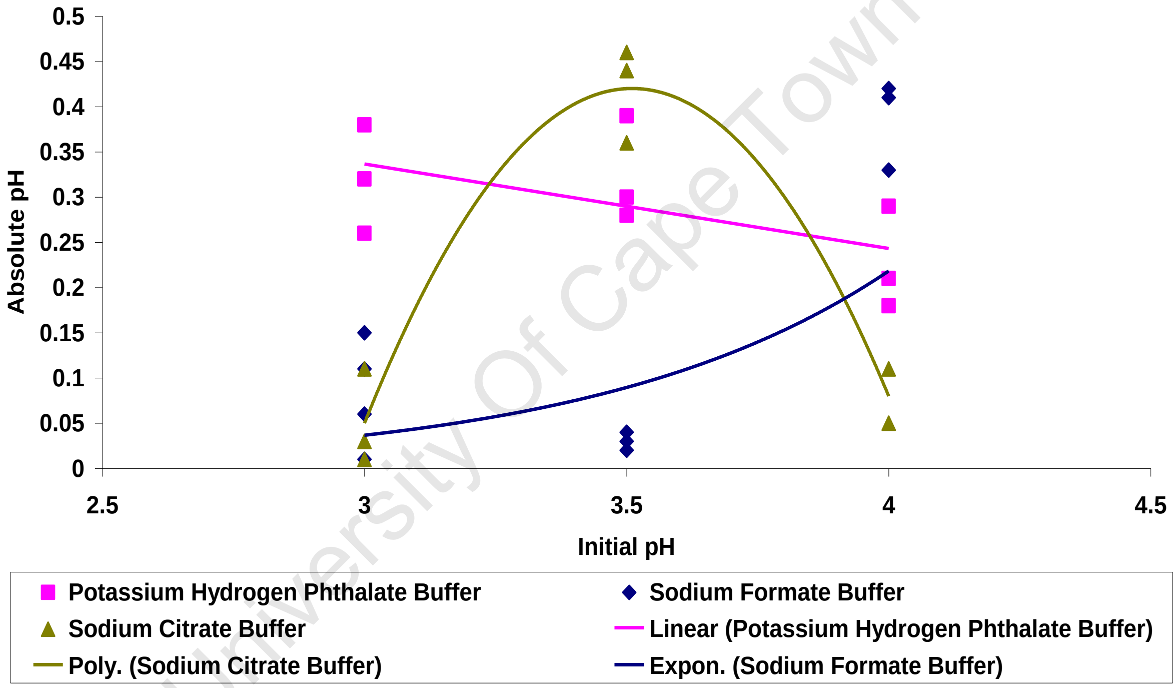

Figure 2.13 *Plot of absolute pH versus pH for buffered ammonium nitrate solutions reacting with sodium nitrite:*

2.3.5.4 Rate constants for the buffered ammonium nitrate-sodium nitrite reactions

The buffered solutions had similar average rate constants at the measured pHs. As pH increases the rate constants were found to decrease as indicated by the trend lines of formate and phthalate buffers and slightly increasing for citrate buffer as shown in **Figure 2.14.**

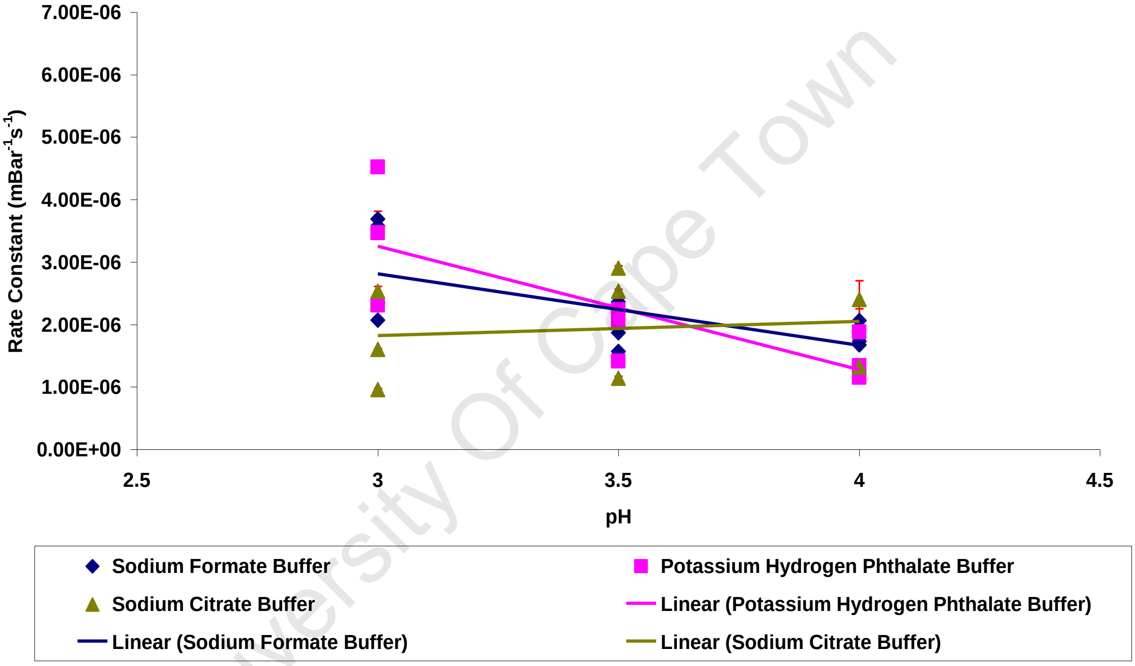

Figure 2.14: *Plot of rate constants and error bars versus pH for buffered ammonium nitrate solutions reacting with sodium nitrite*

2.3.5.5 Initial rate of reaction for the buffered ammonium nitrate-sodium nitrite reaction

Figure 2.15, a plot of initial rates of reaction versus pH clearly shows that there is an exponential relationship, with the rates of reaction decreasing with an increasing pH. At pH = 3 the reactions were fast and below pH = 3 they were found to be slow. There is also very little difference between the different buffered solutions. The initial rate of reaction and associated rate errors are reported in **Appendix C**.

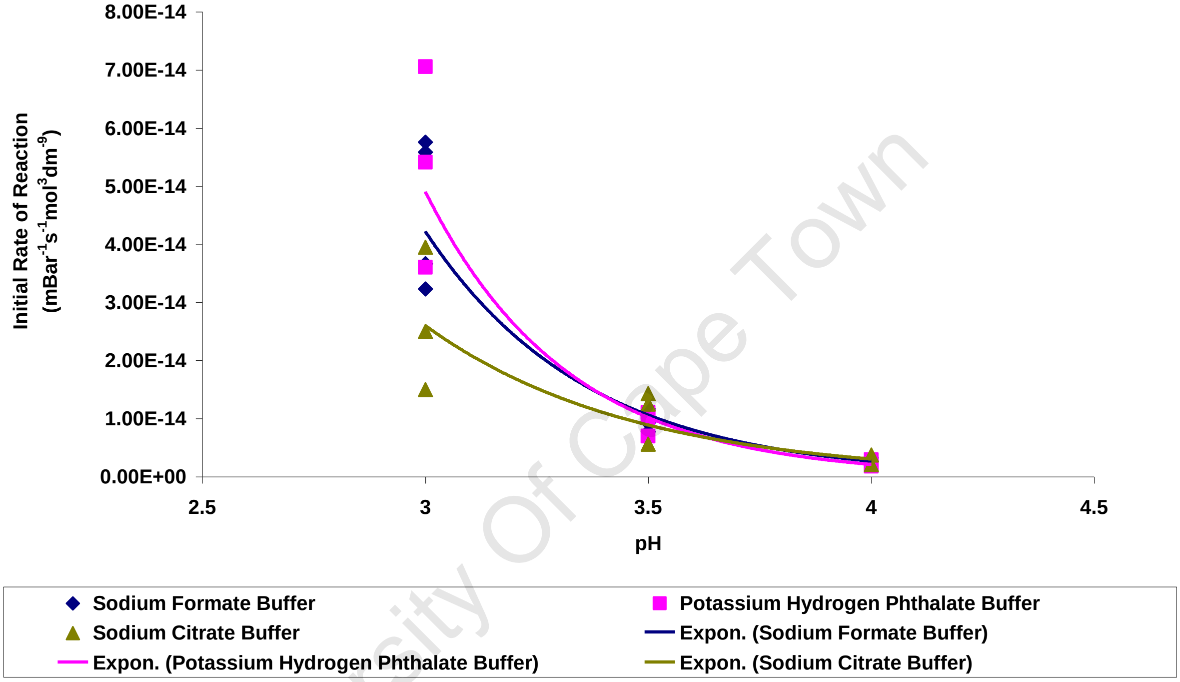

Figure 2.15: *Plot of initial rate of reaction versus pH for buffered ammonium nitrate solutions reacting with sodium nitrite:*

2.3.6 Effect of the Lewis Acid (Zinc Nitrate) on buffered and unbuffered ammonium nitrate-sodium nitrite reactions

Zinc nitrate was added to the buffered and unbuffered ammonium nitrate-sodium nitrite reactions as a pH lowering agent to see whether it would have an effect on pH and also if it would affect the other parameters of the reactions.

2.3.6.1 Pressure variation on buffered and unbuffered reactions with zinc nitrate

Pressure traces for the buffered and unbuffered ammonium nitrate-sodium nitrite reactions over time are illustrated below (**Figure 2.16**, **Figure 2.17** and **Figure 2.18**). At pH = 3 unbuffered and citrate buffer reactions had reached maximum pressure within 2 to 3 hours of starting the reaction and the pressure had reached a stable state (**Figure 2.16**). Formate and phthalate buffers did not reach maximum pressure even after 12 hours of conducting the reaction a plateau that is stable pressure was not attained.

At pH = 3.5 (**Figure 2.17**), phthalate and citrate had similar pressure traces and maximum pressure was reached after 4 hours of starting the reaction. In the case of unbuffered ammonium nitrate-sodium nitrite reaction there was an initial rapid increase in pressure and maximum pressure, in the form of the trace reaching a plateau was attained. In comparison to the previous reactions, the pressure traces for reactions of the formate buffer show a noticeably slower rate of pressure increase. In addition, it is also clear that the pressure did not reach a steady state, and that consequently maximum pressure is not achieved even after 16 hours of reaction.

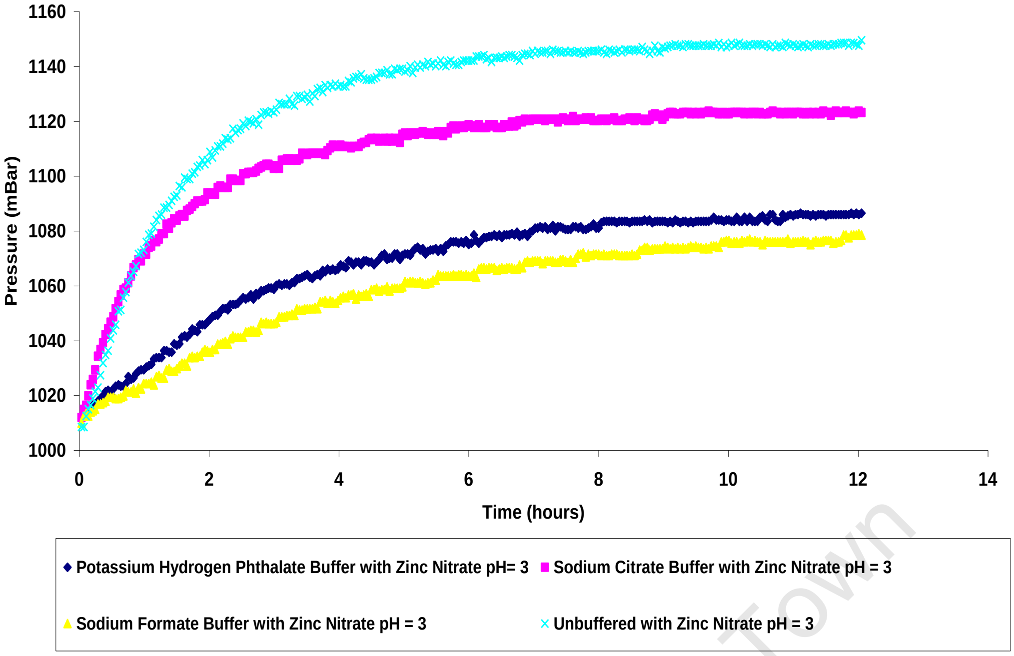

Figure 2.16: *Pressure traces for buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate at pH = 3*

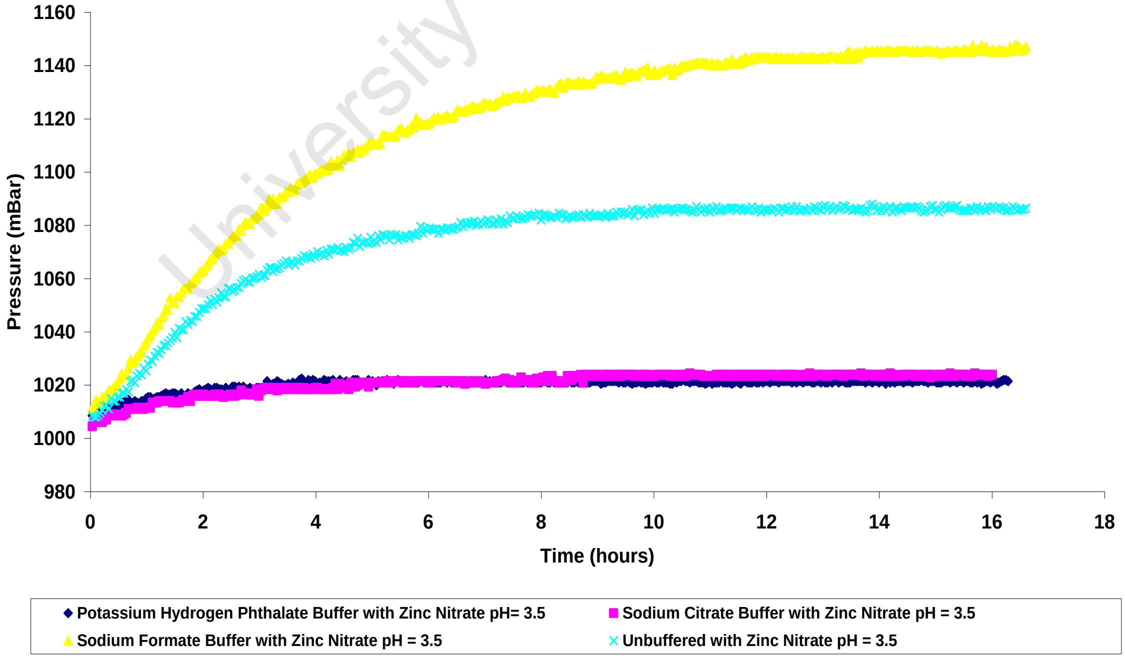

Figure 2.17: *Pressure traces for buffered and unbuffered* ammonium nitrate-sodium nitrite *reactions with zinc nitrate at pH = 3.5*

Gasification reactions for buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate at pH = 4 are shown below (**Figure 2.18**). All the experiments both buffered and unbuffered ammonium nitrate-sodium nitrite reactions had displayed an increase in pressure in different stages or intervals. For example, with phthalate buffer maximum pressure was reached after 3 and 7 hours respectively then a stable state was attained after 8 hours. For the formate buffer and unbuffered experiments the pressure kept on increasing and no stable state was reached. For citrate buffer a steady state was achieved after 3 hours.

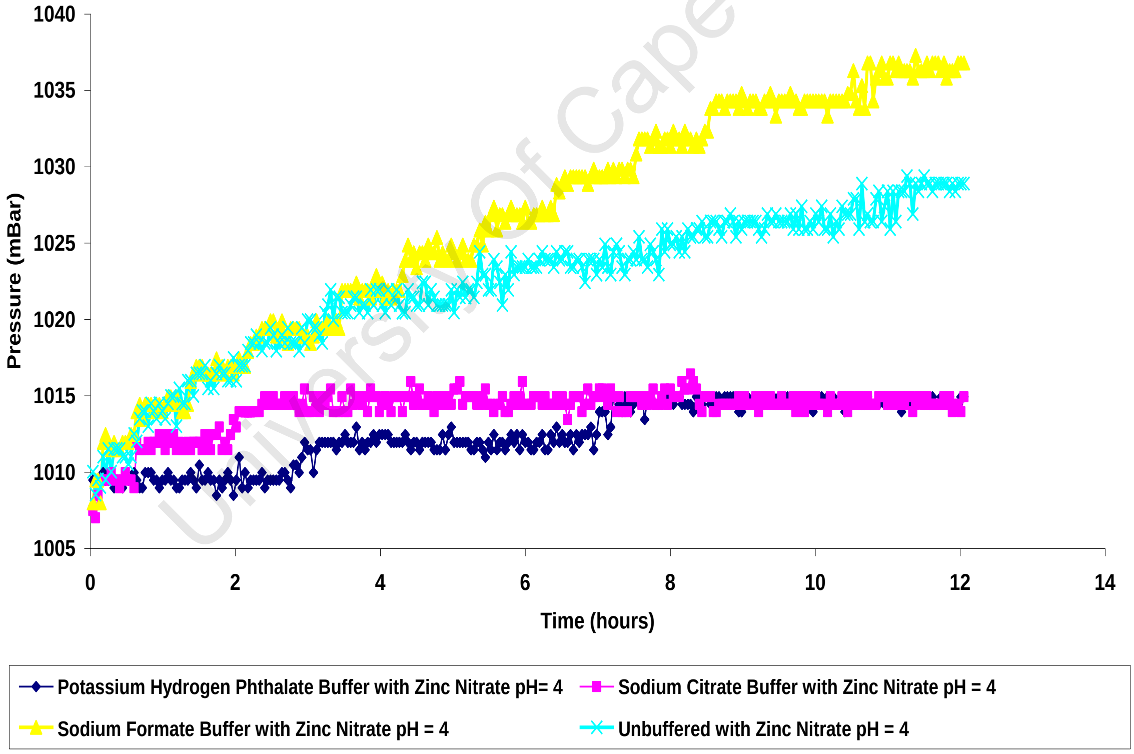

Figure 2.18: *Pressure traces for buffered and unbuffered* ammonium nitrate-sodium nitrite *reactions with zinc nitrate at pH = 4*

2.3.6.2 Pressure changes on the buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate

A plot of pressure change against pH for buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate is shown below (**Figure 2.19**). Citrate and phthalate buffers had the least overall pressure change at all the measured pHs as compared to formate buffer. Unbuffered reactions had a largest pressure increase at pH = 3 and 3.5. In addition, the pressure change decreased with increasing pH (shown by the downward trend lines). Overall the average pressure increase clearly indicates that the unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate result in a greater total pressure change than the buffered ammonium nitrate-sodium nitrite reactions with zinc nitrate at equivalent pH. This suggests that in terms of extent of the reactions, the addition of the Lewis Acid had made a difference on the buffered ammonium nitrate-sodium nitrite reactions than the unbuffered ammonium nitrate-sodium nitrite reactions.

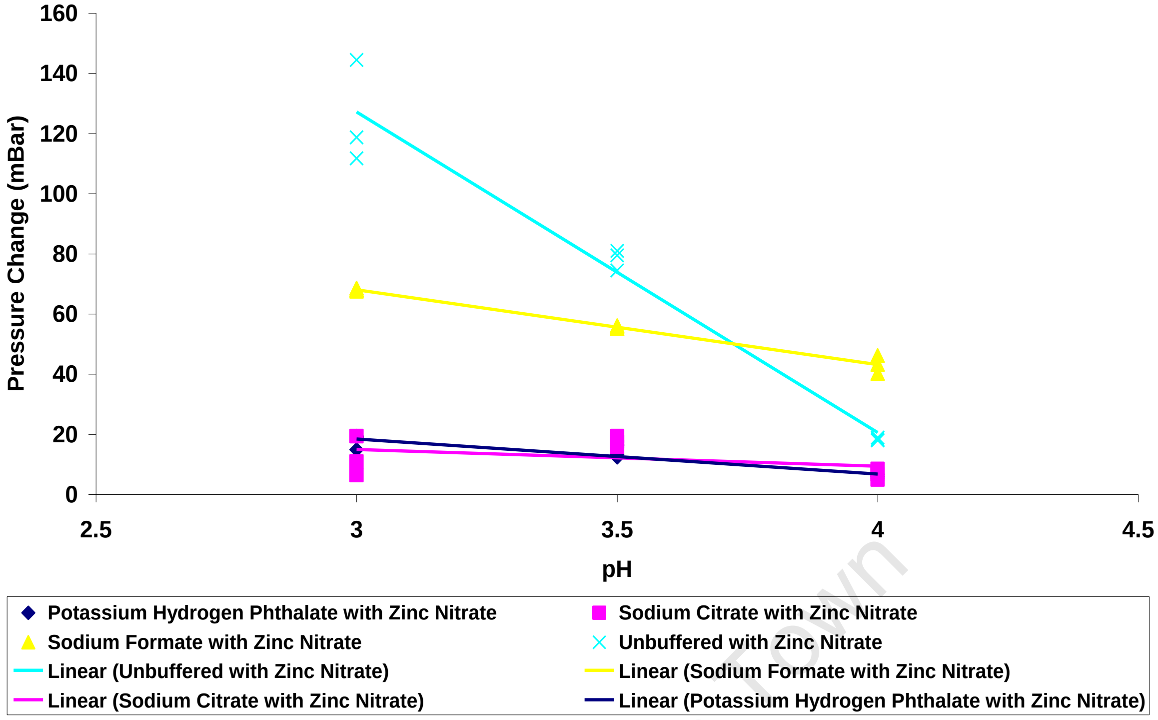

Figure 2.19: *Plot of change in pressure versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite and zinc nitrate*

2.3.6.3 Effect of the buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate upon pH

pH was measured before and after the reactions and **Figure 2.20** illustrates the results of the buffered and unbuffered reactions with zinc nitrate. There was a variation in the overall pH change. Unbuffered reactions had a significantly small pH change at all the pHs measured. For the buffered reactions, the citrate buffer had a greater overall absolute pH change compared to the phthalate and formate buffers and as the pH increases the absolute pH decreases (shown by the trend lines). This is most likely due to the complexation of the Zn(II) by the citrate as opposed to the phthalate and formate buffers.

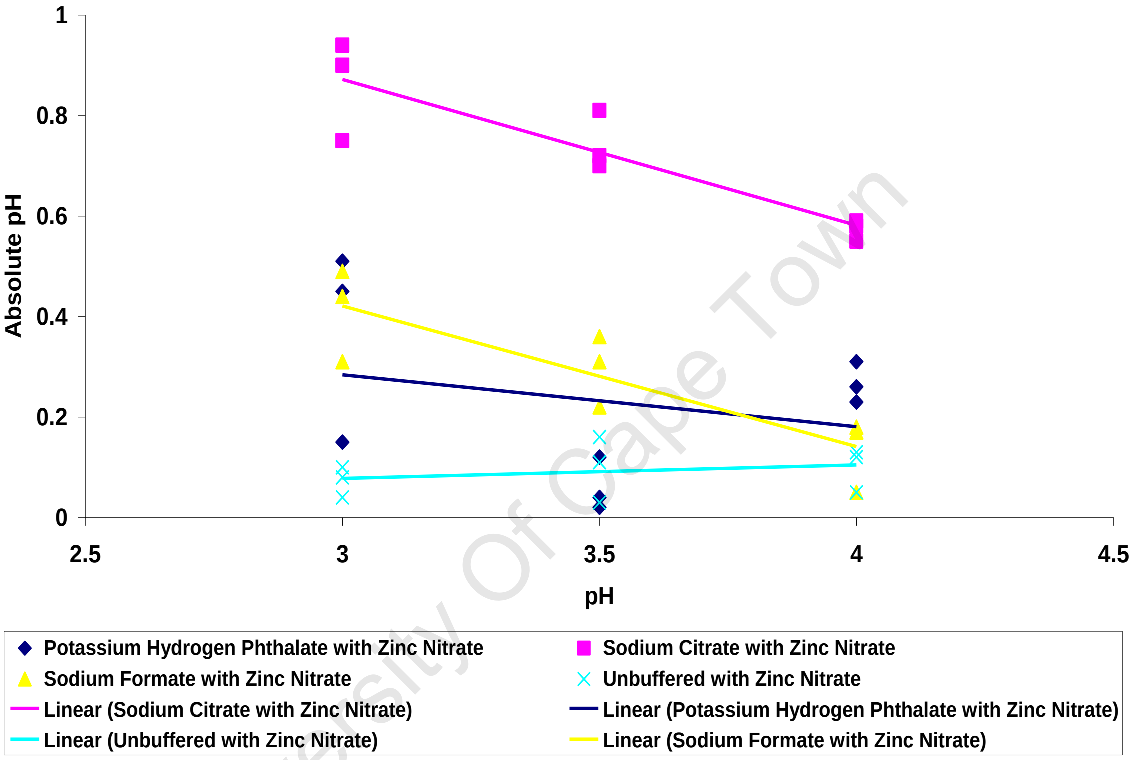

Figure 2.20: *Plot of absolute pH versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite and zinc nitrate*

2.3.6.4 Rate constants for the buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate

Rate constants were calculated using the gasification reactions results obtained in section 2.3.6.2. The rate constants and associated errors are reported in **Appendix C**. **Figure 2.21**, a plot of the rate constants versus pH and trendlines for both buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate, clearly shows that the buffered experiments have greater rate constants (faster reaction) than the unbuffered reactions. At pH = 3 formate, phthalate and citrate buffered solutions had a greater rate constants as compared to the unbuffered solutions while at pH = 4 citrate had shown a greater rate constant. At pH = 3.5 the buffered solutions were indiscernible from the unbuffered solutions.

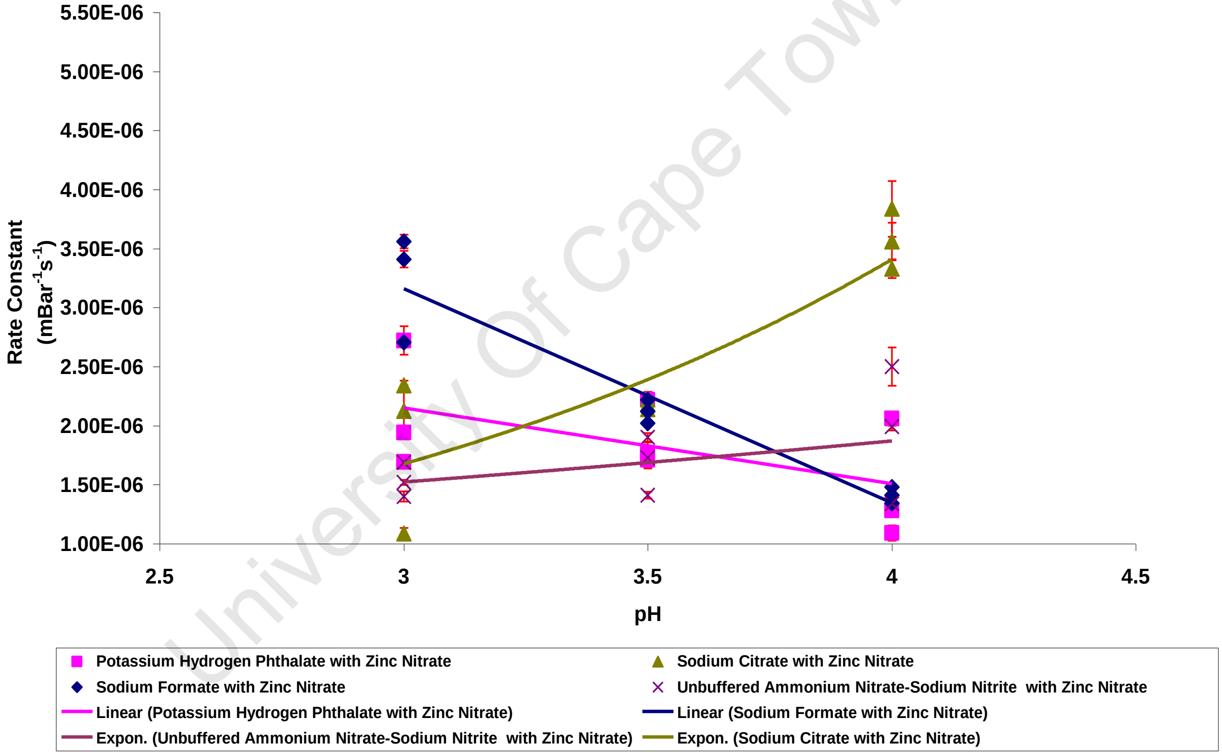

Figure 2.21: *Plot of calculated rate constants and error bars versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite and zinc nitrate*

2.3.6.5 Initial rate of reaction for the buffered and unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate

The initial rates of reaction were calculated from the rate constants determined in section 2.3.6.4. The calculated initial rates of reaction and their associated errors are reported in **Appendix D**.

Plots of the initial rate of reaction versus pH are shown in **Figure 2.22**, which clearly indicates that reactions of the buffered ammonium nitrate-sodium nitrite reaction with zinc nitrate were much faster than the unbuffered ammonium nitrate-sodium nitrite reaction with zinc nitrate reactions. However both the buffered and unbuffered reactions displayed an exponential relationship and the rate of reaction was found to be decreasing as the pH increased.

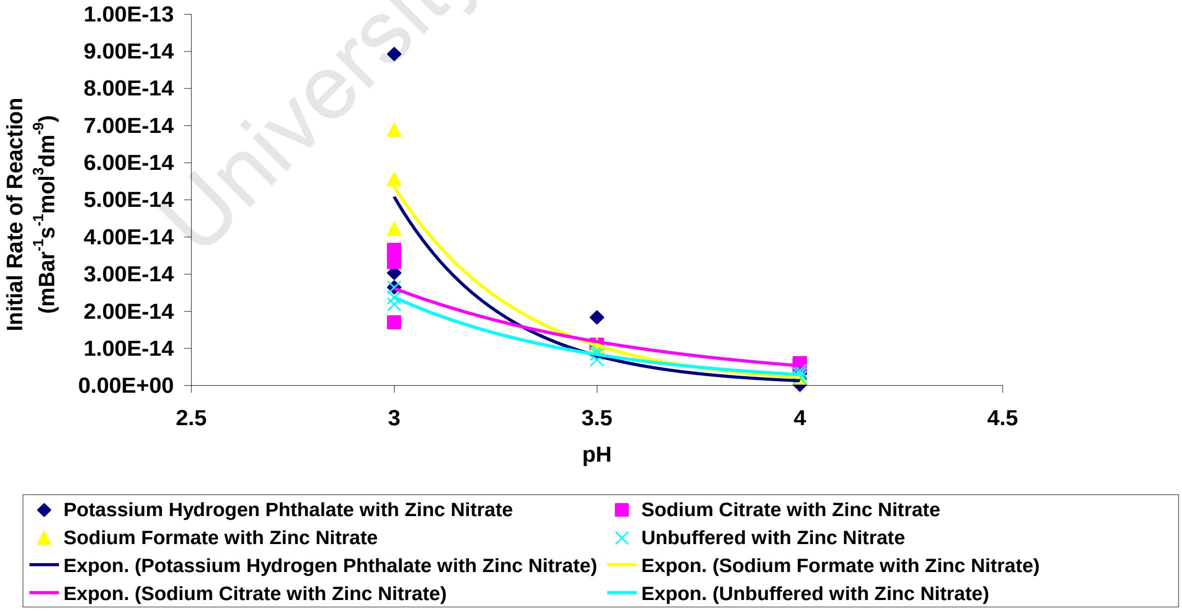

Figure 2.22: *Plot of rate of reaction versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite and zinc nitrate.*

2.4 Discussion

For purposes of comparing the results for the buffered and unbuffered ammonium nitrate-sodium nitrite gassing reactions are reported below, they are illustrated graphically.

Nitrogen gas is the product of the ammonium nitrate-sodium nitrite gassing reaction. One of the reasons for conducting this study was to try and measure the rate at which nitrogen gas is produced. This means that nitrogen gas can be measured through pressure increase over time and from pressure measurements the rate of the reaction can be calculated using pressure results.

2.4.1 Gasification reactions (Pressure traces and pH results) for buffered and unbuffered ammonium nitrate-sodium nitrite gassing reaction

Figures 2.23, 2.24 and 2.25 illustrate plots for pressure over time for buffered and unbuffered ammonium nitrate-sodium nitrite reactions at pH = 3, 3.5 and 4 respectively. **Figure 2.23** clearly shows that all the reactions at pH = 3 had reached maximum pressure within 3 hours of starting the reaction and that a stable pressure was reached. The diagram illustrates that unbuffered ammonium nitrate-sodium nitrite reactions had attained maximum pressure increase faster as compared to the buffered ammonium nitrate-sodium nitrite reactions.

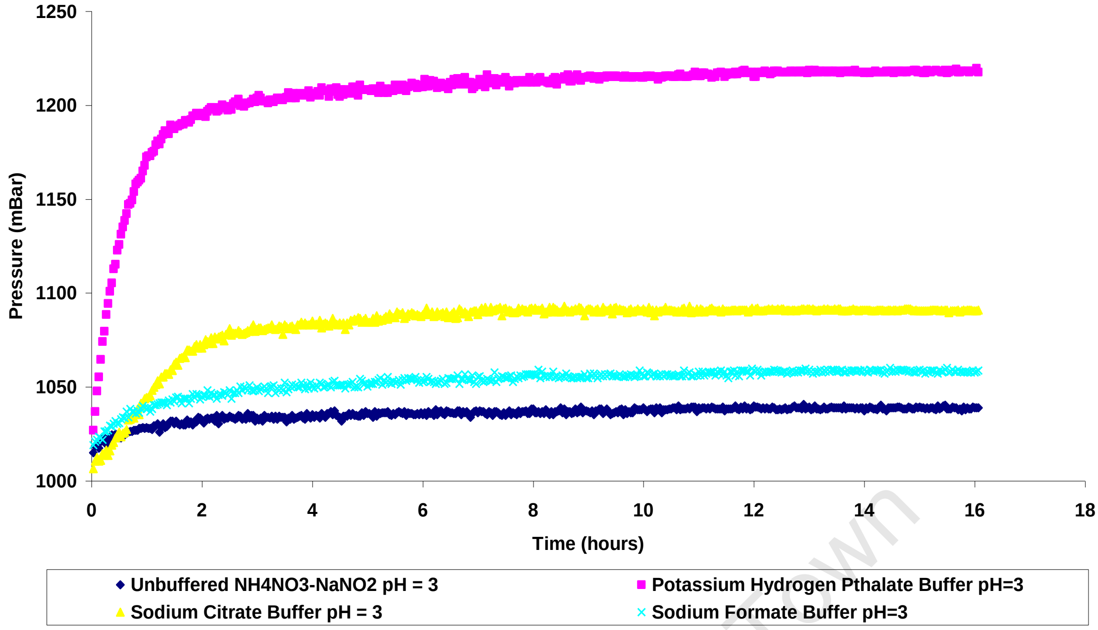

Figure 2.23: *Plot of pressure versus time for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite at pH = 3*

An inverse of what had occurred at pH = 3 was observed at pH 3.5 and pH = 4, that is buffered ammonium nitrate-sodium nitrite reactions had a rapid rate pressure increase over unbuffered ammonium nitrate-sodium nitrite reactions, however only citrate buffer and unbuffered reactions had reached maximum pressure at pH 3.5 (**Figure 2.24**). At pH = 4 (**Figure 2.25**) reactions for formate buffer showed that the reaction was still continuing without reaching maximum pressure and this led to a plateau not being reached.

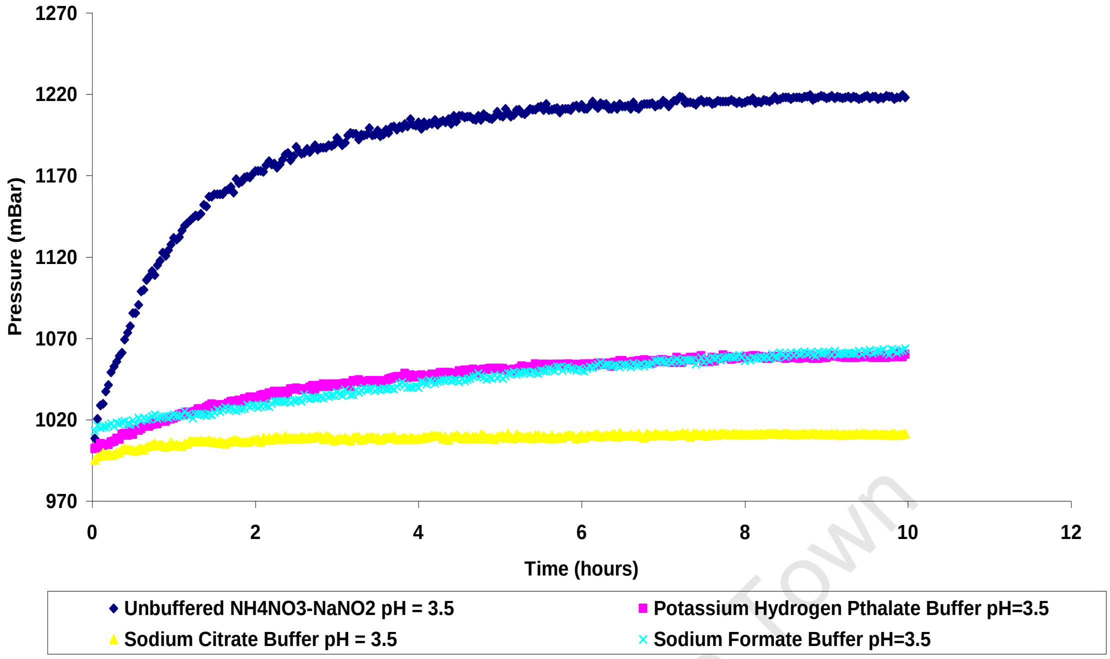

Figure 2.24: *Plot of pressure versus time for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite at pH = 3.5*

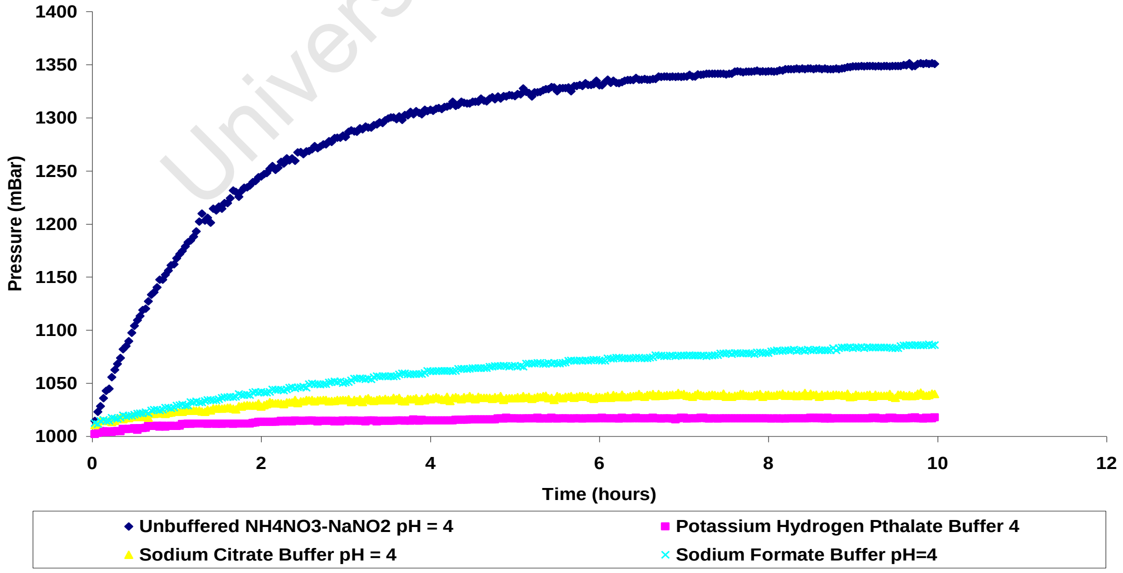

Figure 2.25: *Plot of pressure versus time for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite at pH = 4*

These above gasification rates clearly show that buffering the ammonium nitrate-sodium nitrite reaction has an effect in pressure and its rate. As pH increases the rate of pressure slows down for unbuffered reactions, while for buffered reactions the rate of pressure increase was rapid as pH increases. Furthermore, buffered ammonium nitrate-sodium nitrite reactions had an overall pressure change that was lower than that of unbuffered ammonium nitrate-sodium nitrite reactions (**Figure 2.26**).

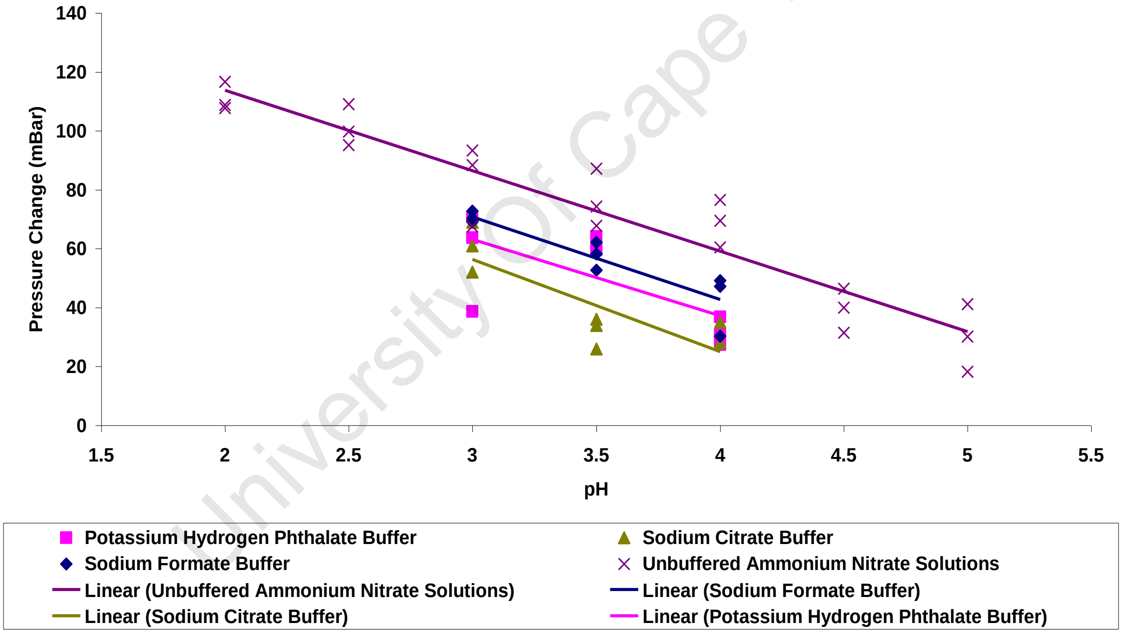

Figure 2.26: *Plot of pressure versus time for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite*

The pH changes for the unbuffered reactions did not show much difference compared to the buffered solutions at the pH investigated as shown in **Figure 2.27**. It was expected that buffering the ammonium nitrate-sodium nitrite reaction would result in a smaller difference or change to the unbuffered ammonium nitrate-sodium nitrite reaction and that was not the case. It is suggested that measuring the pH during the reaction would be an advantage in understanding the reaction and the interaction between the reactants and buffers.

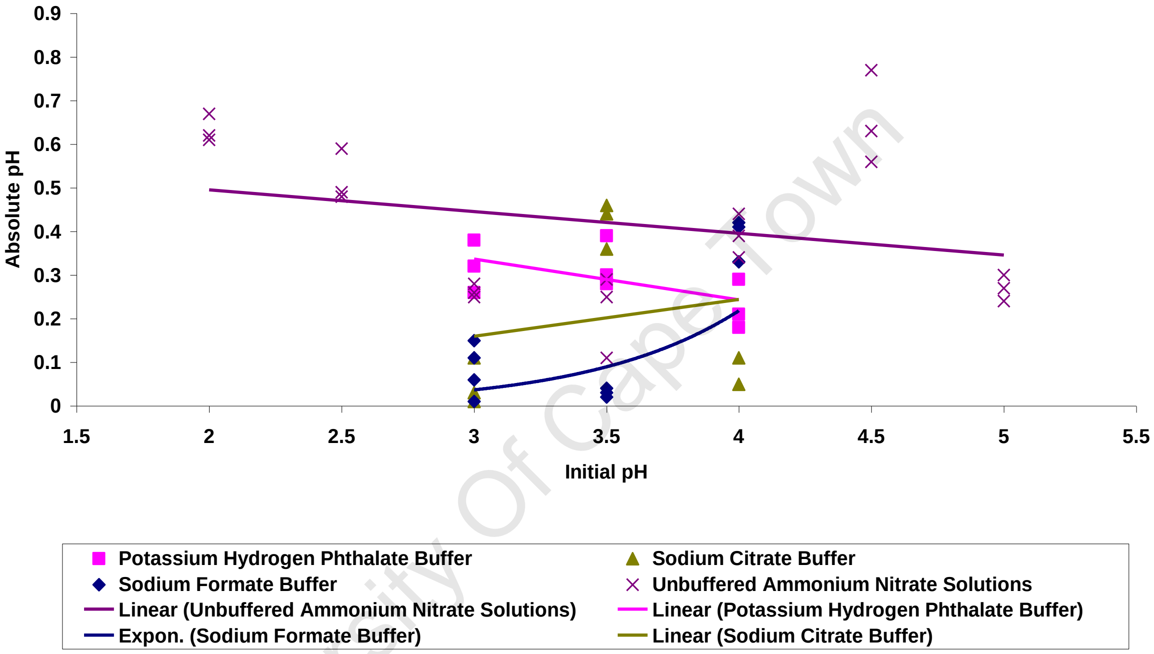

Figure 2.27: *Plot of Absolute pH change versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite*

2.4.2 Rate constants and initial rate of reaction for buffered and unbuffered ammonium nitrate-sodium nitrite gassing reaction

The rate constants for the unbuffered experiments showed a variation similar to the buffered experiments shown in **Figure 2.28**. However, the rate constants for the three buffers (citrate, formate and phthalate) were found to be greater at the pH's that were investigated (i.e. pH = 3, 3.5 and 4) compared to the unbuffered solutions. This evidently shows that buffering the ammonium nitrate solutions has an effect in the rate of reaction.

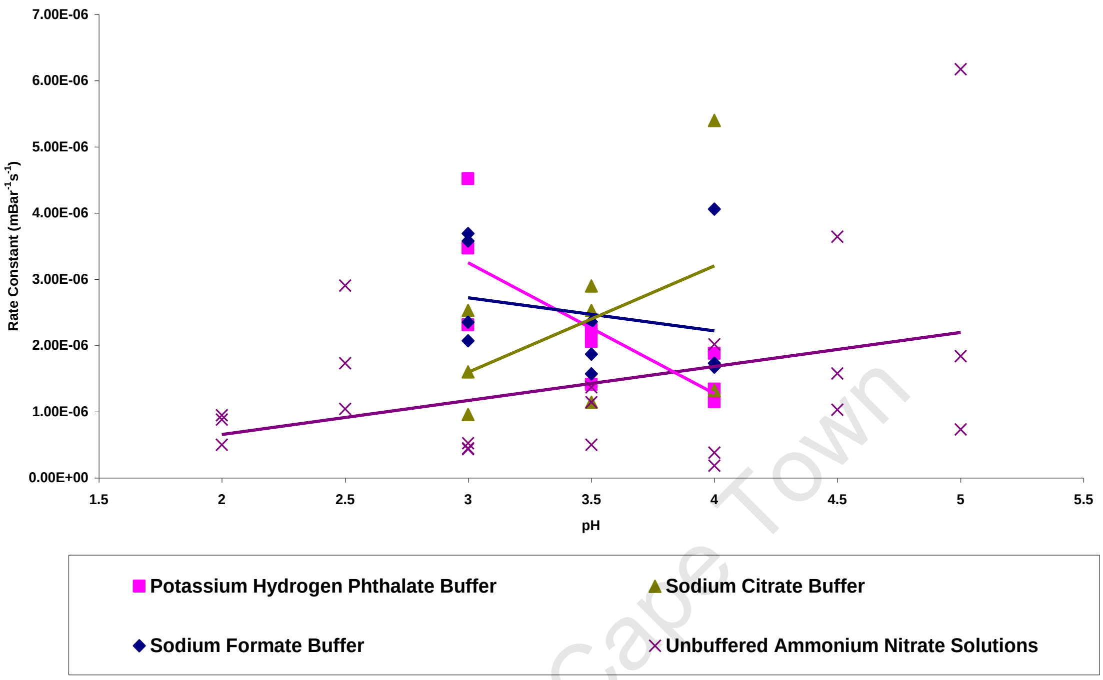

Figure 2.28: *Plot of rate constants versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite.*

In the case of the initial rate of reaction both the buffered and unbuffered experiments were found to have an exponential trend (**Figure 2.29**). At pH = 3 all three buffers were found to have significantly greater initial rates of reaction. Nonetheless, at pH = 3.5 and 4 the initial rates had dropped to be approximately the same as the unbuffered solutions.

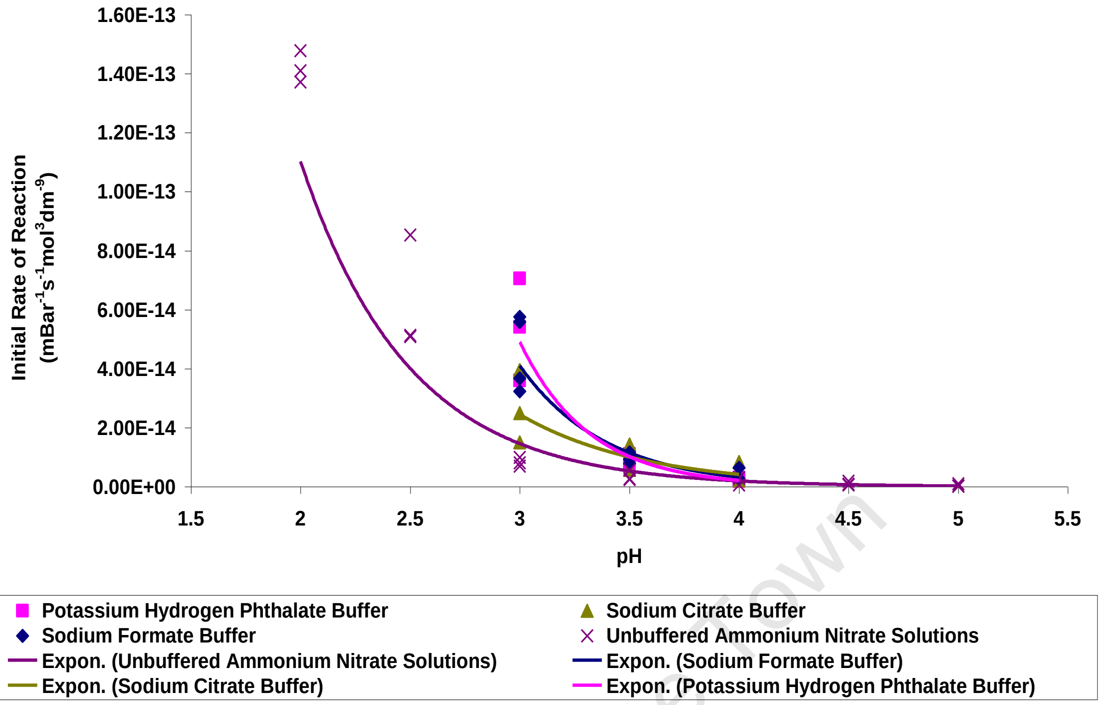

Figure 2.29: *Plot of initial rate of reaction versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite*

A difficulty was encountered in this study, which is the problem of repeatability in measuring the reaction as shown by the level of variation in the rate constants, pressure change and absolute pH change. This deviation occurred regardless of substantial attempt to ensure the reproducibility of the experiments. A possible rationalization to this occurrence may be due to the reaction possessing an oscillatory nature suggested by Rubin *et al.* 1987 [3]. The buffered solutions were found to have a positive effect on the rates of the reaction, but they did not produce similar overall pressure increase as the unbuffered solutions. The reason for this finding might be that there is some interaction between the buffers and the reactive species of the nitrogen gas gasification reaction. However, given that there is enough variability in the reaction measurements, this might not be the case. It might be important to determine if there is any sensitivity of the reaction to the presence of the buffers. For the initial rate of reactions, phthalate and formate buffers had a positive effect at pH =3.5 and that alone leads to a further investigation.

2.4.3 Addition of zinc nitrate on the buffered and unbuffered ammonium nitrate-sodium nitrite gassing reaction

Alilovic and Reckzin [4] patented a method for producing a gassed emulsion explosive. The gassing reaction had a pH lowering agent which comprised of a Lewis Acid (zinc nitrate). According to their findings addition of zinc nitrate produced better results than the gassed emulsion explosives that did not contain zinc nitrate. For example, they discovered that gassed emulsion explosives with zinc nitrate displayed a significant reduction in gassing reaction times as compared to the gassed emulsion explosives without zinc nitrate.

Zinc nitrate was added to the buffered and unbuffered ammonium nitrate-sodium nitrite gassing reaction and this was done to see if the Lewis Acid would have an effect on the gasification rates of the ammonium nitrate-sodium nitrite reaction. Gasification results for buffered and unbuffered ammonium nitrate-sodium nitrite gassing reaction with zinc nitrate are reported below.

For comparison between reactions with and without zinc nitrate, buffered and unbuffered reactions with zinc nitrate are illustrated graphically on the same plot of axis with reactions without zinc nitrate.

A plot of pressure versus time (**Figure 2.30**) for unbuffered with and without zinc nitrate is shown below. Looking at the pressure traces for all the reactions, the unbuffered reactions with zinc nitrate had a rapid pressure rate increase as compared to the unbuffered reactions without zinc nitrate. At all pHs measures except for pH = 4, maximum pressure and steady pressure were reached. At pH = 4 no plateau was reached and the reaction was still continuing even after 10 hours.

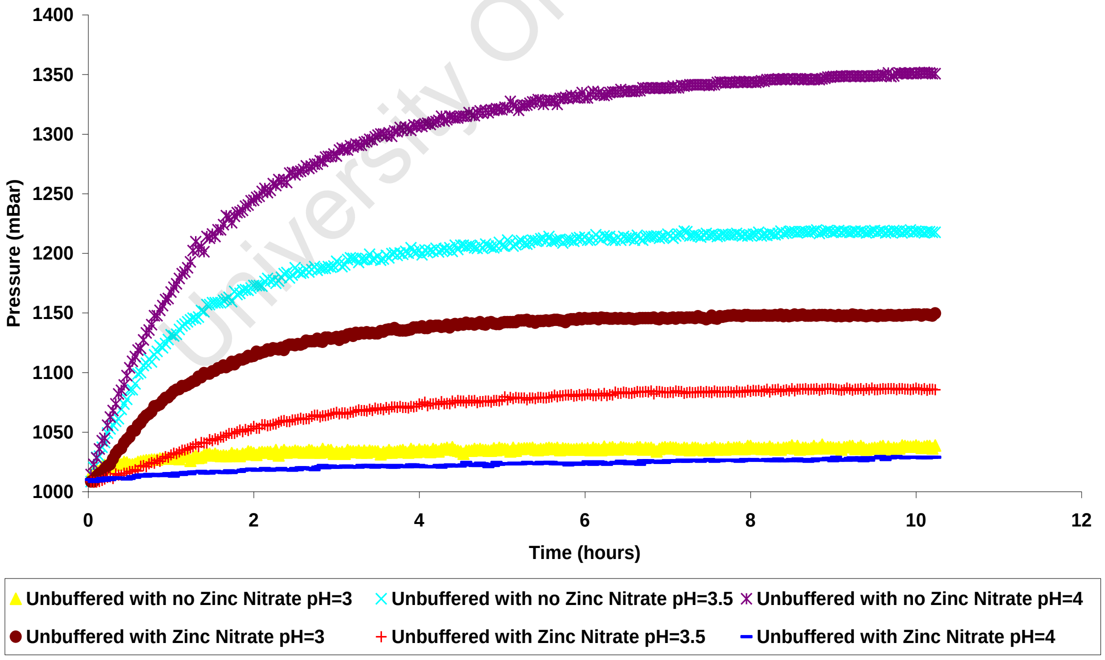

Figure 2.30: *Plot of pressure versus pH for unbuffered ammonium nitrate-sodium nitrite reactions with and without zinc nitrate*

In the case of pressure change, the unbuffered ammonium nitrate-sodium nitrite experiments with zinc nitrate resulted in an overall pressure change increase **(Figure 2.31**) mirroring the findings mentioned above, that is having a rapid pressure rate. Both the unbuffered ammonium nitrate-sodium nitrite with and without zinc nitrate reactions had a linear relationship with pH (shown by the linear trendlines) and pressure change was decreasing as pH increases.

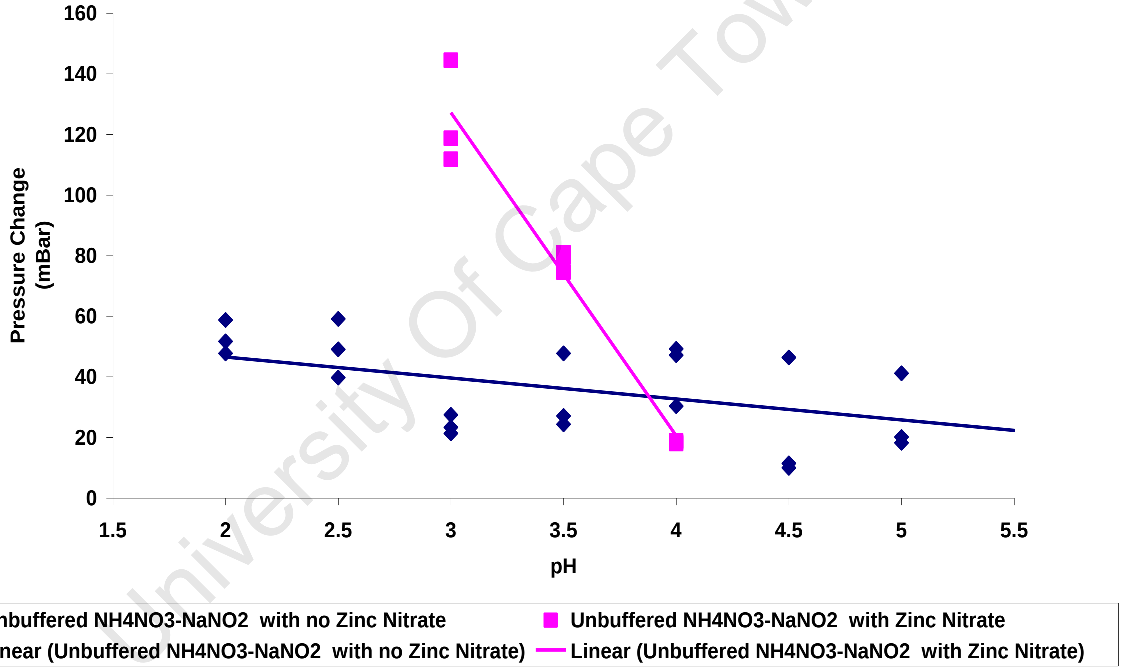

Figure 2.31: *Plot of pressure change versus pH for unbuffered ammonium nitrate-sodium nitrite reactions with and without zinc nitrate*

Looking at the effect of absolute pH change on the unbuffered ammonium nitrate-sodium nitrite reactions with and without zinc nitrate, a scattered plot was observed and unbuffered ammonium nitrate-sodium nitrite reaction without zinc nitrate displayed an increase in absolute pH change as compared to the unbuffered ammonium nitrate-sodium nitrite reaction with zinc nitrate (**Figure 2.32**). This clearly shows that addition of zinc nitrate had an effect on the pH of the unbuffered ammonium nitrate-sodium nitrite reaction.

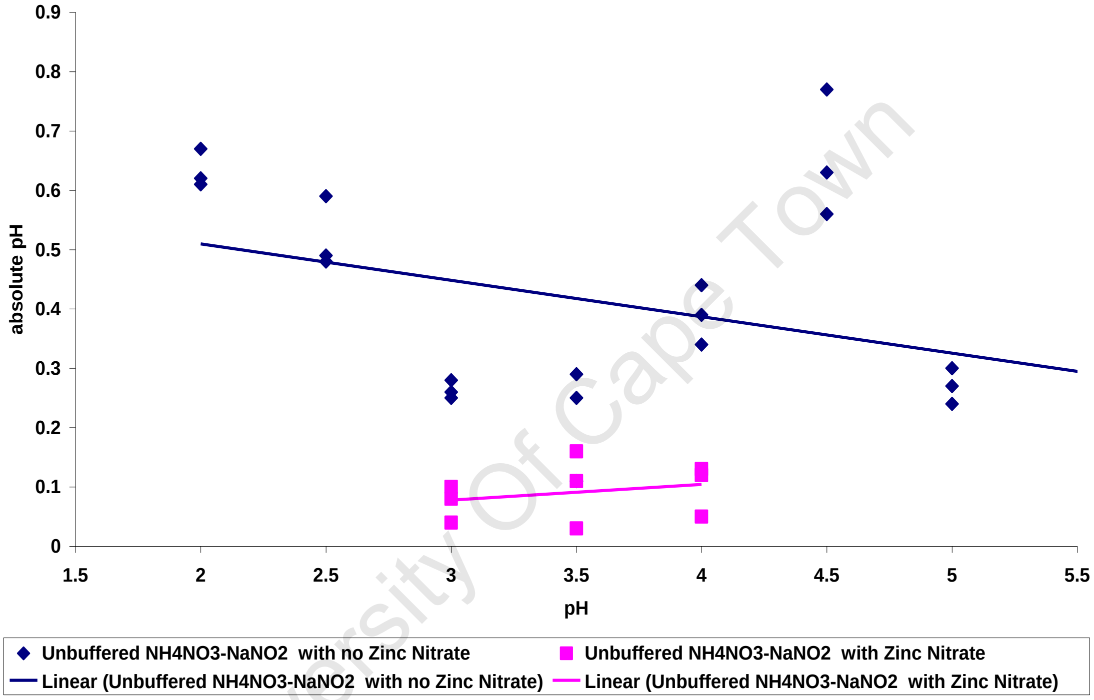

Figure 2.32: *Plot of absolute pH change versus pH for unbuffered ammonium nitrate-sodium nitrite reactions reacting with and without zinc nitrate*

2.4.4 Rate constants and Initial rate of reaction for unbuffered ammonium nitrate-sodium nitrite gassing reaction with and without zinc nitrate

A plot for rate constants against pH (**Figure 2.33**), clearly shows that the reactions with zinc nitrate had greater rate constants than the reactions without zinc nitrate and this means that the reactions with zinc nitrate were faster than the reactions without zinc nitrate.

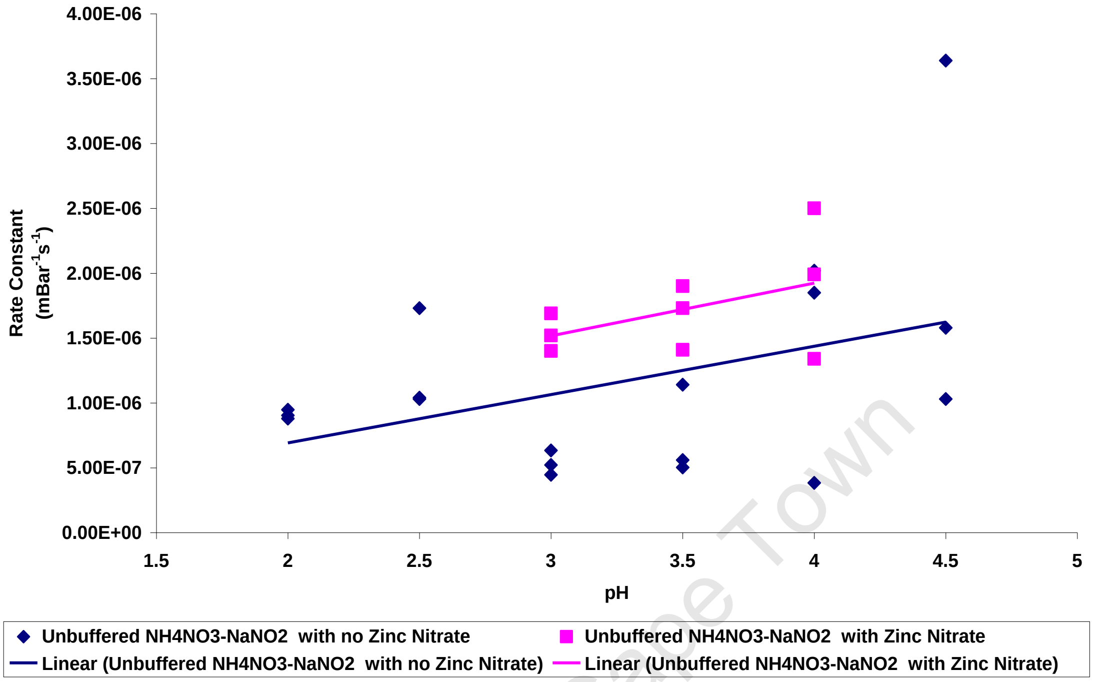

Figure 2.33: *Plot of Rate Constants versus pH for unbuffered* NH_4NO_3 *Solutions reacting with and without Zinc Nitrate and* $NaNO_2$

Initial rate of reaction for the unbuffered with and without zinc nitrate are depicted in **Figure 2.34.** The unbuffered with and without zinc nitrate reaction had an exponential relationship with the pH, as the pH increases the initial rate of reaction decreases. The unbuffered with zinc nitrate had a greater initial rate of reaction than the unbuffered without the zinc nitrate and this clearly indicates that the unbuffered with zinc nitrate reactions had a faster rate of reaction than the unbuffered without zinc nitrate.

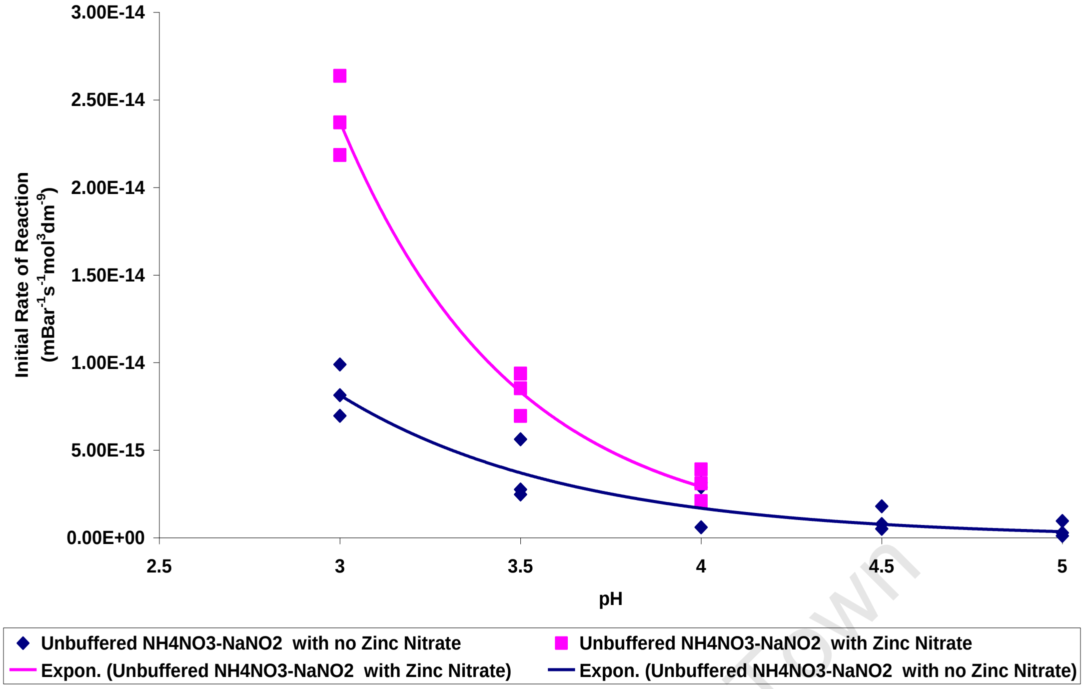

Figure 2.34: *Plot of initial rate of reaction versus pH for unbuffered ammonium nitrate-sodium nitrite reactions reacting with and without zinc nitrate*

2.4.5 Gasification rates for buffered ammonium nitrate-sodium nitrite gassing reactions with and without zinc nitrate

Pressure was measured for the buffered ammonium nitrate-sodium nitrite gassing reactions with and without zinc nitrate and the results are shown below (**Figure 2.35**, **Figure 2.36** and **Figure 2.37**).

Figure 2.35 illustrates a plot of buffered ammonium nitrate-sodium nitrite reaction with and without zinc nitrate at pH = 3. Phthalate buffer with no zinc nitrate had reached maximum pressure within 2 hours of starting the reaction, while phthalate buffer with zinc nitrate did not reach maximum pressure but had a rapid pressure increase. However, citrate buffer with and without zinc nitrate had reached maximum pressure and both attained a stable state (fixed pressure). As for formate buffer with zinc nitrate no maximum pressure was reached while formate buffer without zinc nitrate had reached maximum pressure with steady pressure state.

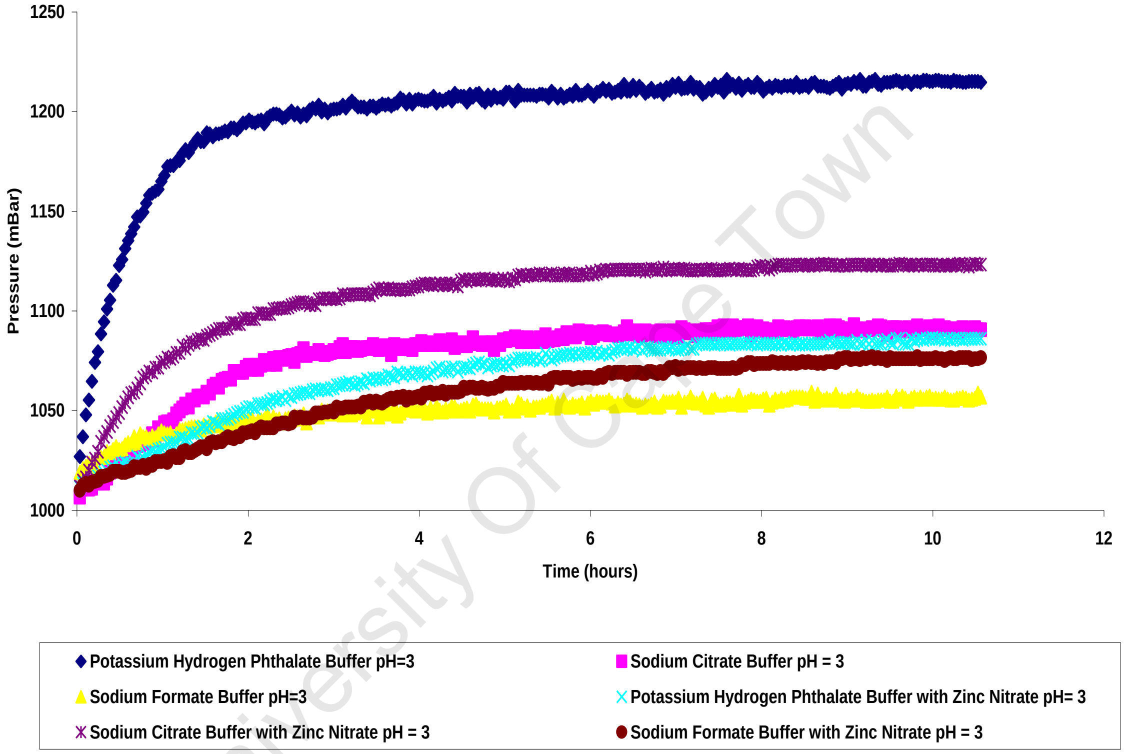

Figure 2.35: *Plot of pressure versus pH for buffered* NH_4NO_3*-*$NaNO_2$ *with and without zinc nitrate at pH = 3*

At pH = 3.5, citrate and phthalate buffered reactions with zinc nitrate had similar pressure traces and they both had a rapid pressure increase, reached maximum pressure and plateau was reached (**Figure 2.36**). Formate buffer reaction with zinc nitrate had the slowest maximum pressure increase and the reaction was still continuing even after 10 hours, same pattern was observed for the formate and phthalate buffers without zinc nitrate.

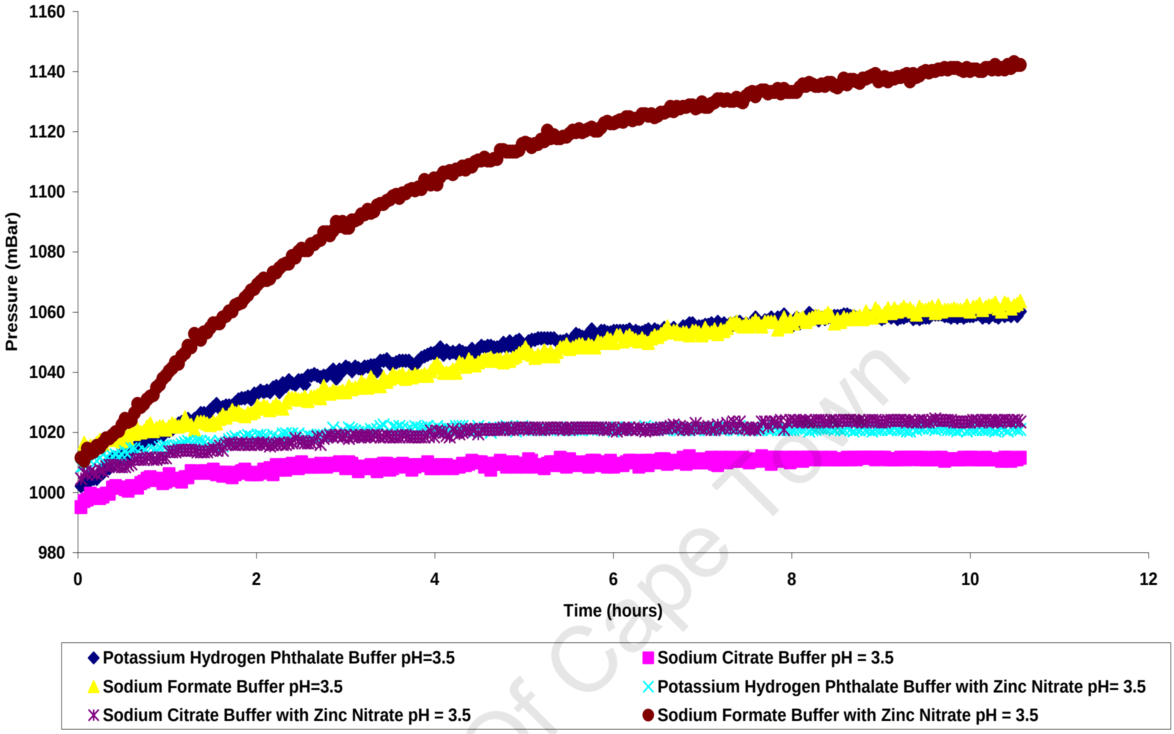

Figure 2.36: *Plot of pressure versus pH for buffered* NH_4NO_3-$NaNO_2$ *with and without zinc nitrate at pH = 3.5*

Gasification rates for the buffered ammonium nitrate-sodium nitrite reaction with and without zinc nitrate at pH = 4 are shown in **Figure 2.37**. The plot clearly shows that as the pressure increases the rate of the reaction slows down, that is the rate at which maximum pressure is reached is very slow and it (maximum pressure) was reached in different intervals for all the reactions except for formate buffer without zinc nitrate.

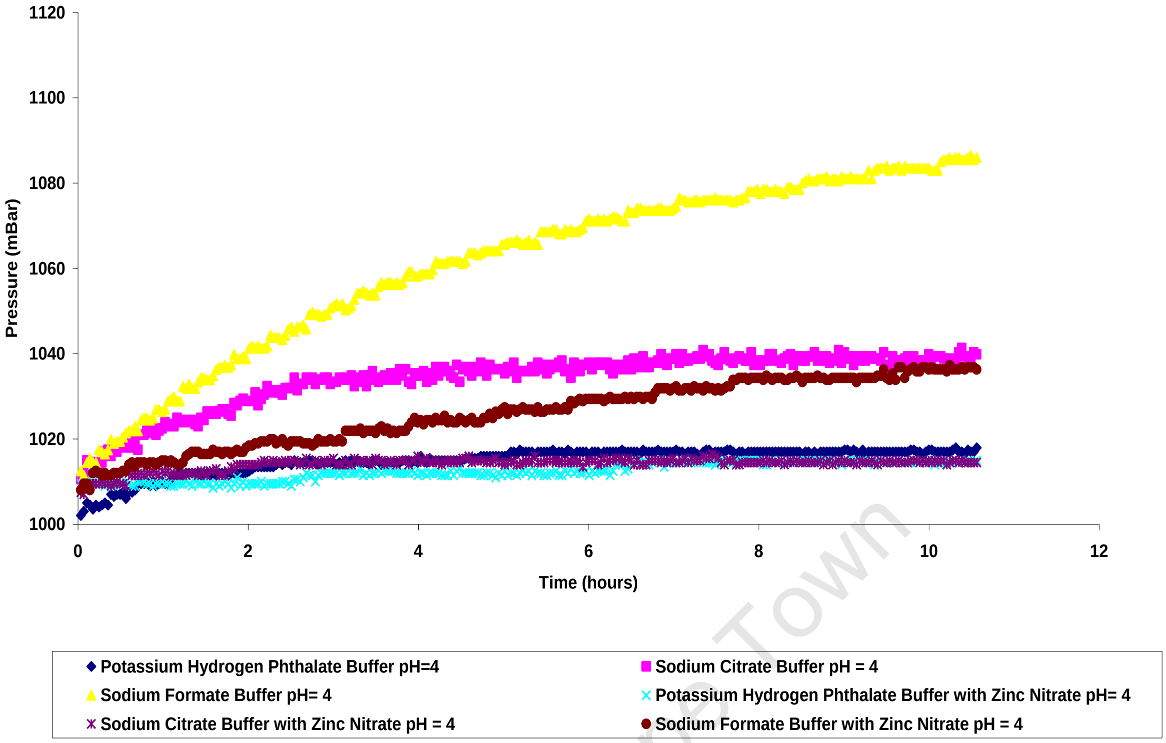

Figure 2.37: *Plot of pressure versus time for buffered ammonium nitrate-sodium nitrite reactions with and without zinc nitrate at pH = 4*

In terms of pressure, the buffered reactions without zinc nitrate were found to have an overall pressure increase/change higher than the buffered with zinc nitrate (**Figure 2.38**), so this means that the zinc nitrate didn't have any effect to the buffered reactions, furthermore pressure was decreasing with increasing pH.

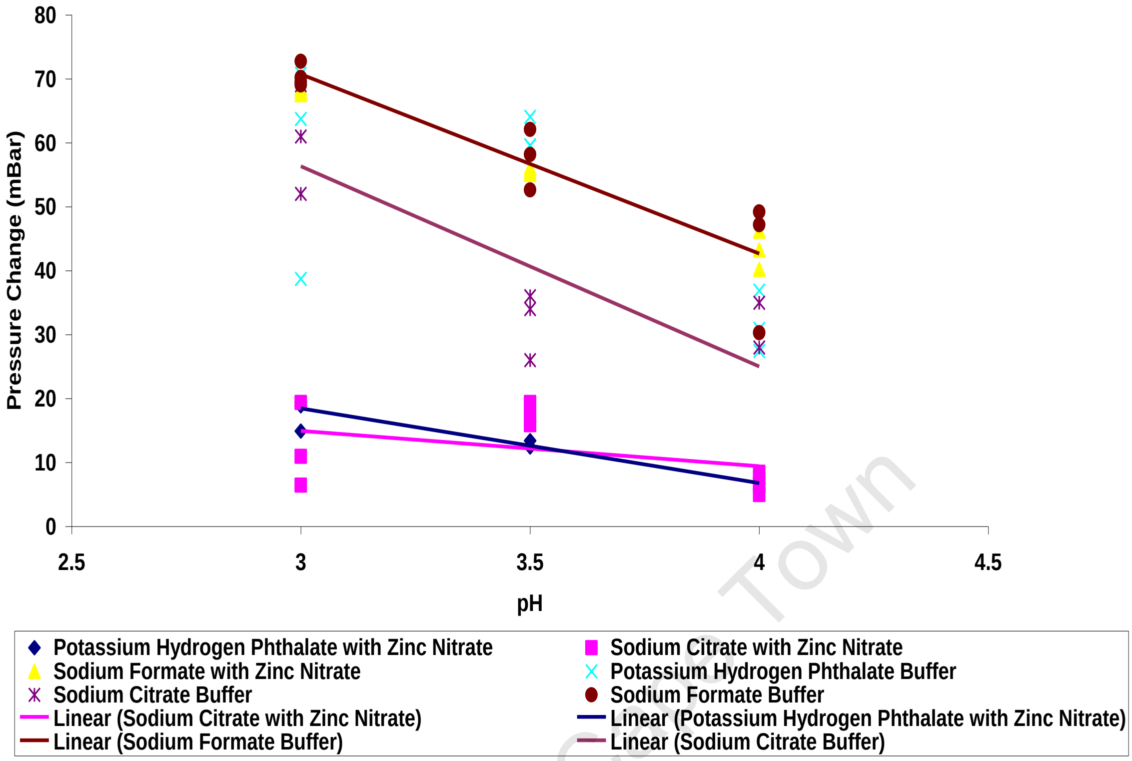

Figure 2.38: *Plot of pressure change versus pH for buffered ammonium nitrate-sodium nitrite solutions reacting with and without zinc nitrate*

For buffered reactions the Lewis Acid didn’t have as much effect as it did with the unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate, the pH change did not decrease instead it went up for the buffered ammonium nitrate-sodium nitrite reaction with zinc nitrate (**Figure 2.39**). Citrate buffer with zinc nitrate had the highest overall absolute pH change. The overall absolute pH for the buffered reactions with the Lewis Acid was found to be higher than the buffered experiments without the Lewis Acid.

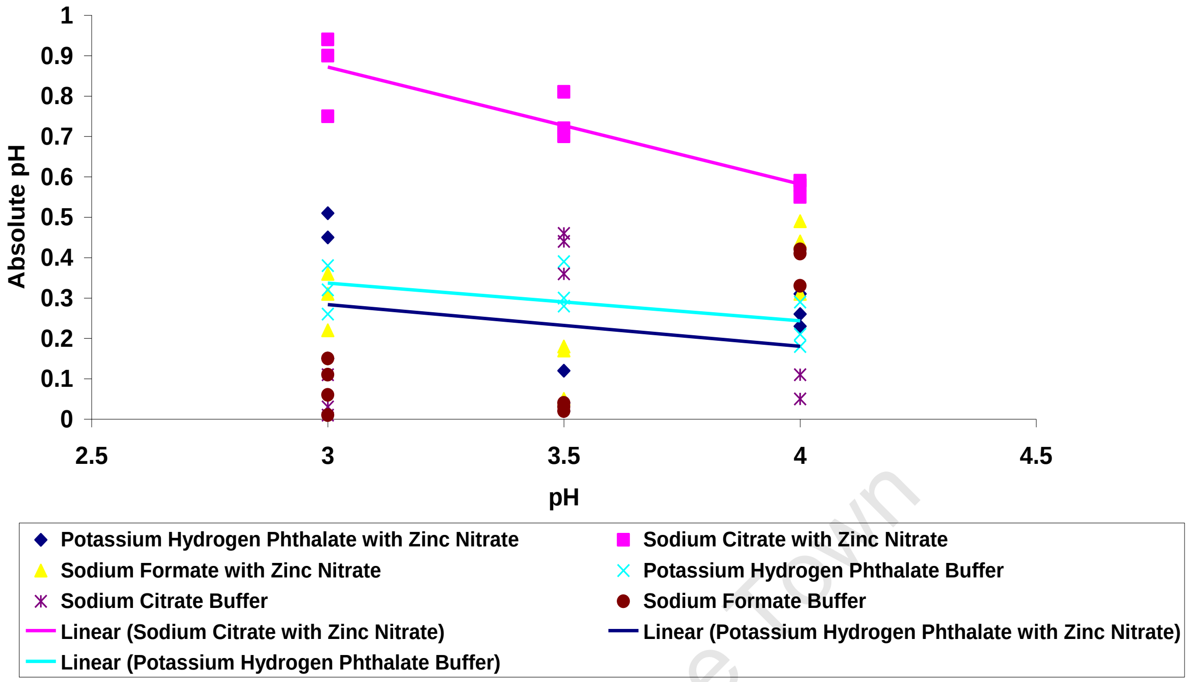

Figure 2.39: *Plot of absolute pH versus pH for buffered ammonium nitrate-sodium nitrite reactions reacting with and without zinc nitrate*

2.4.6 Rate Constants and Initial Rates of Reaction for buffered ammonium nitrate-sodium nitrite gassing reactions with and without zinc nitrate

A plot of rate constants versus pH for the buffered ammonium nitrate-sodium nitrite gassing reactions with and without zinc nitrate (**Figure 2.40**) shows that there was no significant difference that was observed between the buffered with and without zinc nitrate. For an example the citrate buffer's rate constants (without zinc nitrate) are increasing with increasing pH same applies to the citrate with zinc nitrate and they have overall rate constants that are similar to one another. Another example is the phthalate buffer where the rate constants are decreasing with increasing pH and to show that they have similar rate constants the trend lines overlap each other (**Figure 2.40**).

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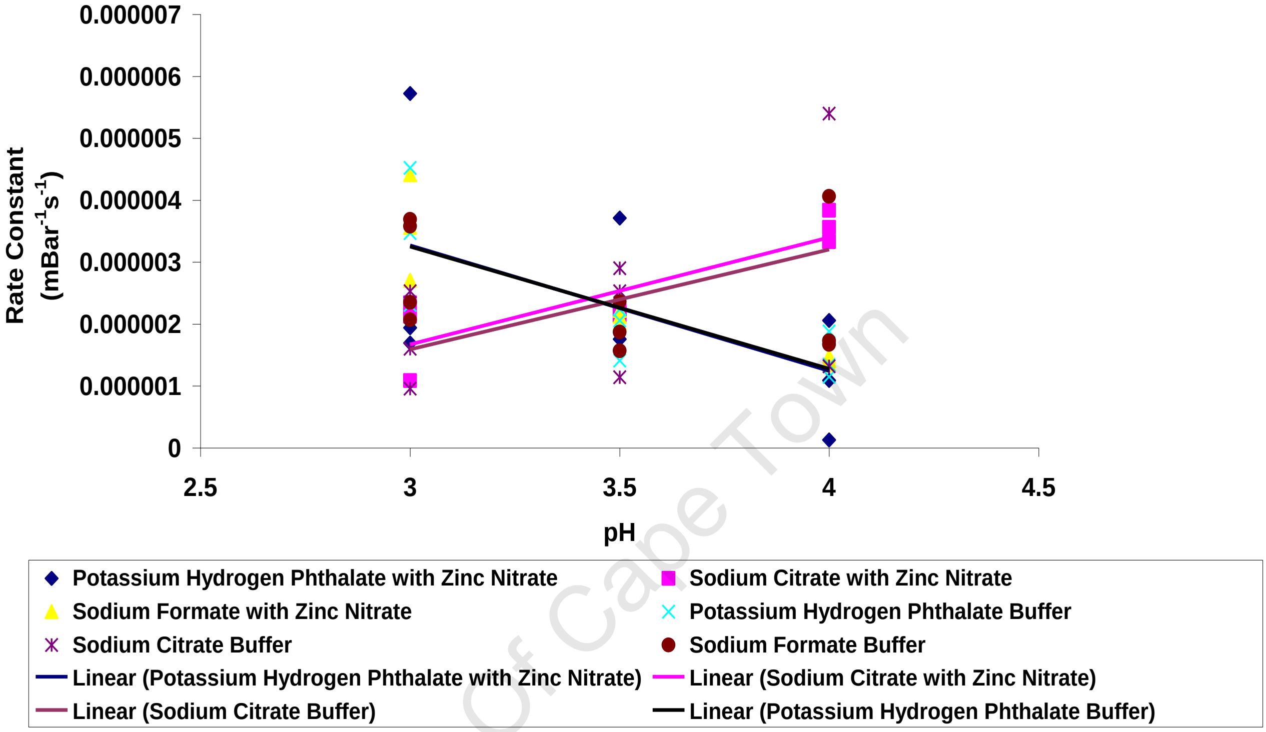

Figure 2.40: *Plot of rate constants versus pH for buffered ammonium nitrate-sodium nitrite solutions reacting with and without zinc nitrate*

In the case of initial rate of reaction the same pattern that was displayed by the rate constants was observed for all the buffered ammonium nitrate-sodium nitrite gassing reactions with and without zinc nitrate. That is there was not much difference in the initial rate of reaction for the buffered with and without zinc nitrate. They all had an exponential relationship (**Figure 2.41**) with an overall rate of reaction that is similar to one another (that is the rate of buffered with zinc nitrate is similar to the initial rate of the buffered without zinc nitrate), with decreasing initial rate of reaction as pH increases. Zinc nitrate did not have as much effect on the initial rate of reaction as it did with the absolute pH change. However, looking at the pressure traces (section 2.4.4) that were obtained for the unbuffered ammonium nitrate-sodium nitrite gassing reactions with and without zinc nitrate this outcome was expected due to the fact that there was not much difference in the pressure traces of these reactions and also the initial rates of reaction are derived or calculated using the gasification or pressure results.

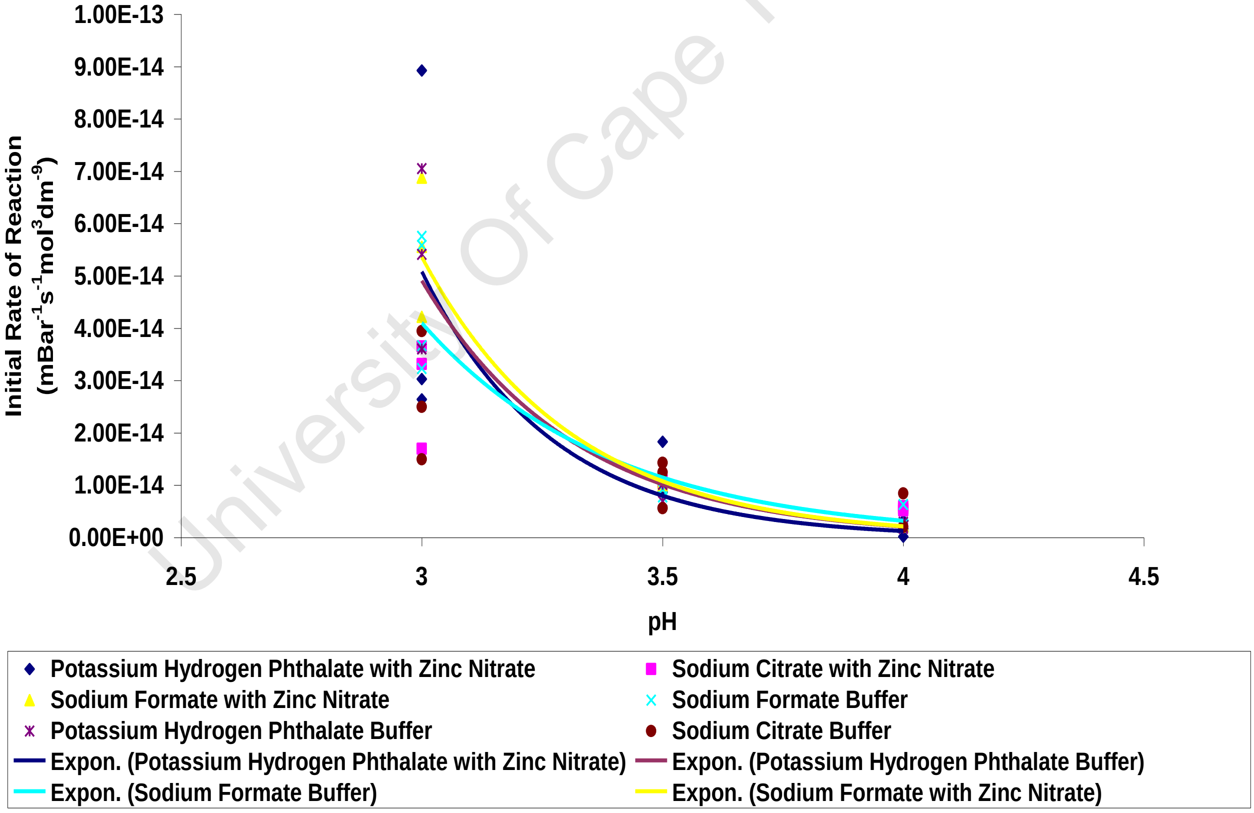

Figure 2.41: *Plot of initial rate of reaction versus pH for buffered ammonium nitrate-sodium nitrite solutions reacting with and without zinc nitrate*

Addition of zinc nitrate to the unbuffered ammonium nitrate-sodium nitrite gassing reactions certainly improved the performance of these reactions, the unbuffered reactions with zinc nitrate had produced better pressure rate increase, faster rate constant and initial rate of reaction and enhanced on the absolute pH change as compared to the unbuffered ammonium nitrate-sodium nitrite gassing reactions without zinc nitrate. These findings agree with the invention of Alilovic and Reckzin that zinc nitrate improves performance of a reaction. However, addition of the Lewis Acid on the buffered ammonium nitrate-sodium nitrite reactions did not have a significant effect as it did with unbuffered reactions. The pressure rate increase, rate constants and initial rate of reactions had similar outcomes as with the buffered without zinc nitrate; furthermore the absolute pH was found to be higher than that of buffered without zinc nitrate and this was not expected as zinc nitrate is known as a pH lowering agent.

2.5 Conclusion

A system and apparatus were designed for the ammonium nitrate-sodium nitrite reaction. Then a method for the kinetic reactions of ammonium nitrate-sodium nitrite reaction was developed and this method was tested and used in this study.

Gasification rates for the ammonium nitrate-sodium nitrite reaction were measured by monitoring the pressure change accompanying the reaction in a closed vessel. The assumption was that only nitrogen gas was produced and so this was responsible for the pressure increase and that the increase in pressure was too small to significantly affect the rate. The ammonium nitrate-sodium nitrite reaction was buffered with three different buffers (sodium citrate, sodium formate and potassium hydrogen phthalate) and zinc nitrate was added to the buffered and unbuffered reactions. At low pH it was found that pressure over time had a rapid pressure. For buffered reactions, citrate buffer had displayed consistency in the pressure rate increase at all the measured pHs, it had reached maximum pressure as well as a steady state (fixed pressure). Upon addition of zinc nitrate, buffered ammonium nitrate-sodium nitrite reactions were found to have a fast rate pressure increase as compared to the unbuffered ammonium nitrate-sodium nitrite reactions with zinc nitrate.

Given that the ammonium nitrate and sodium nitrite is sensitive to pH, pH was measured to see its effect on the buffered an unbuffered reactions. The matter of pH change is essential since the dependence of the reaction on the concentration of H_3O^+. In the presence of buffers, the overall pH change is much lesser than that of corresponding unbuffered experiments. However, addition of the Lewis Acid (zinc nitrate) resulted in the decrease of overall pH change for unbuffered and buffered experiments had a greater overall pH change.

In the case of pressure, the unbuffered solution of ammonium nitrate showed a decrease in the overall pressure change with increasing pH. The presence of the three buffers resulted in a reduced pressure change comparative to the unbuffered experiments. With regards to the presence of zinc nitrate there was no significant difference that was observe to both the buffered and unbuffered experiments. Interestingly, the profile of the formate buffer (pKa 3.75) showed a maximal pressure increase at a pH close to its pKa.

The unbuffered ammonium nitrate solutions produced rate constants with a marginal dependency on pH, increasing slightly with increasing pH. Significantly, the ammonium nitrate buffered solutions had larger rate constants as compared to the corresponding unbuffered solutions. Zinc nitrate had the same effect, that is buffered solutions resulted in a greater increase than unbuffered solutions.

Rates of reaction were calculated using the rate constants, the unbuffered with and without zinc nitrate solutions showed an exponential relationship to pH, decreasing rapidly with increasing pH. This relation mirrored the logarithmic relation of H_3O^+ to pH. Significantly, the presence of the buffers with and without zinc nitrate showed a distinct influence upon the initial rates of reaction attributable to their larger rate constants.

References

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2. L. Rayleigh and W. Ramsay, *Argon, the new constituent of the atmosphere*, Philos.*Trans. R. Soc*. London, 1895, **186**, 187.
3. M. B. Rubin, R. M. Noyes and K. W. Smith, *Gas-evolution oscillators. 9. A study of the ammonium nitrate oscillator*; J. *Phys. Chem*.,1987, **91**, 1618.
4. I. Alilovic *et.al*, *Methods of gassing emulsion explosives and explosives produced thereby*, U.S. Patent 20040065396, 2004.

Chapter 3

Gasification Reaction Rate for Emulsified Ammonium Nitrate with aqueous Sodium Nitrite

3.1 Introduction

Ammonium nitrate was first prepared in 1654 by Glauber, but it was not until the beginning of the 19th century that it was considered for use in explosives by Grindel and Robin as a replacement for potassium nitrate in black powder. Its explosive properties were also reported in 1849 by Reise and Millon when a mixture of powdered ammonium nitrate and charcoal exploded on heating. In 1867, Swedish chemists Ohlsson and Norrbin patented an explosive called *Ammoniakust*. Ammonium nitrate is not considered to be an explosive although in the first half of the last century small fires and explosions involving ammonium nitrate occurred throughout the world [1, 2].

Ammonium nitrate is used extensively in commercial explosives and propellants. It is the most important raw material in the manufacture of commercial explosives. It is used by itself in conjunction with fuels or in a mixture with solid fuels and sensitizers, such as nitroglycerine and TNT to give more sensitive explosives [3]. Water explosives, developed since 1956, based on solutions of nitrates have been another are where ammonium nitrate is used. More cost effective ammonium nitrate based w/o and o/w emulsion explosives were developed in 1962 [4]. W/O emulsion explosives have been made as typified by the formulation containing 20 % water, 12 % oil, 2 % microspheres, 1 % emulsifier and 65 % ammonium nitrate. Areas like coal mining, non metal mining and quarrying find extensive use of ammonium nitrate as an explosive. Some of the known military explosives which use ammonium nitrate are amatol, ammonals and minols.

The aim of this chapter is to investigate the role of pH and buffer type in the gasification reactions of emulsified Ammonium Nitrate with aqueous Sodium Nitrite applying the same methodology that was used in Chapter 2.

3.2 Experimental Methods

3.2.1 Pressure Measurements

Ammonium Nitrate Emulsions were prepared by African Explosives Limited (AEL).

All experiments were conducted in a 100 ml reagent bottle fitted with a rubber cap seal and a pressure sensor linked to a PC. The bottle was mounted on a stirrer assembly in a temperature controlled, insulated cupboard at 25 °C.

50.0 g of ammonium nitrate emulsion was placed into the reagent bottle along with a small stirrer bar and the reaction initiated by the addition of 1.25 ml of an aqueous 6.25% (m/m) sodium nitrite solution. The bottle was sealed and pressure recording started. At this point the reaction mixture was vigorously shaken and swirled for approximately 90 seconds to ensure adequate mixing. Data capture was continued until the pressure reading had stabilised, typically 24 hours. Three to four samples were investigated for each of the five prepared emulsions.

3.2.2 Emulsion Separation:

25 ml of a 1:2:2 Hexane: Ethanol: Water solvent blend was added to each 50 g emulsion sample and the resultant emulsion solvent mixture thoroughly mixed by vigorous shaking before being placed in a 100ml Nalgene centrifuge bottle and immersed in hot water for approximately 15 minutes. The mixture was centrifuged at 10000 rpm (30°C) for between 40 and 60 minutes or until the two solvent layers were clear. The sample was carefully poured into a

clean, dry separating funnel and the aqueous layer decanted into a clean, dry, labelled, sealable sample vial and the pH determined.

3.2.3 Data Analysis:

Data were analysed using Microsoft Excel and the PRISM graphing package. Rate constants were determined by linear regression of plots of 1/ (P_{eq} – P_t) versus time. Initial rates of reaction were calculated using the known H^+ and NO_2^- concentrations and the determined rate constants.

3.3 Results

3.3.1 Pressure Measurements

3.3.1.1 Pressure measurements for acetic acid/sodium acetate emulsion

Gasification reaction experiments were conducted for the acetic acid/sodium acetate (AA/NA) emulsions at an initial pH of 3.20. The pressure traces for the AA/NA emulsion are shown in **Figure 3.3.1**. Three different curves were observed due to the variation of pH after the reaction. The maximum pressure was reached within 3 hours of starting the reaction.

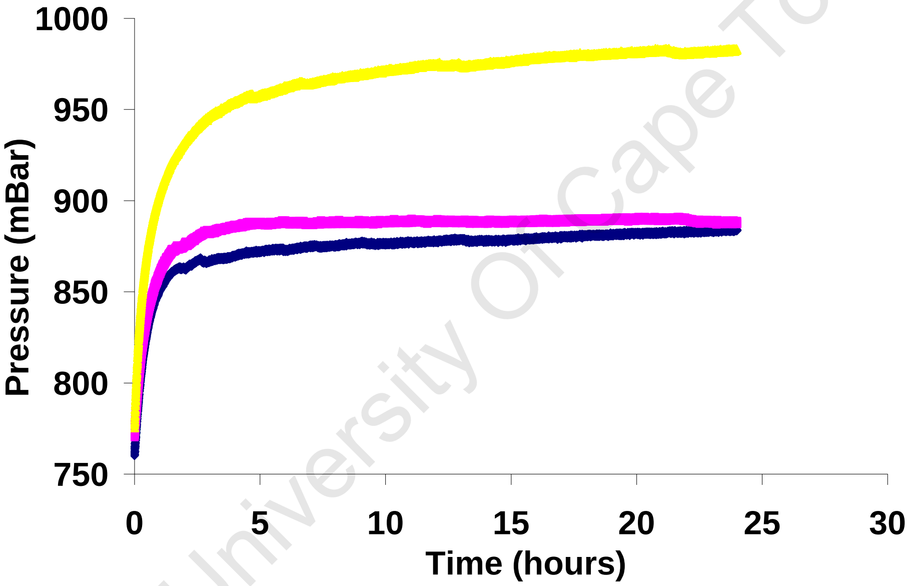

Figure 3.3.1: *Pressure Traces for Gasification Rates of 50 g Emulsion A (AA/NA) with 6.25 % (m/m) $NaNO_2$ pH = 3.20*

The plot of pressure versus time for AA/NA (emulsion B) at pH = 4.01 (**Figure 3.3.2**) shows that there was a rapid increase in pressure traces, but with no maximum pressure reached, that is in the form of reaching a plateau even after 24 hours.

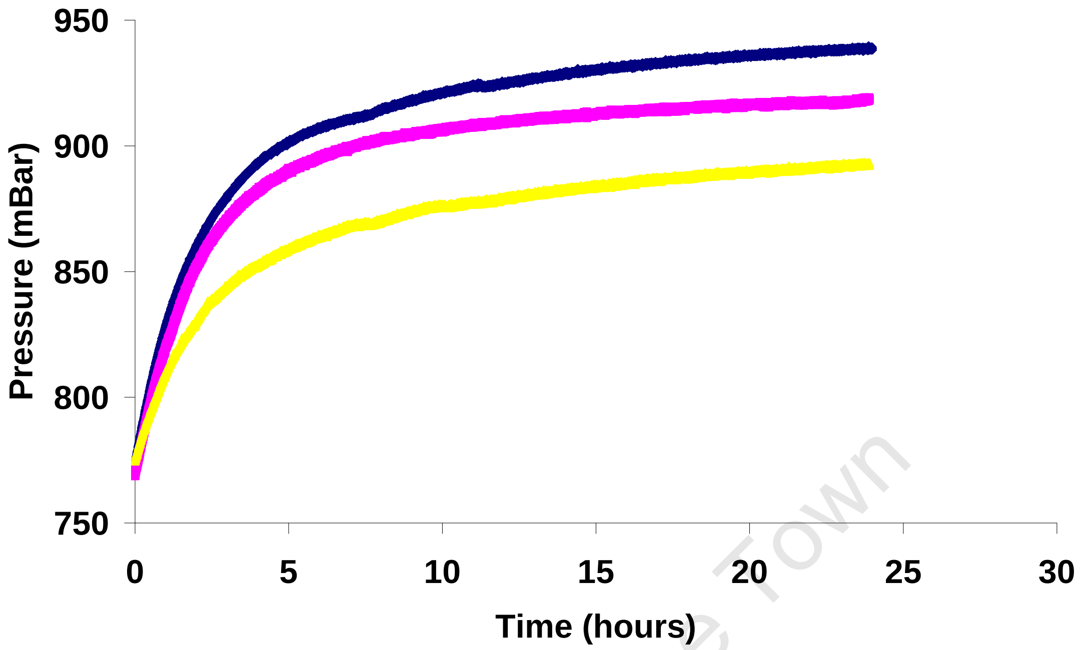

Figure 3.3.2: *Pressure traces for Gasification Rates of 50 g Emulsion B (AA/NA) with 6.25 % (m/m)* $NaNO_2$ *at pH = 4.01*

The pressure traces for emulsion C (AA/NA pH = 4.50) showed a slowest pressure increase as compared to emulsions A and B, **Figure 3.3.3** illustrates that the pressure had not reached a stable state and that resulted in a maximum pressure not being reached.

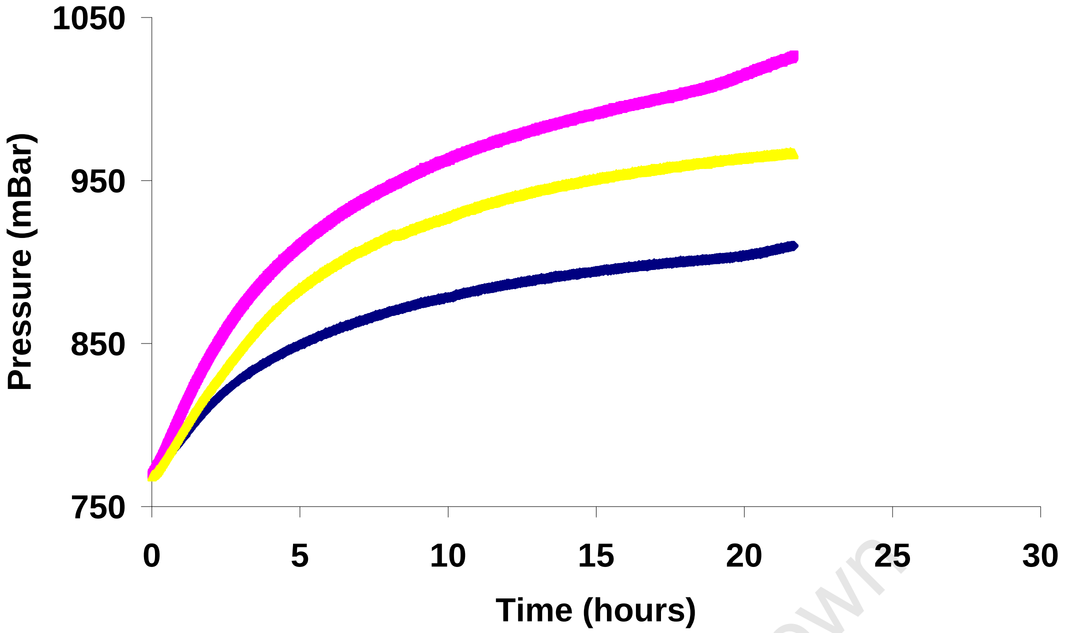

Figure 3.3.3: *Pressure Traces for Gasification Rates of 50 g Emulsion C (AA/NA) with 6.25 % (m/m)* $NaNO_2$ *pH = 4.50*

3.3.1.2 Pressure measurements for citric acid/sodium citrate emulsion (CA/NC)

Three experiments were conducted for emulsion D (CA/NC) pH= 3.20. Even though maximum pressure (stable pressure) was not reached the plots show that there was a pressure increase. **Figure 3.3.4** shows the pressure traces for CA/NC (emulsion D pH = 3.20).

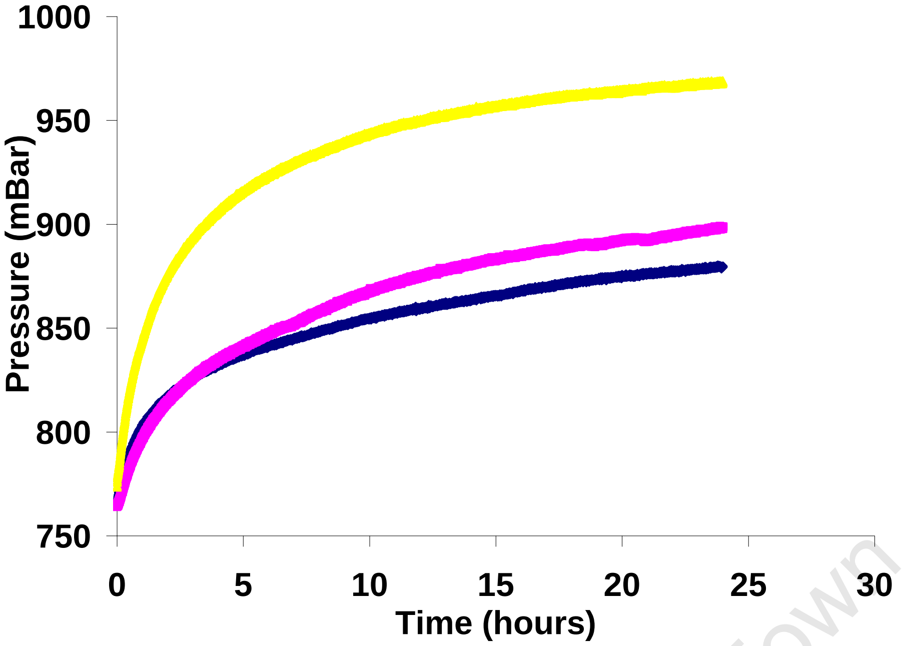

Figure 3.3.4: *Pressure Traces for Gasification Rates of 50 g Emulsion D (CA/NC) with 6.25 % (m/m)* $NaNO_2$ *pH = 3.20*

Emulsion E (CA/NC pH = 4.50) showed a slow rate pressure increase that is the reaction took long to finish and no maximum pressure was reached. This conclusion is emphasized by **Figure 3.3.5**

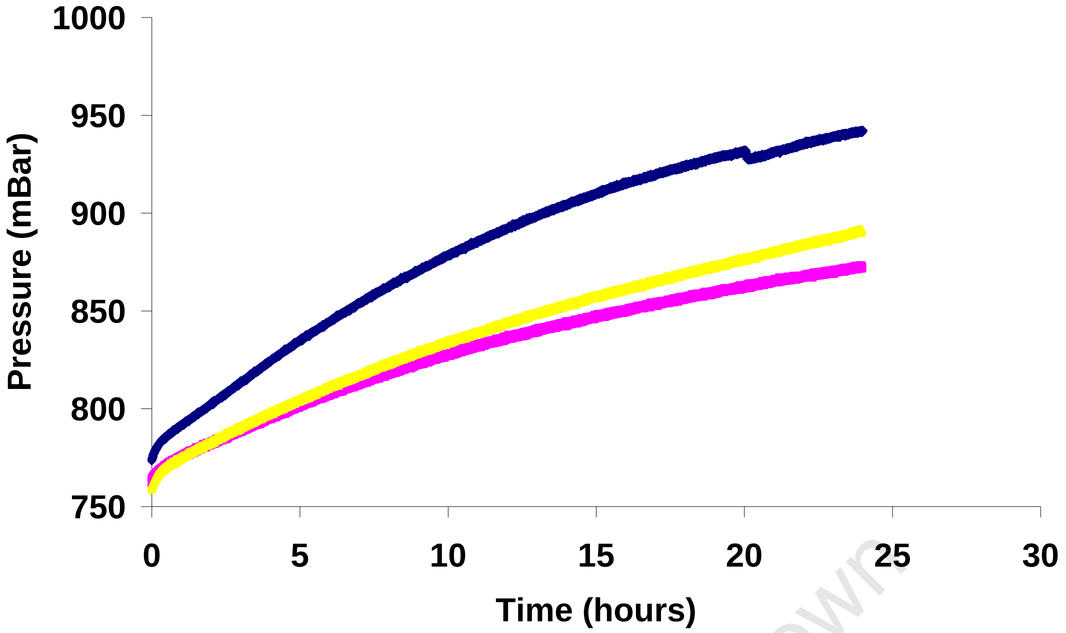

Figure 3.3.5: *Pressure Traces for Gasification Rates of 50 g Emulsion E (CA/NC) with 6.25 % (m/m)* $NaNO_2$ *pH=4.50*

3.3.1.3 Pressure changes on the acetic acid/sodium acetate and citric acid/sodium citrate emulsions

The pressure increases recorded for the various gasification reactions and their averages are reported in **Table 3.3.1**. At different pHs the pressure increase for the acetic acid/ sodium acetate emulsion was higher than that for citric acid/ sodium citrate. Overall the average pressure increase for AA/NA is 10 mBar higher than the average of CA/NC emulsion with standard deviation of 5.40 and 3.70 and this clearly indicate that the AA/ NA emulsions result in a greater total pressure change than the CA/NC emulsions at all pH measurements.

***Table 3.3.1:** Recorded Pressure Increases and Averages for the Gasifaction Reactions of Acetic Acid/ Sodium Acetate (AA/NA) and Citric Acid/ Sodium Citrate (CA/NC) Emulsions between pH 3.30 and 4.50.*

Emulsion	Pressure Increase (mBar)	Average Pressure Increase (mBar)	Standard Deviation
AA/NA pH=3.20	176.29 181.41 183.46	} 182.37	5.40
AA/NA pH=4.00	176.62 177.39 187.33		
AA/NA pH=4.50	192. 29 179.29 184.25		
CA/NC pH=3.20	173.13 179.78 182.59	} 171.99	3.70
CA/NC pH=4.50	170.54 168.83 157.05		

This conclusion is emphasised by **Figure 3.3.6**, where a plot of the observed pressure increases against the pH of the emulsions show a slight upward trend in total pressure change with increasing pH, whereas the CA/NC emulsions showed a downward trend.

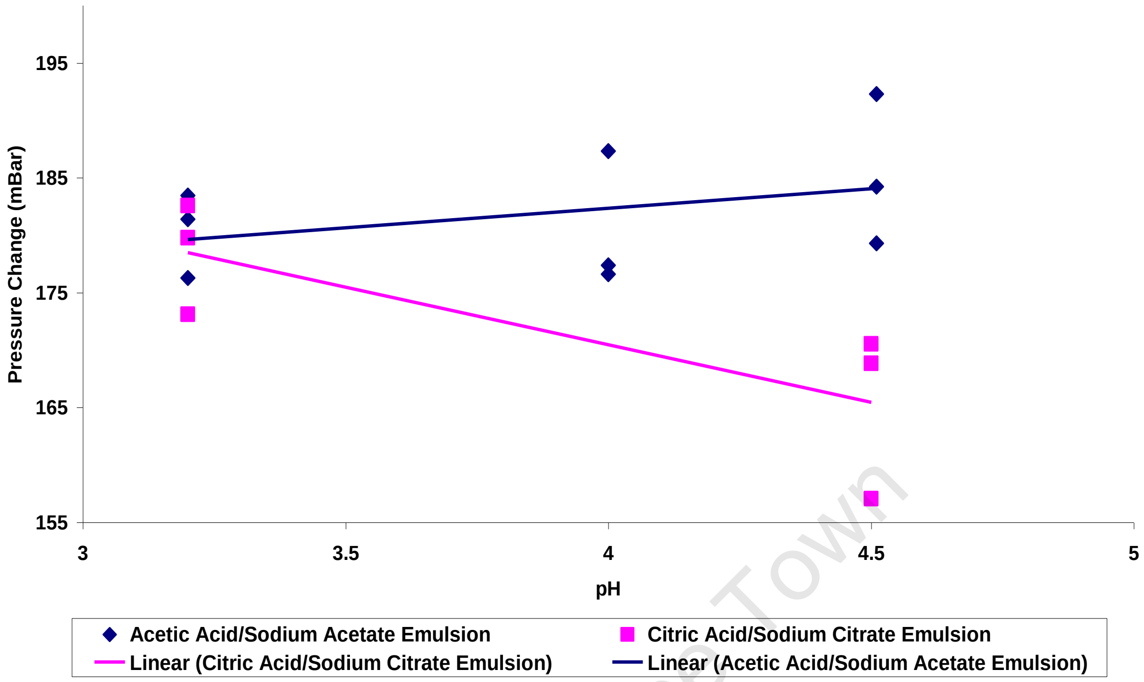

Figure 3.3.6: *Observed Pressure Increases (mBar) versus Initial pH for the Gasification Reactions of the AA/ NA and CA/ NC Emulsions*

3.3.2 Reaction induced pH changes for the acetic acid /sodium acetate and citric acid /sodium citrate emulsions

3.3.2.1 Effect of the emulsions on initial pH:

A method was developed for separating the ammonium nitrate emulsions. This involved the addition of a 1:2:2 mixture of hexane: ethanol: water to the ammonium nitrate emulsion followed by centrifuging for between 20 and 60 minutes. The effect of the formation of emulsion upon the initial pH was investigated using this method and the pH of the aqueous component was determined.

Table 3.3.2: *Reacted and unreacted emulsion pH split and pH changes*

Emulsion	Initial pH of pre-emulsified AN	Unreacted emulsion split pH	Reacted emulsion split pH	Absolute pH Change	Corrected pH Change
AA/NA pH=3.20	3.20	3.68	3.70	0.50	0.02
	3.20	3.68	3.76	0.56	0.01
	3.20	3.68	3.80	0.60	0.12
AA/NA pH=4.00	4.00	4.50	4.55	0.55	0.05
	4.00	4.50	4.56	0.56	0.06
	4.00	4.50	4.59	0.59	0.09
AA/NA pH=4.50	4.51	5.10	5.16	0.65	0.06
	4.51	5.10	5.14	0.63	0.04
	4.51	5.10	5.12	0.61	0.02
CA/NaC pH=3.20	*3.20*	4.01	4.11	0.91	0.11
	3.20	4.01	4.07	0.87	0.06
	3.20	4.01	4.04	0.84	0.03
CA/NaC pH=4.50	*4.50*	5.21	5.25	0.75	0.04
	4.50	5.21	5.28	0.78	0.07
	4.50	5.21	5.31	0.81	0.10

The pH difference between the unreacted split and the pre-emulsified aqueous nitrate solution for the acetic acid /sodium acetate (AA /NA) emulsion was between 0.48 and 0.59. At pH 3.2, the emulsion set was found to have an unreacted emulsion split of 3.68 giving a pH difference 0.48. The AA / NA emulsion set at pH 4.00, the split was 4.50 giving a pH difference of 0.50. Finally for the pH 4.50 the emulsion split was found to be 5.10 resulting in a pH difference of 0.59. These findings are shown in **Table 3.3.2**.

The pH difference between the unsplit and split emulsions for the citric acid/ sodium citrate (CA/NC) were found to be higher than those of AA/NA emulsion where pH was equivalent and the pH difference was found to be between 0.71 and 0.81. At pH 3.2, the CA/ NC emulsion set was found to have pH 4.01 after splitting yielding a difference of 0.81. The pH 4.50 emulsion had a split pH of 5.21, resulting to a pH difference of 0.71.

3.3.2.2 Absolute pH change for acetic acid/sodium citrate and citric acid/sodium citrate emulsions

The absolute difference in pH was calculated by subtracting the initial pH of the unsplit (unreacted) emulsions from the pH of the reacted (split) emulsions. A plot of the absolute pH change versus initial pH (**Figure 3.3.7**) shows that there is a large pH difference between the two buffered emulsions, with an average of 0.58 for the AA/NA emulsions and 0.83 for the CA/NC emulsions. This clearly indicates that the acetic acid buffer is a better buffer than the citric acid at pH=3.20 and 4.50.

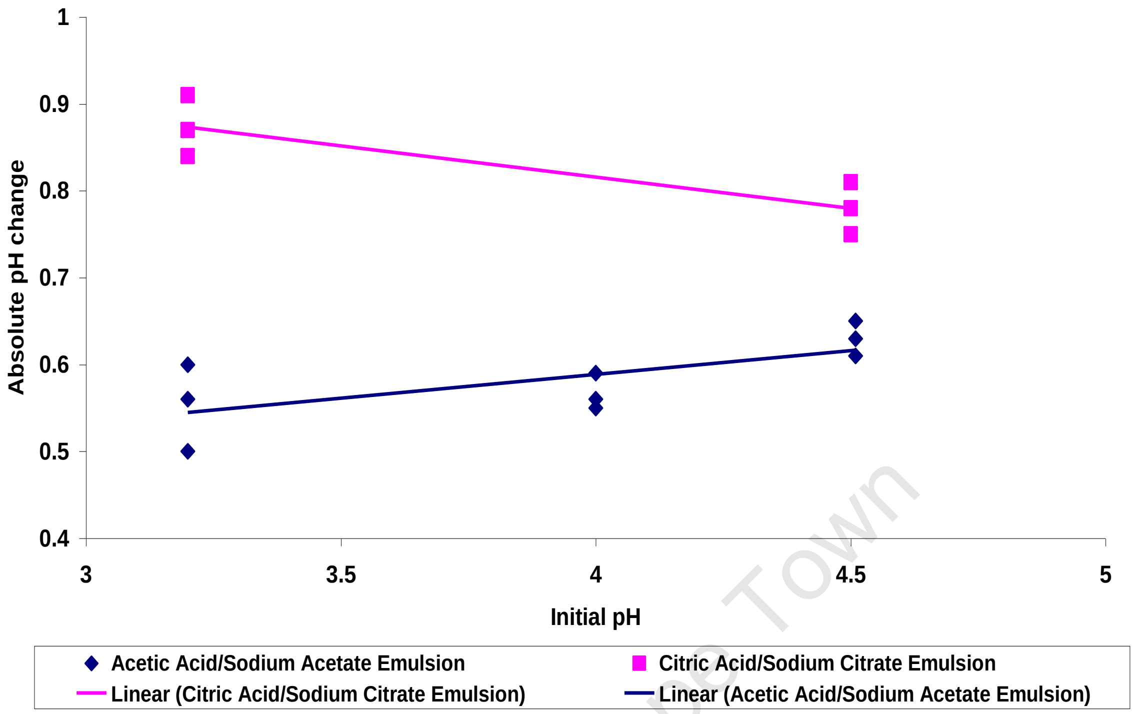

Figure 3.3.7: *Plot of Absolute (Uncorrected) pH Change versus Initial pH for the Gasification Reactions of the AA/ NA and CA/ NC Emulsions*

3.3.2.3 Corrected pH change for acetic acid/sodium acetate and citric acid/sodium citrate emulsions

The change in pH due to the reaction was calculated by subtracting the initial pH determined in Section 3.3.2.1 from the reacted split pH. Comparing the two buffers used, the AA/NA emulsions had an average of 0.05 while the CA/NC emulsions had an average of 0.07, which is an insignificant corrected pH difference.

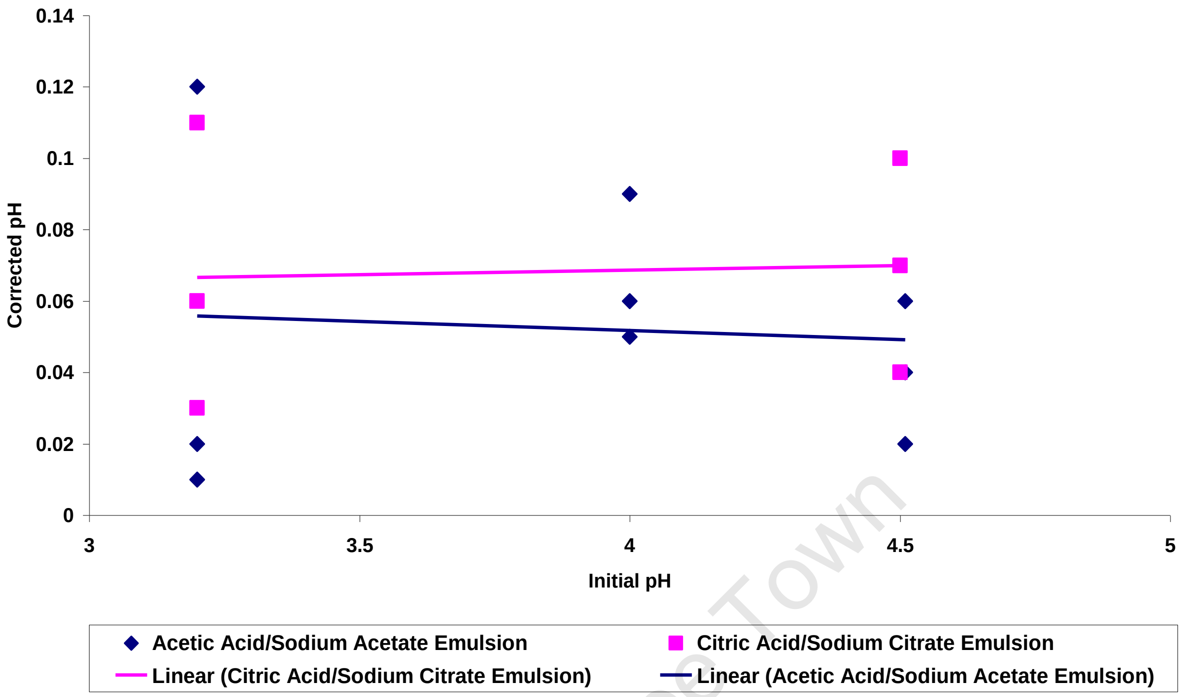

Figure 3.3.8: *Plot of Corrected pH Changes versus Initial pH for the Gasification Reactions of the AA/ NA and CA/ NC Emulsions*

3.3.3 Rate Constants and Initial Rates of Reaction for the emulsions:

3.3.3.1 Rate constants for acetic acid/sodium acetate and citric acid/sodium citrate emulsions

Rate constants were calculated by plotting 1/ (P_{eq} – P_t) against time, with the slope of the straight line, obtained by linear regression, equal to the rate constant. The associated rate constant errors are reported in **Appendix E**. **Figure 3.3.9**, a plot of the rate constants versus pH and trend lines for acetic acid/sodium acetate and citric acid/sodium citrate emulsions. At a pH less than 4 the AA/NA emulsions have a faster reaction rate than the CA/NC emulsions.

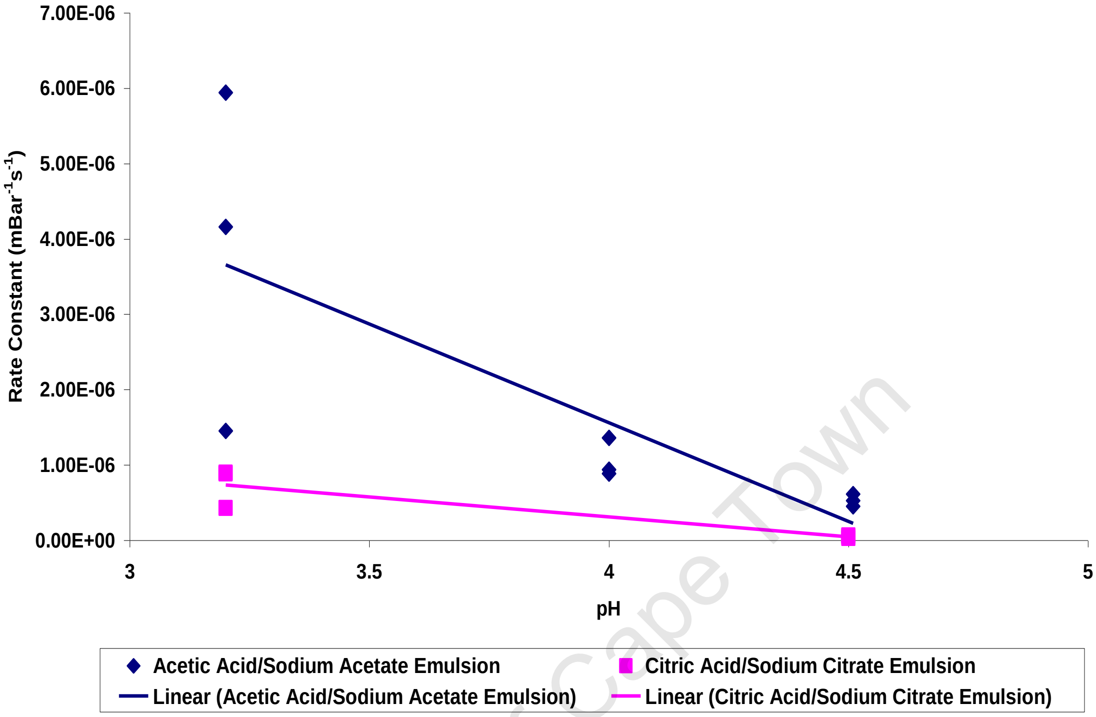

Figure 3.3.9: *Calculated Rate Constants and Trend lines versus pH for the Gasification Reactions of the AA/ NA and CA/ NC Emulsions.*

3.3.3.2 Initial rates of reaction for acetic acid/sodium acetate and citric acid/sodium citrate emulsions:

The initial rates of the reaction were calculated from the rate constants determined in section 3.3.3.1 and the known initial concentrations of H^+ and NO_2^-. The calculated initial rates of reaction and their associated errors are reported in **Appendix E**. Plots of the initial rate constants versus pH are shown in **Figure 3.3.10**, which clearly indicates that reactions of the AA/ NA emulsions are much faster at low pH (that is pH lower than 4) than those of CA/ NC, mirroring the trends seen for the rate constants in section 2.4.1.

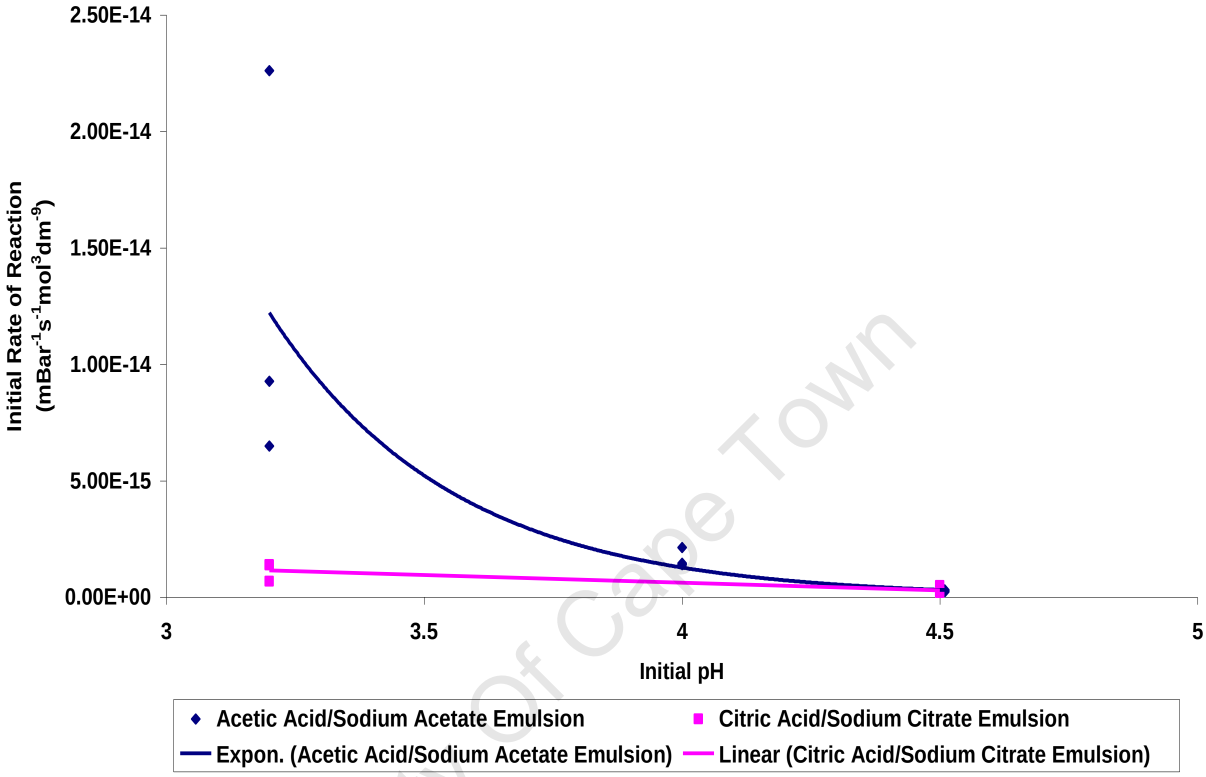

Figure 3.3.10: *Initial Rates of Reaction and Trend lines versus Initial pH for the Gasification Reactions of the AA/ NA and CA/ NA Emulsions*

3.4 Discussion

Two different buffered emulsions were investigated, that is the acetic acid/sodium acetate and citric acid/sodium citrate emulsions with a pKa of 4.75 and 3.15 respectively.

The gasification reactions of this study have shown that acetic acid is a better buffer as compared to the citric acid when used in the ammonium nitrate emulsions; furthermore at low pH, pressure increased rapidly and slowed down with increasing pH as indicated by the rate constants and initial rates of acetic acid buffered emulsions. At pH = 3.2, AA/NA emulsion reached maximum pressure increase within 3 hours of starting the reaction, whereas CA/NC emulsion did not attained maximum pressure at the corresponding pH; furthermore same pattern was observed for pH greater than 3.2 in both emulsions no stable pressure state was reached even after 24 hours as evidenced by plots of pressure versus time.

A method was developed to separate the emulsions into their aqueous and organic components. This involved the addition of a 1:2:2 mixture of hexane: ethanol: water to the ammonium nitrate emulsion followed by centrifuging for between 20 and 60 minutes. Upon separation it was found that emulsion formation appreciably changes the pH of its pre-emulsified aqueous component. Although the action of splitting the emulsion also has an insignificant effect on pH, AA/NA emulsions had an average pH increase of 0.5 higher than while citric acid was found to have an increase of 0.76 pH units.

On emulsification, the gasification reactions were found to have a small effect on pH. After reacting with sodium nitrite, the acetic acid emulsion had a mean corrected pH of 0.05, while citric acid showed a slight increase of 0.07. The results of the corrected pH showed that there is an insignificant difference (0.02) between AA/NA and CA/NC emulsions after emulsification. These findings led to a conclusion that both weak acids are exerting a buffer effect.

The pressure monitoring methodology for determining gasification rates has proved that it can be used for the ammonium nitrate emulsions. However, with viscosity of the emulsion, there was an increased difficulty in assuring adequate mixing of the sodium nitrite solution. The sodium nitrite solution was used to initiate the gasification reactions. Acetic acid emulsions were more efficient in generating pressure increase compared to the citric acid emulsions. Citric acid emulsion had an average pressure of 172 mBar, whereas acetic acid emulsion was found to have a mean of 182 mBar.

In overall, acetic acid buffer was a better buffer than the citric acid buffer; It generated a bigger pressure increase than the citric acid buffered emulsion and it had a minimal pH increase than the citric acid buffer.

3.5 Conclusion and Future works

This study has shown that the pressure monitoring methodology for determining reaction rates is suitable for the ammonium nitrate emulsions. Furthermore, acetic acid buffered emulsions were found to be faster and better than the citric acid buffered emulsions. However, with the increased viscosity of the emulsions, there was an increased difficulty in assuring adequate mixing of the sodium nitrite solution which was used to initiate the gasification reactions. Due to poor mixing the reactions showed signs of cracking in the emulsion with the formation of large pockets of gas. For future investigation it would be better to design or build an injection and mixing system to pump and mix the emulsions and sodium nitrite solution into the reaction vessel. Also, use of sodium nitrite emulsion instead of sodium nitrite solution to sensitize the ammonium nitrate emulsion may result in greater increase in pressure.

The fact that the gasification reaction is pH sensitive means that it is important to know the pH of the emulsion. A method was designed or developed to split the ammonium nitrate emulsions into its aqueous and organic components. This methodology has proved that emulsion formation significantly changes the pH of its pre-emulsified aqueous components. With the methods developed in this study further investigations can be done in the ammonium nitrate emulsions. It would be interesting to determine if the rate of the reaction has an effect on gas bubble size. In addition, it would be possible to investigate the stability, robustness and shelf life of the sensitized emulsion.

References

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2. M. A. Cook, *The science of high explosives*, Robert Krieger Publishing Company, New York, 1971.
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Chapter 4

General Discussion and Conclusion

4.1 Introduction

Gasification is an important method of sensitising emulsion explosives. It is also a process that is difficult to control. In this study the kinetics of the most commonly used gasification reaction, the ammonium nitrate and sodium nitrite reaction was studied.

A system and a method were designed to study the gasification rates of ammonium nitrate solution reacting with sodium nitrite by virtue of the N_2 gas generated in the reaction. In this system the reaction vessel was designed so that the pressure can be monitored at the same time as being able to withstand high pressures and to be able to control the temperature. The method and apparatus were used to conduct the kinetic reactions for the ammonium nitrate-sodium nitrite reaction and the results are depicted in Chapter 2 of this study.

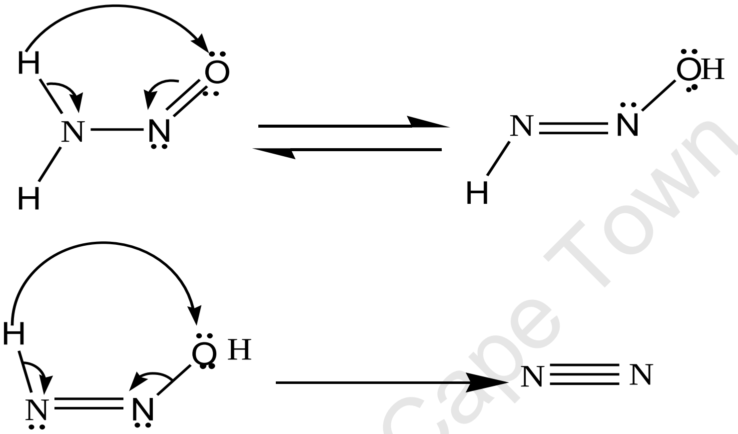
4.2 Reaction Mechanisms

Rubin *et.al* [1] has described the reaction mechanism leading to the formation of nitrogen gas and water as final products. According to the reaction pathway described in Chapter 2, H_2NNO (reaction 7) is the intermediate responsible for the formation of N_2 and H_2O.

$$H_2NNO \rightleftharpoons N_2 + H_2O$$

H_2NNO is kinetically and thermodynamically unstable due to the fact that it can self dissociate to the final two products and only one bond needs to be broken in order to produce N_2 and H_2O. A possible reaction mechanism for the production of N_2 and H_2O is shown below

Reaction mechanisms for $H_2NNO \rightleftharpoons N_2 + H_2O$

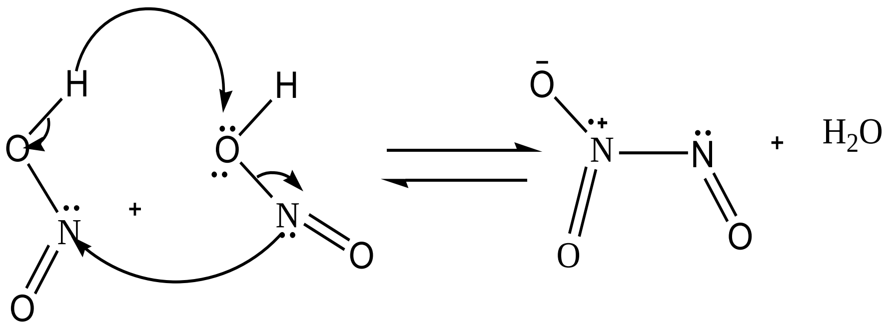


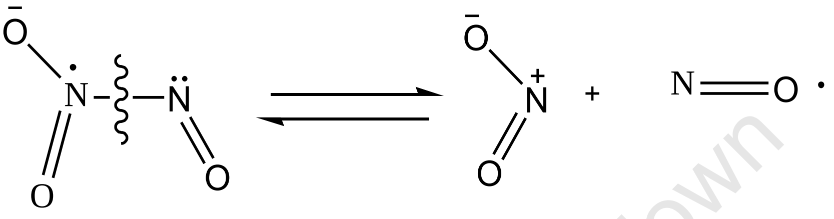
Looking at the reaction pathway there are reactants that are responsible for the formation of the intermediate nitrosamine. Their mechanisms are depicted below:

NH_3 molecule can react directly with the two molecules of HNO_2 or two of them may participate in a prior equilibrium followed by a reaction with the third molecule to generate nitrosamine. HNO_2 is in equilibrium with N_2O_3 which in turn is in equilibrium with NO and NO_2

Reaction mechanism for $2\ HNO_2 \rightleftharpoons N_2O_3 + H_2O$

$N_2O_3 \rightleftharpoons NO + NO_2$



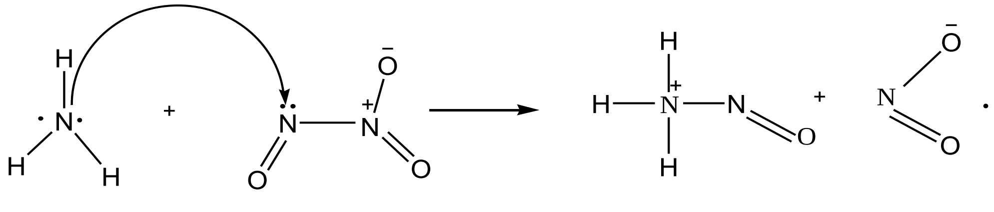


HNO2 is less reactive so its derivatives are used to form the nitrosamine intermediate.

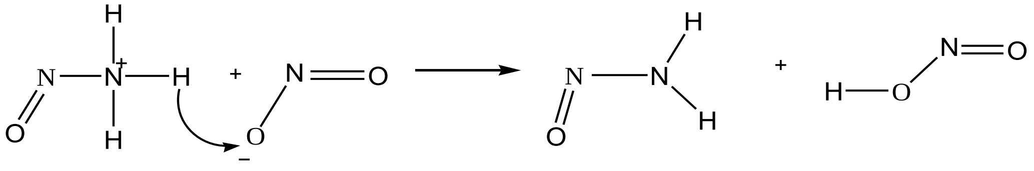
Reaction mechanism for $NH_3 + N_2O_3 \rightleftharpoons H_3NNO^+ + NO_2^-$

$H_3NNO^+ + NO_2^- \rightleftharpoons H_2NNO + HNO_2$

Slow step



Fast step



As can be seen, in this complex mechanism, HNO_2 is a reactant in one step of the reaction but a product in another step. This may give rise to an oscillatory kinetics as noted by Rubin *et.al*. If this proposed mechanism is correct it should be possible to interpret the experimental results below

4.3 Gasification reactions of unbuffered ammonium nitrate-sodium nitrite reaction

The ammonium nitrate-sodium nitrite reaction produces nitrogen gas and this is observed by the increase in pressure over time. **Figure 4.1** depicts pressure traces for unbuffered ammonium nitrate-sodium nitrite gassing reactions. The method that was designed had proven to be working but there was a problem in reproducibility; this was shown by the different pressure traces that were observed for the same reaction at the same pH and temperature (**Figure 4.2**). Furthermore, it was discovered that at low pH the pressure increases rapidly while at higher pH the extent of reaction slows down (**Figure 4.1**).

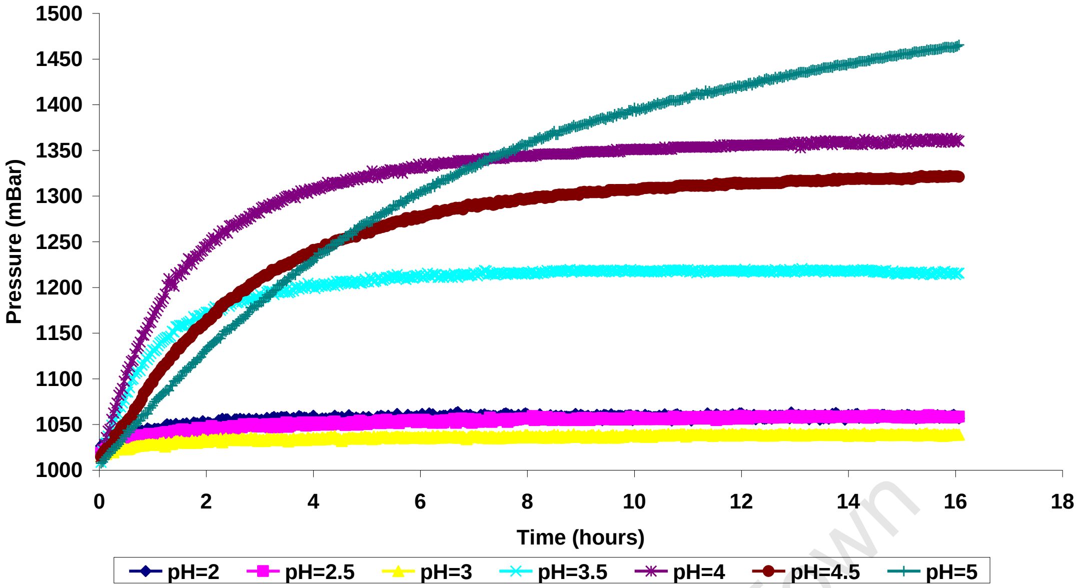


Figure 4.1: *Plot of pressure versus time for the gasification reactions of the unbuffered ammonium nitrate-sodium nitrite solution at various pHs*

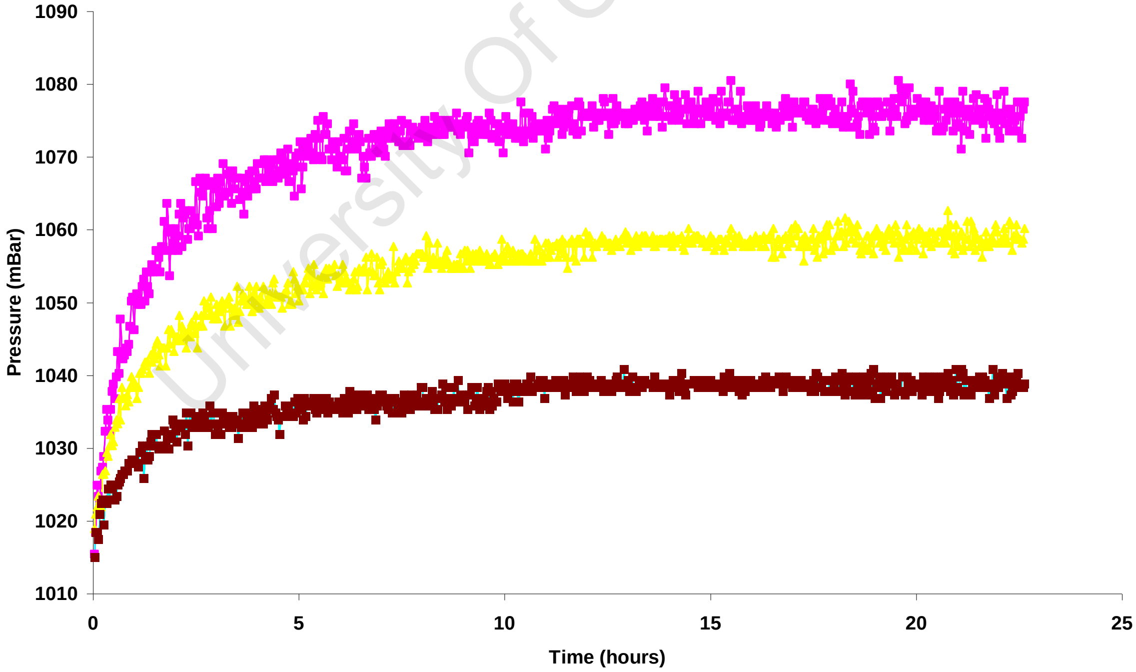


Figure 4.2: A plot of pressure versus time for unbuffered reactions at pH = 3.5

Since the ammonium nitrate-sodium nitrite reaction is sensitive to pH. pH was measured before and after the reaction had taken place in order to see if it had changed. It was discovered that the pH does change and that the pH change varies. For example **Figure 4.3**, at pH = 2 and 2.5 there was an increase in the absolute pH change while at pH = 3 and 3.5 there was the lowest absolute pH changes. This might be due to the fact that NO_2^- has a pKa of approximately 3.27 and hence acts as a buffer in the intermediate pH range.

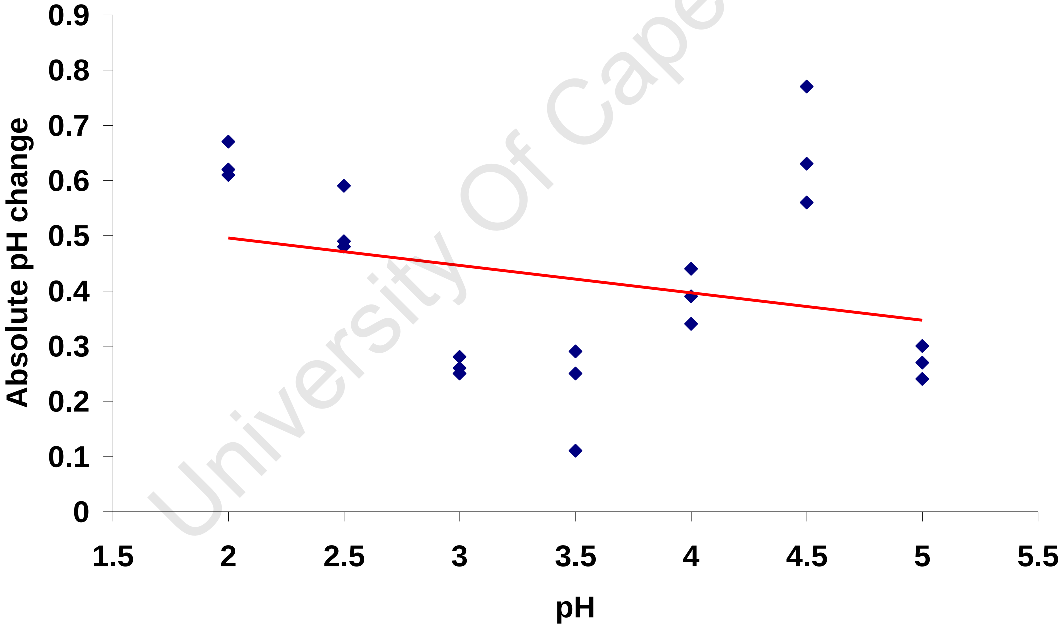


Figure 4.3: *Plot of absolute pH change versus pH for unbuffered ammonium nitrate-sodium nitrite reaction*

Since the pressure increase is assumed to be due to the nitrogen gas produced in the reaction, the pressure change can be used as a measure of the extent of the reaction. The question then arises does the pH affect the extent of reaction. **Figure 4.4** illustrates a plot of pressure changes against pH. From this it is seen that at different pHs the extent of the reaction does change. Thus not only is the rate of the reaction pH dependent, but also the extent of the reaction.

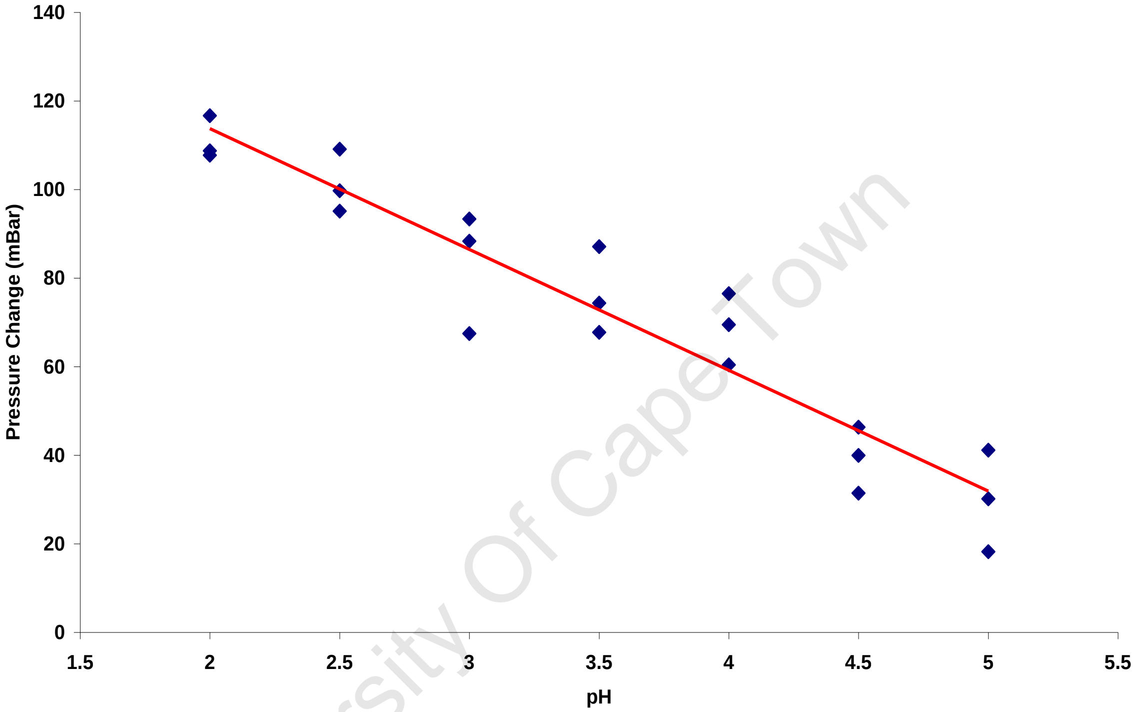


Figure 4.4: *Plot of pressure change versus pH for unbuffered ammonium nitrate-sodium nitrite reaction*

Since the nitrite anion or the nitrous acid is involved in the reaction it is important to know how their relative concentrations change with pH. To this end, speciation of the nitrite ion was calculated using the JESS simulation program and illustrated graphically using Microsoft Excel program (**Figure 4.5**).

$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

The pKa of this dissociation is 3.27 at ionic strength = 0, but this will change under the very high ionic strength conditions that exist in saturated ammonium nitrate solution. The effect of ionic strength on pKa, under these conditions is difficult to predict [2]. Using the JESS simulation program [3, 4] we can only reliably extrapolate to an ionic strength of 10. The nitrite speciation at this ionic strength is shown in **Figure 4.5.** From this plot it can be seen that in the pH range of 3 – 5 there is an inflection with the speciation of the nitrite changing rapidly. Since the reaction producing N_2 gas is dependent on the HNO_2 concentration it is easy to see why the reaction is pH sensitive and so difficult to control. It also explains why the rate slows down dramatically as the pH increase.

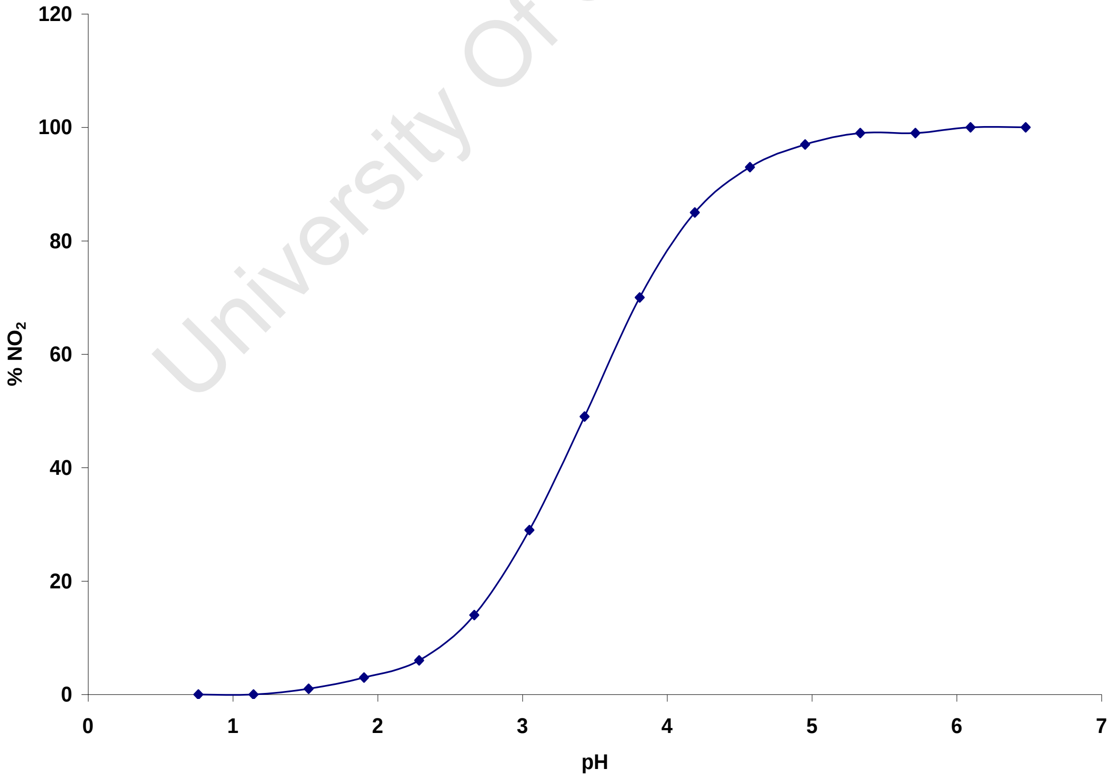


Figure 4.5: Nitrite *speciation at an ionic strength = 10*

4.4 Effect of buffers on gasification reaction

Since it was shown that the gasification reaction is pH sensitive and that the pH changes during the experiment it was decided to buffer the reaction using potassium hydrogen phthalate (pKa = 2.94) , sodium citrate (pKa = 4.07) or sodium formate (pKa = 3.75) buffers.

Table 4.1 shows the pH change during the reaction when these three buffers are employed at a concentration of   0.1 M. As can be seen these buffers are able to minimise the pH changes during the reaction. However, in order to be useful, they must not themselves affect the reaction.

Table 4.1: pH changes for the buffered reactions

Buffers	Initial pH	Final pH	Absolute pH change
Potassium hydrogen phthalate	3.0	3.32	0.32
	3.0	3.38	0.38
	3.0	3.26	0.26
	3.5	3.22	0.28
	3.5	3.11	0.39
	3.5	3.20	0.30
	4.0	3.71	0.29
	4.0	3.79	0.21
	4.0	3.82	0.18
Sodium citrate	3.0	2.99	0.01
	3.0	2.97	0.03
	3.0	2.89	0.11
	3.5	3.86	0.36
	3.5	3.94	0.44
	3.5	3.96	0.46
	4.0	4.05	0.05
	4.0	4.11	0.11
Sodium formate	3.0	3.15	0.15
	3.0	3.11	0.11
	3.0	3.06	0.06
	3.0	2.99	0.01
	3.5	3.52	0.02
	3.5	3.47	0.03
	3.5	3.46	0.04
	4.0	3.59	0.41
	4.0	3.67	0.33
	4.0	3.58	0.42

Figure 4.6 shows that the three buffers have a similar effect on the extent of the reaction depressing it relative to the unbuffered solution. As in before in each case the extent of the reaction decreases with pH.

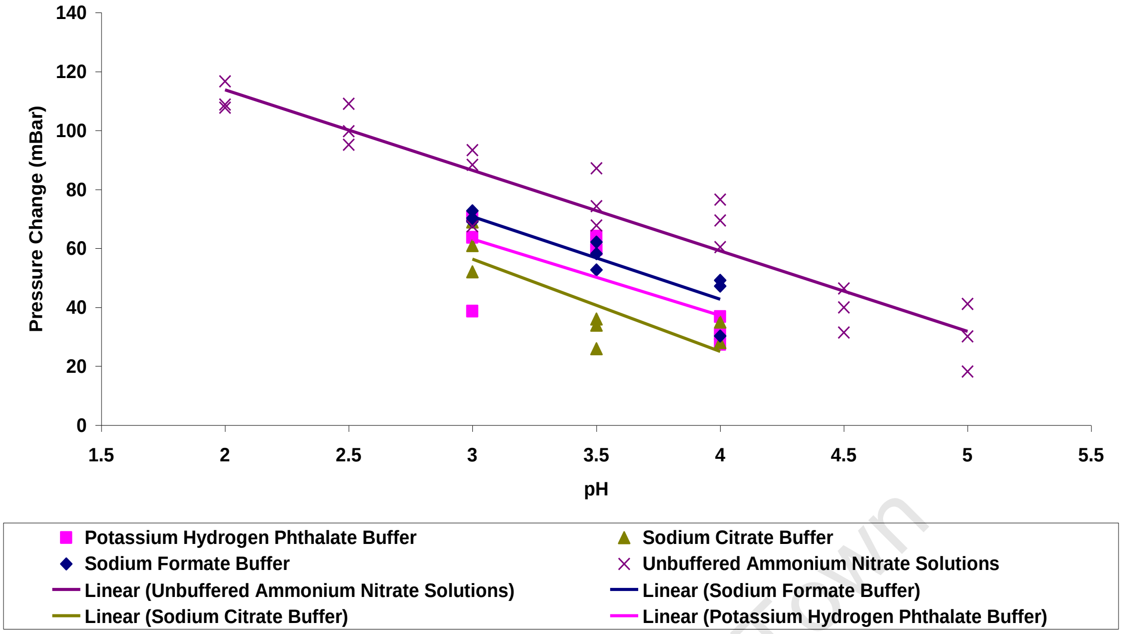


Figure 4.6: Pressure changes versus pH for buffered and unbuffered ammonium nitrate-sodium nitrite reactions

Figure 4.7 shows the effect of pH on the rate constant of buffered and unbuffered reactions. There is a considerable scatter in the data and there does not appear to be any clear trend for the reactions. From the initial rates of reaction the buffered reactions had the fastest reactions with phthalate and formate buffers showing highest rate at pH = 3 (**Figure 4.8**). Therefore buffering the ammonium nitrate-sodium nitrite reaction had improved the rate of the ammonium nitrate-sodium nitrite reaction. Hughes *et.al* has postulated that the nitrosamine reaction may be catalysed by carboxylate [5]. If this is true it is easy to see why these carboxylic acid buffers could affect the rate.

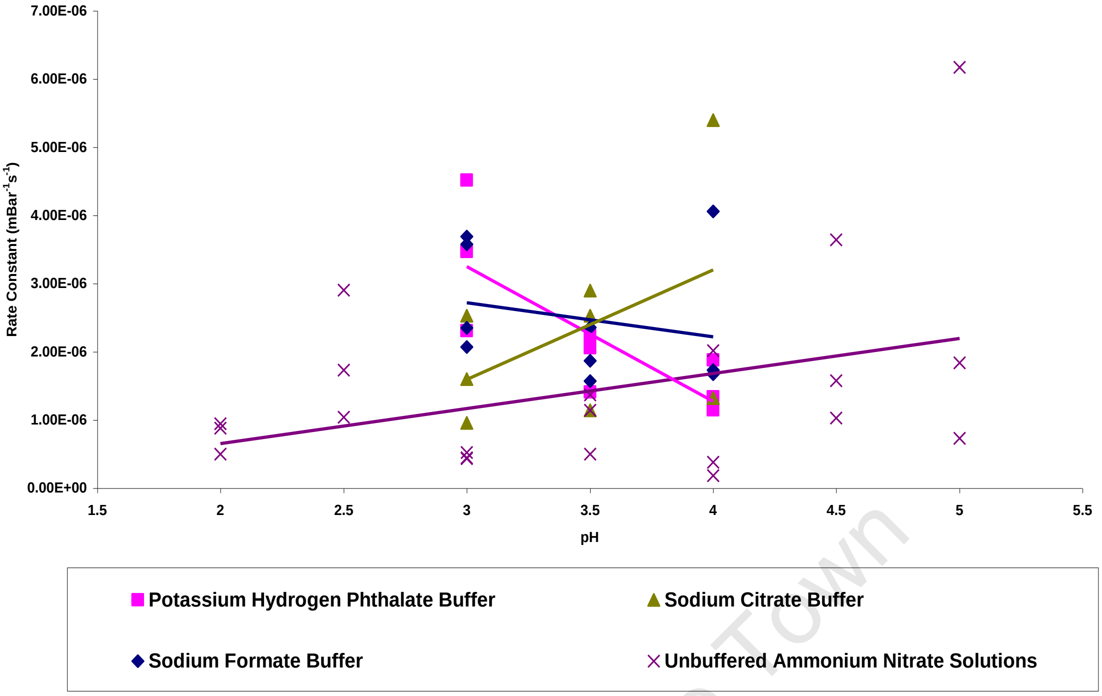


Figure 4.7: *Plot of rate constants versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite*

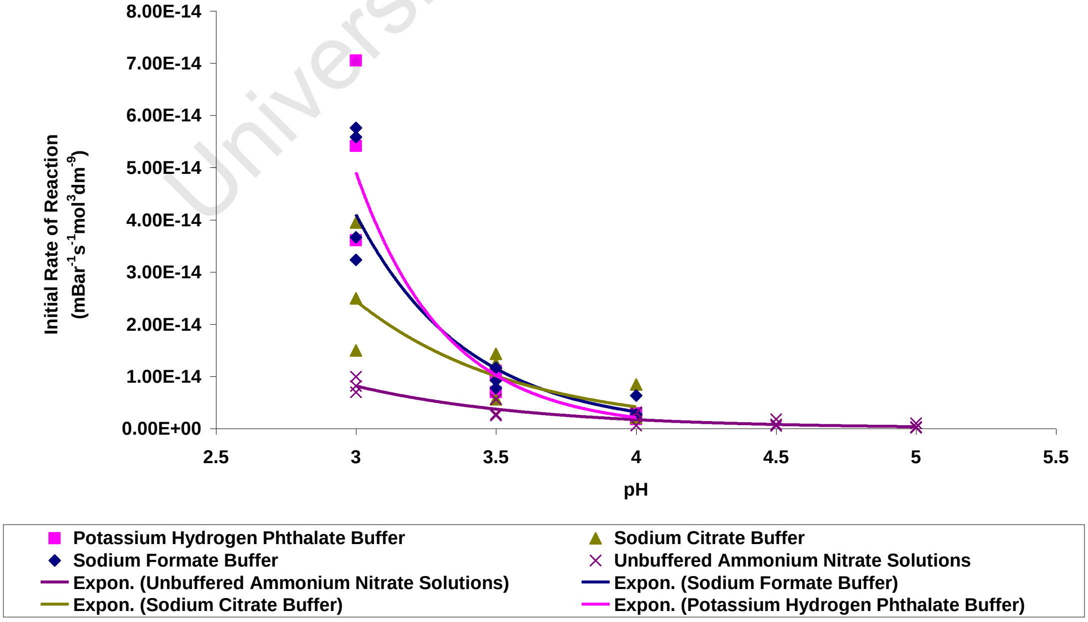


Figure 4.8: *Plot of initial rates of reaction versus pH for buffered and unbuffered ammonium nitrate solutions reacting with sodium nitrite*

4.5 Comparison between buffered ammonium nitrate solutions and ammonium nitrate emulsions

The ammonium nitrate solution was emulsified and buffered with citric acid/sodium citrate and acetic acid/sodium acetate buffers and the same methodology used was used for buffered and unbuffered ammonium nitrate solutions. The results of these reactions are depicted below:

Pressure traces for buffered ammonium nitrate-sodium nitrite reactions and acetic acid/sodium acetate and citric acid/sodium citrate emulsions at corresponding pHs are illustrated graphically (**Figure 4.9** and **Figure 4.10**).

At pH = 3 gasification reaction experiments for buffered ammonium nitrate-sodium nitrite reactions had shown that all three buffers (citrate, formate and phthalate) had an increase in pressure and a stable pressure state was reached, while for the buffered ammonium nitrate emulsions only acetic acid/sodium acetate emulsion had reached a maximum pressure and citric acid/sodium citrate only had an increase in pressure the reaction was still continuing even after 24 hours.

At pH = 4 the pressure traces for buffered ammonium nitrate-sodium nitrite reactions have shown that although there was an increase in pressure, maximum pressure, in the form of the trace reaching a plateau, was not achieved and that the reactions were slow (**Figure 4.9**). The same pattern was observed for the acetic acid/sodium acetate and citric acid/sodium citrate emulsions (pH 4 and 4.5) (**Figure 4.10**) as pH increases the reactions became slower; the only difference was that the pressure increase did not take place in intervals. This leads to a conclusion that at higher pH whether a reaction is emulsified or not the extent of a reaction slows down or the rate at which nitrogen gas is produced slows down.

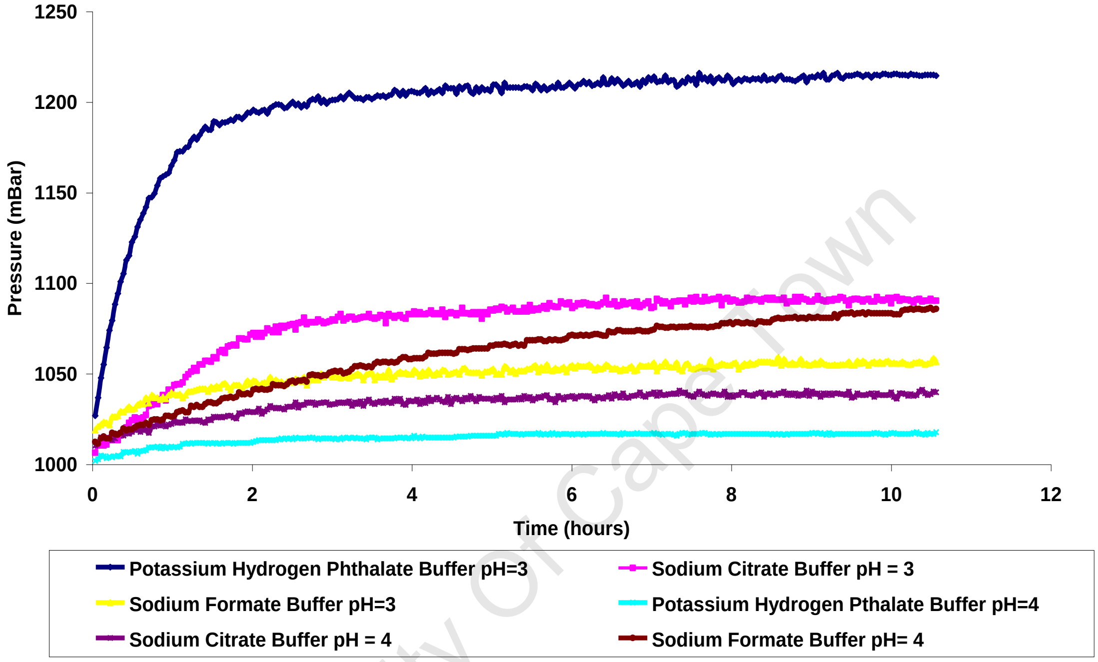


Figure 4.9: *Plot of pressure versus time for the gasification reactions of the buffered ammonium nitrate-sodium nitrite reaction*

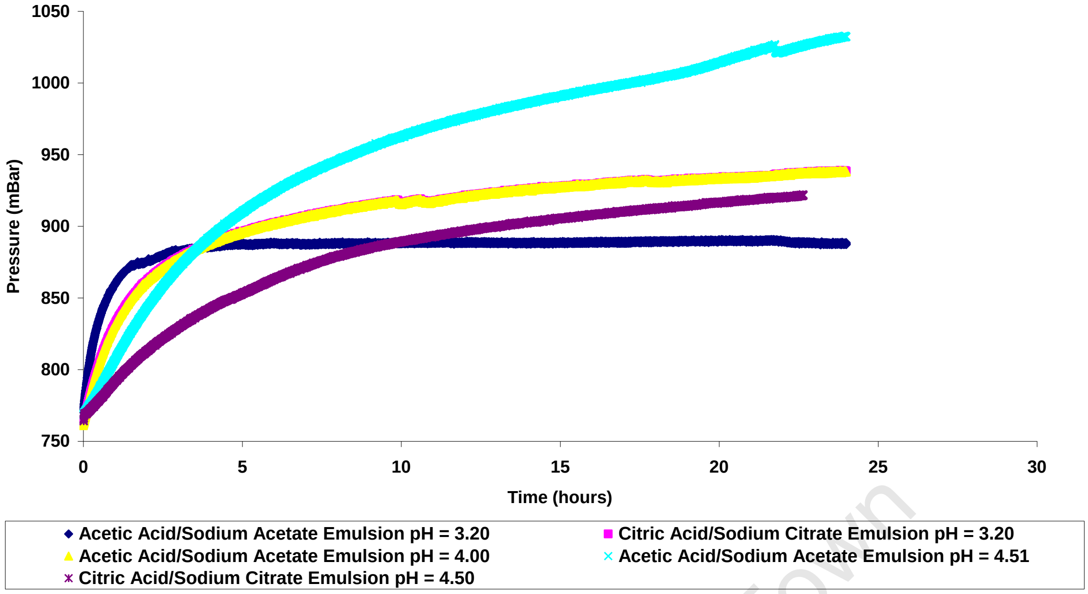


Figure 4.10: *Plot of pressure versus time for the gasification reactions of the buffered ammonium nitrate emulsions*

Pressure changes for the buffered ammonium nitrate-sodium nitrite reactions had a smaller pressure change as compared to the buffered ammonium nitrate emulsions. Furthermore as pH increases the pressure change was decreased while for the buffered ammonium nitrate emulsions the pressure change seemed to be constant for all the measured pHs (that is there was not much variation in the pressure change for the buffered emulsions). **Figure 4.11** illustrates the findings of pressure change against initial pH for buffered ammonium nitrate-sodium nitrite reactions and buffered ammonium nitrate reactions.

This means that even though the buffered emulsions did not reach a stable pressure state more nitrogen gas was being produced as compared to the buffered ammonium nitrate reactions at the same pH.

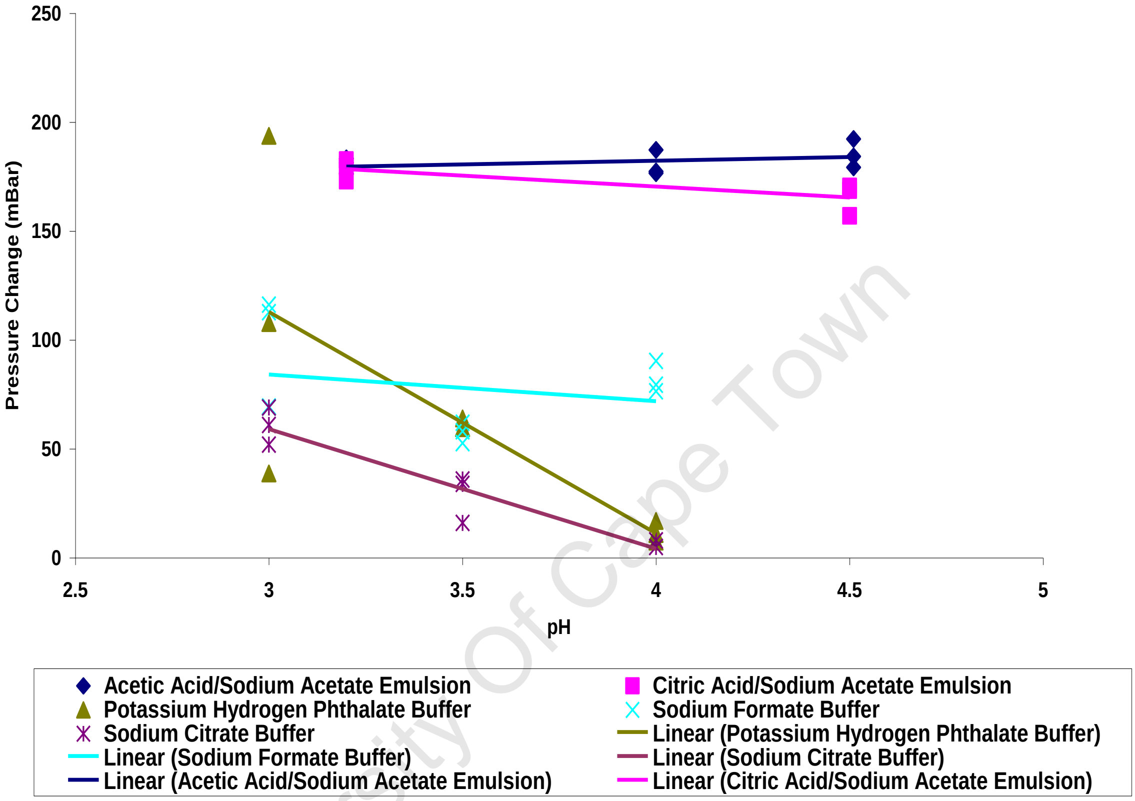


Figure 4.11: *Plot of pressure change versus Initial pH for the gasification reactions of the AA/ NA and CA/ NA emulsions and buffered ammonium nitrate-sodium nitrite reactions*

A plot of absolute pH versus Initial pH (**Figure 4.12**) shows that the buffered ammonium nitrate emulsions had a greater increase in absolute pH, with citric acid/sodium acetate emulsion having an overall pH increase as compared to the buffered ammonium nitrate solutions. This suggests that emulsifying buffered ammonium nitrate solutions leads to a pH increase.

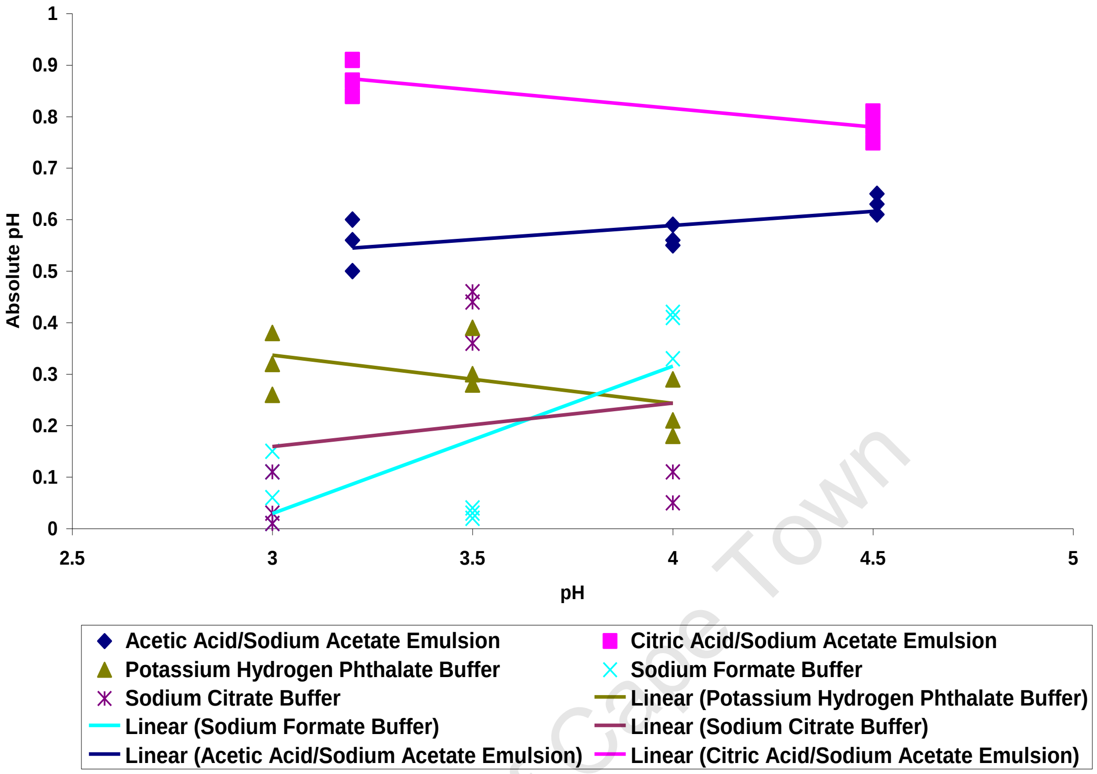


Figure 4.12: *Plot of absolute pH versus initial pH for the gasification reactions of the AA/ NA and CA/ NA emulsions and buffered ammonium nitrate-sodium nitrite reaction*.

Buffered ammonium nitrate emulsions have shown to evolve more nitrogen gas being produced, but buffered ammonium nitrate solutions were found to have a greater overall rate constant (**Figure 4.13**). With these findings a conclusion can be made that the buffered ammonium nitrate-sodium nitrite reactions had a much faster rate as compared to the buffered ammonium nitrate emulsions.

The initial rates of reaction for emulsified experiments were found to be lower than the buffered ammonium nitrate-sodium nitrite reactions (**Figure 4.14**). For example at pH = 3, the buffered ammonium nitrate-sodium nitrite reactions had the highest rates of reaction and at pH = 3.2 the buffered ammonium nitrate emulsions had the lowest rate of reaction and the rates of reaction decreased with increasing pH. This means that buffering the ammonium nitrate emulsions caused the reactions to have a slower rate as compared to the buffered ammonium nitrate-sodium nitrite reactions and this conclusion agrees with the above findings.

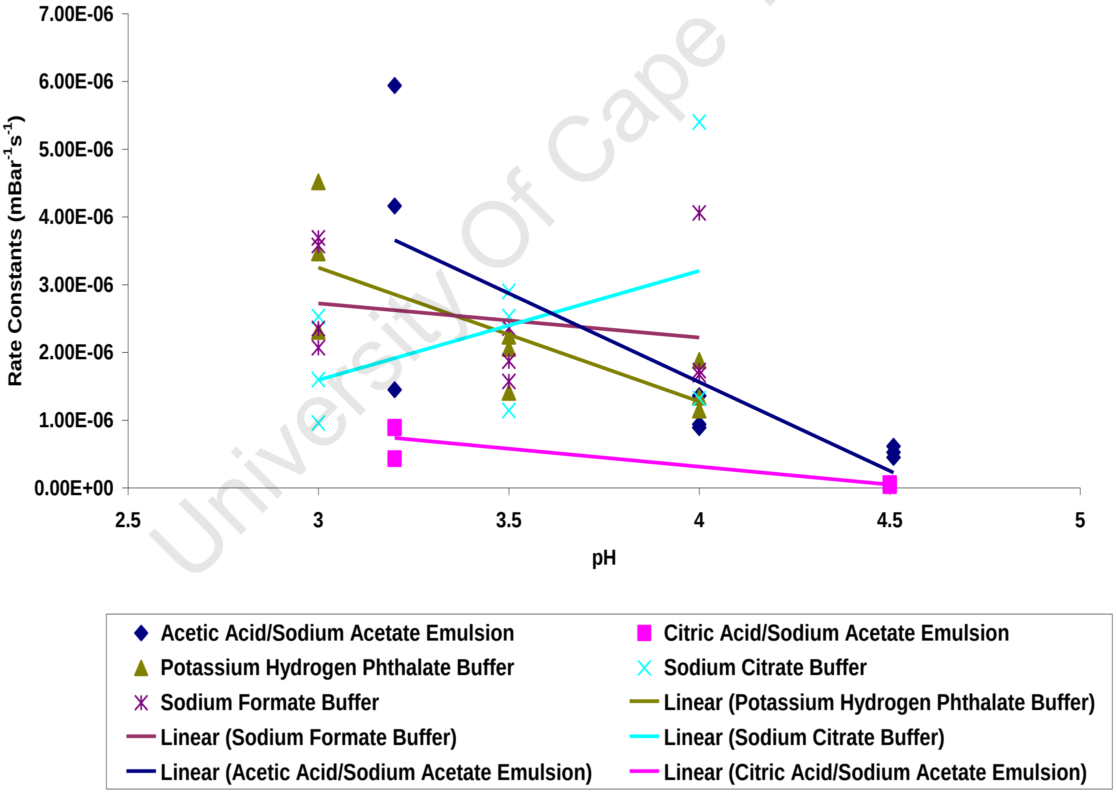


Figure 4.13: *Plot of rate constants versus initial pH for the gasification reactions of the AA/ NA and CA/ NA emulsions and buffered ammonium nitrate-sodium nitrite* reactions

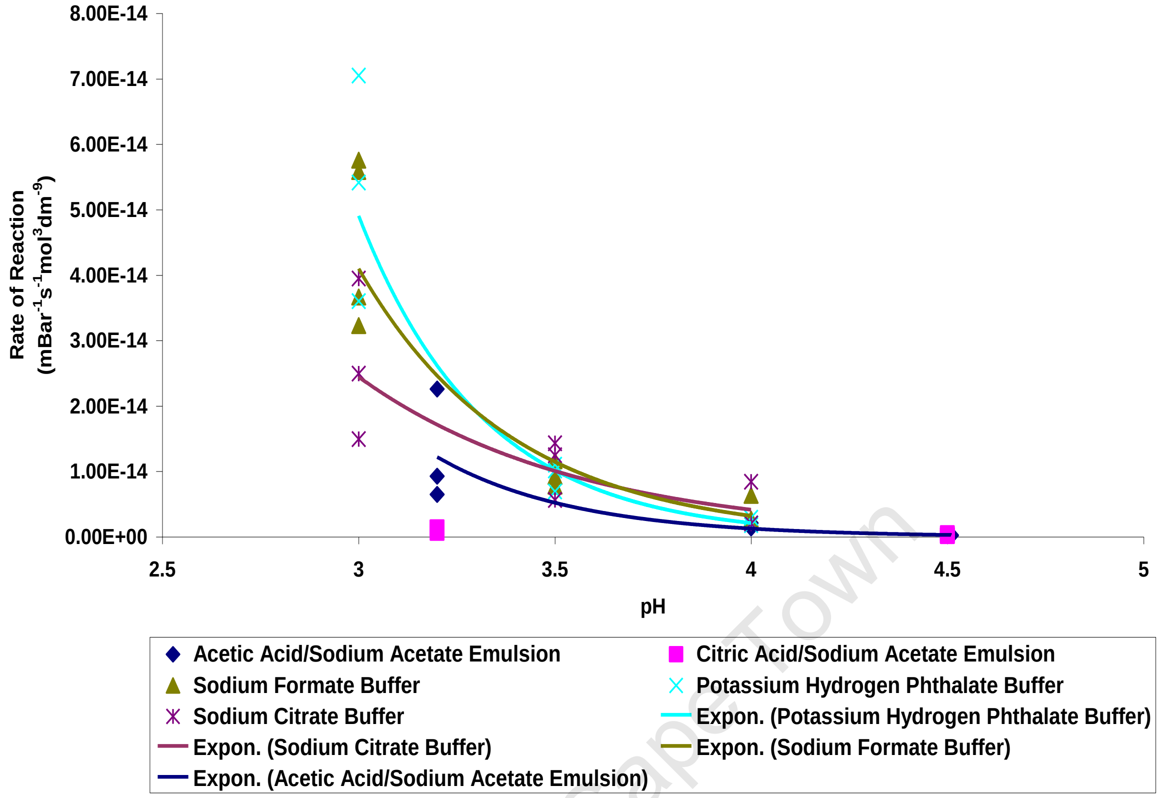


Figure 4.14: *Plot of initial rate of reaction versus Initial pH for the gasification reactions of the AA/ NA and CA/ NA emulsions and buffered ammonium nitrate-sodium nitrite reactions*

Due to these findings, it can be concluded that emulsifying and buffering the ammonium nitrate solutions has an effect in the pH, pressure, rate constant and rate of reaction. In addition a noticeable absolute pH change was observed in the ammonium nitrate emulsion explosives and this was unexpected as the emulsions were buffered in the hope that buffering would lead to a small pH change for the ammonium nitrate emulsion explosives.

4.6 Effect of zinc nitrate on buffered and unbuffered ammonium nitrate reactions

A Lewis acid (zinc nitrate) was also added to the buffered and unbuffered solutions of ammonium nitrate-sodium nitrite reaction. This was done because Lewis Acids are known to improving performance of reactions and act as pH lowering agents

Alilovic *et.al* [6] patented a method of gassing emulsion explosives. In this patent a pH lowering agent was added in order to decrease the pH of the gassing solution. In this case the pH lowering agent was $ZnCl_2$ or $AlCl_3$. Alilovic *et.al* claim that addition of zinc nitrate to the gassing solution improved the performance of the gassing reaction; it showed a significant decrease in the gassing reaction times as compared to the gassing reaction that did not contain zinc nitrate.

In this project a Lewis Acid (zinc nitrate) was added to the buffered and unbuffered ammonium nitrate-sodium nitrite reactions. The pressure changes for the unbuffered reactions with zinc nitrate were found to be higher than those of buffered reactions with zinc nitrate. However rate constants and initial rates of reaction for buffered reactions with zinc nitrate were much faster than the unbuffered reactions with the Lewis Acid. The Lewis Acid had an impact on the ammonium nitrate reactions but did not lower pH changes for buffered ammonium nitrate reactions with zinc nitrate as expected.

Clearly the Lewis Acid had improved the performance of the ammonium nitrate-sodium nitrite gassing reaction and it would be interesting to see if the Lewis Acid would have the same effect with the ammonium nitrate emulsions as it did with the buffered and unbuffered ammonium nitrate-sodium nitrite gassing reactions. Furthermore, it would be ideal to conduct a study with the buffered and unbuffered ammonium nitrate-sodium nitrite reactions and ammonium nitrate emulsions under different temperatures to see what kind of effect temperature would have in these reactions.

4.7 Future Works

While this study has given some insight into the very complex reaction between nitrite and ammonium ions, the study could be extended to include conditions more applicable to industry. Thus the study could be extended to include:

a) Effects of temperature. Underground mining takes place at extremes of temperature and so its effect on the reaction is important. Also, in open caste mining, charging may take place over several days and so a column of explosive maybe subject to extremes of temperature during the day and at night. Similarly there will be seasonal changes in temperature.

b) Effect of pressure. The pressure at the top of a large explosive column may be very different from that at the top of the column. Hence it is important to know what effect, if any, pressure has on the reaction. It is for this reason that the current experimental setup was designed, where ambient pressure could be varied.

c) Since sensitization depends on an intimate mixture of gas bubbles within the emulsion, the size and distribution of the bubbles should be studied using microscopy.

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2. K. S. Pitzer, *Activity coefficients in electrolyte solutions*, CRC Press, Florida, 1991.
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5. E. D. Hughes, C. K. Ingold and J. H. Ridd; *Nitrosation, diazotization, and deamination. VI. Comparative discussion of the mechanisms of N- and O-nitrosation with special reference to diazotization*; *J. Chem. Soc***.**; 1958; 88.
6. I. Alilovic *et.al*, *Methods of gassing emulsion explosives and explosives produced thereby*, U.S. Patent 20040065396, 2004.

Appendix A
Material safety for NH_4NO_3 and $NaNO_2$

Chemical	Chemical Characteristics	Types of Hazard	Prevention	First Aid
NH_4NO_3	Molar mass 80.04 g ⁄mol Boiling point 210 °C Melting point 170 °C Density 1.73 g⁄cm^3 Appearance: white solid Solubility in H_2O: 190 g⁄100ml at 20 °C	**Fire**: enhances combustion of other substances and gives of toxic fumes in a fire. **Explosion:** risk of fire and explosion under confinement and high temperature. **Inhalation:** cough, headache and sore throat. **Skin:** redness. **Eyes:** redness and pain. **Ingestion:** abdominal, pain, diarrhea, dizziness and vomiting.	No contact with combustible or reducing agent Use fume hood or breathing protection Protective gloves and coat Safety goggles Do not eat, drink or smoke during work	Rinse with lots of water Evacuate danger area Get fresh air Rinse with plenty of water Rinse with plenty of water Drink lots of water
$NaNO_2$	Molar mass 69.00 g ⁄mol Boiling point 320 °C Melting point 270 °C Density 2.2 g⁄cm^3 Appearance: white solid Solubility in H_2O 82 g⁄100ml at 20 °C	**Fire:** enhances combustion of other substances and gives of toxic fumes in a fire. **Inhalation:** convulsions, dizziness, headache, nausea and unconsciousness. **Skin:** redness. **Eyes:** redness and pain. **Ingestion:** rapid pulse.	No contact with combustible or reducing agent Use fume hood or breathing protection Protective gloves and coat Safety goggles Do not eat and drink	Rinse with lots of water Get fresh air Rinse with plenty of water Rinse with plenty of water Drink lots of water

Appendix B

Tabulated results from the investigation of different parameters upon the reaction of ammonium nitrate with sodium nitrite

Appendix B1: pH changes, rate constants and initial rates of reaction unbuffered ammonium nitrate reactions

Initial pH	pH after reaction	Absolute pH change	Rate constant (mBar^{-1}s^{-1})	Rate constant error (mBar^{-1}s^{-1})	Initial rate of reaction (mBar^{-1}s^{-1} mol^{3}dm^{-9})	Initial rate of reaction error (mBar^{-1}s^{-1} mol^{3}dm^{-9})
2.0	2.67	0.67	8.79E-07	2.08E-08	1.37E-13	3.25E-15
2.0	2.61	0.61	4.98E-07	2.55E-08	1.41E-13	3.98E-15
2.0	2.62	0.62	9.47E-07	2.42E-08	1.48E-13	3.78E-15
2.5	2.99	0.49	1.04E-06	3.13E-08	5.13E-14	1.54E-15
2.5	2.98	0.48	1.73E-06	3.93E-08	8.54E-14	1.94E-15
2.5	3.09	0.59	2.91E-06	1.95E-08	5.08E-14	9.62E-16
3.0	3.26	0.26	4.46E-07	1.45E-08	6.96E-15	2.26E-16
3.0	3.28	0.28	5.22E-07	2.06E-08	8.14E-15	3.21E-16
3.0	3.25	0.25	4.34E-07	1.60E-08	9.89E-15	2.50E-16
3.5	3.21	0.29	1.14E-06	3.69E-08	5.62E-15	1.82E-16
3.5	3.25	0.25	1.37E-06	2.71E-08	2.76E-15	1.34E-16
3.5	3.39	0.11	5.02E-07	1.32E-08	2.48E-15	6.51E-17
4.0	3.66	0.34	3.83E-07	3.36E-08	5.98E-16	5.24E-17
4.0	3.56	0.44	2.02E-06	5.68E-08	3.15E-15	8.86E-17
4.0	3.61	0.39	1.85E-07	3.32E-08	2.89E-15	5.18E-17
4.5	3.94	0.56	1.03E-06	1.48E-08	5.08E-16	7.30E-18
4.5	3.87	0.63	3.64E-06	4.63E-07	1.80E-15	2.28E-16
4.5	3.73	0.77	1.58E-06	1.60E-08	7.80E-16	7.89E-18
5.0	4.73	0.27	6.17E-06	1.98E-08	1.12E-16	3.09E-18
5.0	4.7	0.3	1.84E-06	5.58E-07	9.63E-16	8.71E-17
5.0	4.76	0.24	7.32E-07	4.44E-08	2.87E-16	6.93E-18

Appendix C

Tabulated results from the investigation into the effect of various buffers upon the reaction of ammonium nitrate with sodium nitrite.

Appendix C1: pH changes, rate constants and initial rates of reaction for potassium hydrogen phthalate ($KHC_8O_4H_4$) buffer

Initial pH	pH after reaction	Absolute pH change	Rate constant ($mBar^{-1}s^{-1}$)	Rate constant error ($mBar^{-1}s^{-1}$)	Initial rate of reaction ($mBar^{-1}s^{-1}$ mol^3dm^{-9})	Initial rate of reaction error ($mBar^{-1}s^{-1}$ mol^3dm^{-9})
3.0	3.32	0.32	2.31E-06	2.47E-08	3.60E-14	3.85E-16
3.0	3.38	0.38	3.47E-06	3.53E-08	5.41E-14	5.51E-16
3.0	3.26	0.26	4.52E-06	6.16E-08	7.05E-14	9.61E-16
3.5	3.22	0.28	2.06E-06	5.88E-08	1.02E-14	2.90E-16
3.5	3.11	0.39	1.41E-06	2.13E-08	6.96E-15	1.05E-16
3.5	3.20	0.30	2.24E-06	2.36E-08	1.11E-14	1.16E-16
4.0	3.71	0.29	1.15E-06	2.04E-08	1.79E-15	3.18E-17
4.0	3.79	0.21	1.88E-06	3.30E-08	2.93E-15	5.15E-17
4.0	3.82	0.18	1.34E-06	1.92E-08	2.09E-15	3.00E-17

Appendix C2: pH changes, rate constants and initial rate of reaction for sodium citrate ($Na_3C_6O_7H_5$) buffer

Initial pH	pH after reaction	Absolute pH change	Rate constant ($mBar^{-1}s^{-1}$)	Rate constant error ($mBar^{-1}s^{-1}$)	Initial rate of reaction ($mBar^{-1}s^{-1}$ mol^3dm^{-9})	Initial rate of reaction error ($mBar^{-1}s^{-1}$ mol^3dm^{-9})
3.0	2.99	0.01	2.53E-06	7.55E-08	3.95E-14	1.18E-15
3.0	2.97	0.03	9.59E-07	1.65E-08	1.50E-14	2.57E-16
3.0	2.89	0.11	1.60E-06	1.64E-08	2.50E-14	2.56E-16
3.5	3.86	0.36	2.90E-06	4.17E-08	1.43E-14	2.06E-16
3.5	3.94	0.44	1.14E-06	3.40E-08	5.62E-15	1.68E-16
3.5	3.96	0.46	2.53E-06	3.55E-08	1.25E-14	1.75E-16
4.0	4.05	0.05	1.32E-06	6.07E-08	2.06E-15	9.47E-17
4.0	4.11	0.11	5.4E-06	3.02E-07	8.43E-15	4.71E-16

Appendix C3: pH changes, rate constants and initial rates of reaction for sodium formate ($NaCO_2H$) buffer

Initial pH	pH after reaction	Absolute pH change	Rate constant ($mBar^{-1}s^{-1}$)	Rate constant error ($mBar^{-1}s^{-1}$)	Initial rate of reaction ($mBar^{-1}s^{-1}$ mol^3dm^{-9})	Initial rate of reaction error ($mBar^{-1}s^{-1}$ mol^3dm^{-9})
3.0	3.15	0.15	3.58E-06	1.04E-07	5.59E-14	1.62E-15
3.0	3.11	0.11	3.69E-06	1.20E-07	5.76E-14	1.87E-15
3.0	3.06	0.06	2.07E-06	3.63E-08	3.23E-14	5.66E-16
3.0	2.99	0.01	2.35E-06	5.77E-08	3.67E-14	9.00E-16
3.5	3.52	0.02	1.57E-06	1.63E-08	7.75E-15	8.04E-17
3.5	3.47	0.03	1.87E-06	1.62E-08	9.23E-15	7.99E-17
3.5	3.46	0.04	2.36E-06	2.08E-08	1.16E-14	1.03E-16
4.0	3.59	0.41	1.73E-06	3.87E-08	2.70E-15	6.04E-17
4.0	3.67	0.33	1.67E-06	3.54E-08	2.61E-15	5.52E-17
4.0	3.58	0.42	4.06E-06	1.88E-07	6.33E-15	2.93E-16

Appendix D

Tabulated results from the investigation of unbuffered experiments and the effect of various buffers upon the reaction of NH_4NO_3 - $NaNO_2$ with zinc nitrate.

Appendix D1: pH changes, rate constants and initial rates of reaction for unbuffered ammonium nitrate-sodium nitrate with zinc nitrate

Initial pH	Final pH	Absolute pH Change	Rate Constant $mBar^{-1}s^{-1}$	Rate Constant Error ($mBar^{-1}s^{-1}$)	Pressure Change (mBar)	Initial Rate of Reaction ($mBar^{-1}s^{-1}$ mol^3dm^{-9})	Initial Rate of Reaction Error ($mBar^{-1}s^{-1}$ mol^3dm^{-9})
3.0	2.92	0.08	1.52E-06	2.23E-08	144.45	2.37E-14	3.48E-16
3.0	2.96	0.04	1.69E-06	3.29E-08	118.71	2.64E-14	5.13E-16
3.0	2.90	0.10	1.40E-06	4.31E-08	111.76	2.18E-14	6.72E-16
3.5	3.47	0.03	1.41E-06	2.91E-08	79.47	6.96E-15	1.44E-16
3.5	3.34	0.16	1.90E-06	3.64E-08	80.96	9.37E-15	1.80E-16
3.5	3.39	0.11	1.73E-06	2.78E-08	74.50	8.54E-15	1.37E-16
4.0	3.88	0.12	1.99E-06	3.17E-08	18.87	3.10E-15	4.95E-17
4.0	3.95	0.05	1.34E-06	2.02E-08	18.38	2.09E-15	3.15E-17
4.0	3.87	0.13	2.5E-06	1.62E-07	17.95	3.90E-15	2.53E-16

Appendix D2: pH changes, rate constants and initial rates of reaction for potassium hydrogen phthalate ($KHC_8O_4H_4$) with zinc nitrate

Initial pH	Final pH	Absolute pH Change	Rate Constant $mBar^{-1}s^{-1}$	Rate Constant Error ($mBar^{-1}s^{-1}$)	Pressure Change (mBar)	Initial Rate of Reaction ($mBar^{-1}s^{-1}$ mol^3dm^{-9})	Initial Rate of Reaction Error ($mBar^{-1}s^{-1}$ mol^3dm^{-9})
3.0	3.15	0.15	1.69E-06	4.52E-08	18.87	2.64E-14	7.05E-16
3.0	3.51	0.51	1.94E-06	2.88E-08	14.91	3.03E-14	4.49E-16
3.0	3.45	0.45	5.72E-06	1.21E-07	19.37	8.93E-14	1.89E-15
3.5	3.54	0.04	3.71E-06	7.44E-08	16.39	1.83E-14	3.67E-16
3.5	3.52	0.02	2.22E-06	6.65E-08	12.41	1.10E-14	3.28E-16
3.5	3.62	0.12	1.76E-06	9.97E-08	13.41	8.67E-15	4.92E-16
4.0	3.74	0.26	2.06E-06	6.12E-08	5.46	3.21E-15	9.55E-17
4.0	3.77	0.23	1.28E-06	3.69E-09	6.69	2.00E-16	5.76E-18
4.0	3.69	0.31	1.09E-06	6.40E-08	5.96	1.70E-15	9.99E-17

***Appendix D3*:** pH changes, rate constants and initial rates of reaction for sodium citrate ($Na_3C_6O_7H_5$) with zinc nitrate

Initial pH	Final pH	Absolute pH Change	Rate Constant $mBar^{-1}s^{-1}$	Rate Constant Error ($mBar^{-1}s^{-1}$)	Pressure Change (mBar)	Initial Rate of Reaction ($mBar^{-1}s^{-1}$ mol^3dm^{-9})	Initial Rate of Reaction Error ($mBar^{-1}s^{-1}$ mol^3dm^{-9})
3.0	2.41	0.94	2.13E-06	2.14E-07	10.94	3.32E-14	3.34E-15
3.0	2.42	0.90	1.09E-06	4.58E-08	6.46	1.70E-14	7.15E-16
3.0	2.45	0.75	2.34E-06	4.24E-08	19.37	3.65E-14	6.62E-16
3.5	2.69	0.81	2.22E-06	4.20E-08	19.37	1.10E-14	2.07E-16
3.5	2.80	0.70	2.14E-06	4.04E-08	15.89	1.05E-14	1.99E-16
3.5	2.78	0.72	2.18E-06	4.12E-08	17.49	1.08E-14	2.03E-16
4.0	3.06	0.59	3.33E-06	7.98E-08	4.97	5.19E-15	1.25E-16
4.0	3.10	0.58	3.84E-06	2.36E-07	8.45	5.99E-15	3.68E-16
4.0	3.25	0.55	3.56E-06	1.57E-07	6.71	5.55E-15	2.45E-16

***Appendix D4*:** Sodium formate ($NaCO_2H$) with zinc nitrate

Initial pH	Final pH	Absolute pH Change	Rate Constant ($mBar^{-1}s^{-1}$)	Rate Constant Error ($mBar^{-1}s^{-1}$)	Pressure Change (mBar)	Initial Rate of Reaction ($mBar^{-1}s^{-1}$ mol^3dm^{-9})	Initial Rate of Reaction Error ($mBar^{-1}s^{-1}$ mol^3dm^{-9})
3.0	2.51	0.49	4.41E-06	7.13E-08	67.55	6.88E-14	1.11E-15
3.0	2.56	0.44	2.70E-06	4.22E-08	68.54	4.22E-14	6.58E-16
3.0	2.69	0.31	3.56E-06	5.68E-08	68.05	5.55E-14	8.86E-16
3.5	3.19	0.31	2.22E-06	2.15E-08	56.09	1.10E-14	1.06E-16
3.5	3.28	0.22	2.02E-06	1.51E-08	55.09	9.97E-15	7.45E-17
3.5	3.14	0.36	2.12E-06	1.83E-08	55.58	1.05E-14	9.03E-17
4.0	3.83	0.17	1.48E-06	2.45E-08	40.23	2.31E-15	3.82E-17
4.0	3.82	0.18	1.34E-06	2.17E-08	46.19	2.09E-15	3.39E-17
4.0	3.95	0.05	1.41E-06	2.31E-08	43.21	2.20E-15	3.60E-17

Appendix E

Rate constants and initial rates of reactions for the gasification rates of the acetic acid/sodium acetate and citric acid/sodium citrate emulsions

Appendix E1: Rate constants and initial rates of reaction for acetic acid/ sodium acetate emulsions

Emulsion	Rate constant (mBar^{-1}s^{-1})	Rate constant error (mBar^{-1}s^{-1})	Initial rate of reaction (mBar-^{1}s^{-1} mol^{3}dm^{-9})	Initial rate of reaction error (mBar-^{1}s^{-1} mol^{3}dm^{-9})
AA/NA pH=3.30	1.45E-06	2.73E-09	2.26E-14	4.26E-17
AA/NA pH=3.31	5.94E-07	5.88E-09	9.27E-15	9.17E-17
AA/NA pH=3.36	4.16E-07	1.90E-09	6.49E-15	2.96E-17
AA/NA pH=4.20	1.36E-06	3.50E-09	2.12E-15	5.46E-18
AA/NA pH=4.23	8.88E-07	8.65E-10	1.39E-15	1.35E-18
AA/NA pH=4.25	9.38E-07	1.12E-09	1.46E-15	1.75E-18
AA/NA pH=4.49	5.25E-07	1.08E-09	2.59E-16	5.32E-18
AA/NA pH=4.52	4.49E-07	2.28E-09	2.21E-16	1.12E-18
AA/NA pH=4.56	6.13E-07	2.98E-09	2.98E-16	1.47E-18

Appendix E2: Rate constants and initial rates of reaction for citric acid/sodium citrate emulsions

Emulsion	Rate constant (mBar^{-1}s^{-1})	Rate constant error (mBar^{-1}s^{-1})	Initial rate of reaction (mBar-^{1}s^{-1} mol^{3}dm^{-9})	Initial rate of reaction error (mBar-^{1}s^{-1} mol^{3}dm^{-9})
CA/NA pH=376	8.846E-07	2.79E-09	1.38E-15	4.35E-18
CA/NA pH=3.86	4.28E-07	5.51E-10	6.68E-16	8.80E-19
CA/NA pH=3.91	8.94E-07	1.71E-09	1.39E-15	2.67E-18
CA/NA pH=4.73	5.39E-08	2.12E-12	2.17E-16	3.31E-19
CA/NA pH=4.76	6.18E-08	2.20E-12	1.84E-16	3.43E-19
CA/NA pH=4.82	3.13E-08	2.03E-12	4.88E-16	3.17E-19