

Thermally Activated Nitrogen/Heat Generating Reaction: A Kinetic Study

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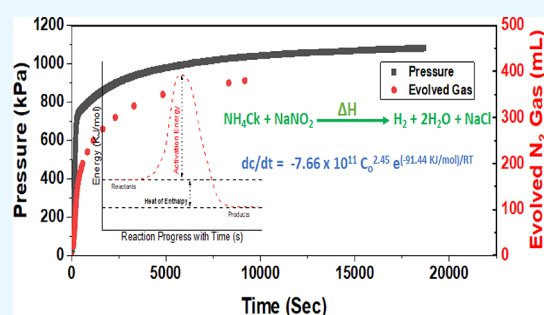
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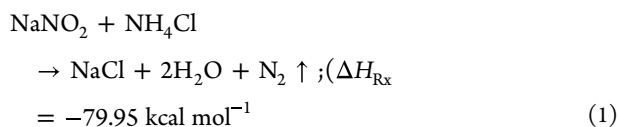
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ABSTRACT: Sodium nitrite and ammonium chloride are the most widely used thermochemicals in the oil and gas industry. The kinetics of this reaction when activated with acids or acid precursors were the subject of extensive research by several researchers. The activation of such a highly spontaneous/vigorous reaction by heat is considered a promising reaction control. In this work, a kinetic study was carried out for the reaction of sodium nitrite and ammonium chloride salt activated by heat at 1–5 M and temperatures of 50–90 °C. The study was carried out in both closed and open systems, with the monitoring of gas evolution and generated pressure. The study showed a relatively higher order for ammonium chloride than sodium nitrite. The excess amount of ammonium chloride, a weak acid, enhanced the reaction as it could be catalyzed by both heat and acid. The obtained kinetics of the nitrogen generating reaction is given as $dc/dt = -7.66 \times 10^{11} C_0^{2.45} e^{(-91.44 \text{ kJ/mol})/RT}$. The reaction kinetics in this study differs from what is reported in the literature regarding the order of NH_4Cl , which was reported to be higher than that of NaNO_2 under examined conditions. This study has practical significance for controlling the reactivity of the $\text{NH}_4\text{Cl}/\text{NaNO}_2$ nitrogen/heat generating system and calculating/optimizing nitrogen generation for a specific field application.



1. INTRODUCTION

The most commonly used thermochemicals in the oil industry are ammonium chloride and sodium nitrite where their reaction is given below:^{1–3}



)irreversible $K_{\text{eq}} = 3.9 \times 10^{71} \text{ Pa}\cdot\text{mol}\cdot\text{m}^{-3}$ at 25 °C)

To control this very vigorous reaction and utilize it in different applications, the reaction kinetics of NH_4Cl and NaNO_2 has been studied by several researchers as a function of pH, reactant concentration, initial pressure, and temperature.^{1,4,5} Contradicting findings for the kinetics reaction order were reported, which might be attributed to different examined concentrations of reactants and catalysts. In agreement with Hughes et al.,⁶ Rubin et al.,⁷ and Harrison et al.,⁸ Nguyen et al.¹ examined reactant concentrations of 0.1–2.5 M and pH values of 3–7 and found that the reaction rate followed first-order kinetics for the concentration of ammonia and second-order kinetics for the concentration of nitrite species for all examined concentration ranges. Dusenbury and Powell⁹ observed the second-order kinetics (first order with respect to the total concentration of nitrite species) at a very

low concentration of nitrite species (from 0.00243 to 0.094 mol dm^{-3}) and low pH (about 2.9).

The effect of the acid concentration was found to influence the reaction rate and was considered in the kinetic equation in some studies.^{4,10} Qian et al.⁴ found that with the increasing reactant concentration, $c(\text{H}^+)$, and temperature, the volume of produced nitrogen increased. Based on their study, the optimal molar ratio of $\text{NaNO}_2/\text{NH}_4\text{Cl}$ was 1. The experimental kinetic equation determined through the N_2 generating process by NaNO_2 and NH_4Cl was $dc/dt = -7.103 \times 10^7 c_{\text{H}^+}^{1.3291} c_0^{2.0949} e^{(-51.28 \text{ kJ/mol})/RT}$.

Bispo et al.⁵ studied ammonium chloride and sodium nitrite reaction to optimize and ensure the greatest and fastest heat production with minimum side production of nitrous oxides. They found that the optimum conditions included ammonium/nitrite equal to 1 and a catalyst concentration of 0.07 mol·L⁻¹, for a case in which the temperature was 5 °C (seafloor level). Also, they found that adding the catalyst over

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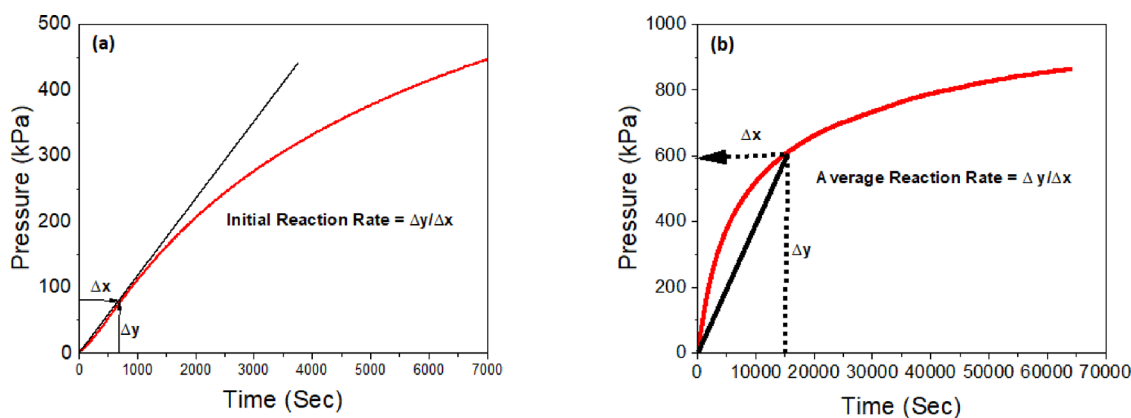


Figure 1. Methodology used to determine the (a) initial reaction rate and (b) average reaction rate.

time was a good strategy to decrease NO_x. To sum up, the reaction kinetics of ammonium chloride and sodium nitrite can be a first order of both reactants or first order for ammonium chloride and a second order for sodium nitrite, depending on the reaction conditions.

Different acids were investigated as thermochemicals (sodium nitrite and ammonium chloride) and reaction catalysts, including HCl acid, citric acid, and acid precursors (esters). In addition, oxidizers, such as ammonium persulfate, were investigated as the thermochemical reaction activator. The acid-activated thermochemical reaction is associated with the generation of side products and pollutant gases such as nitrogen oxides. Bispo et al.⁵ reported that the percentage of nitrogen oxides could reach more than 25% of the produced gases for the acid-activated reaction under certain conditions.

As promising techniques, in situ nitrogen gas/heat generation reactions have been given more attention by several researchers nowadays. In situ generated N₂ can be utilized to provide better foam quality for different field applications, including well cleanout, enhanced oil recovery (EOR), and fracturing operations.^{11–14} Therefore, understanding the rate of nitrogen gas generation is crucial to design required foam quality under specific field conditions. In this study, the reaction kinetics of a thermally activated NH₄Cl/NaNO₂ reaction was studied. Salt concentrations of 2, 3, 4, and 5 M and a temperature range of 70, 80, and 90 °C were investigated. Thermally activated NaNO₂ and NH₄Cl reactions are not anticipated to produce NO_x since nitrite solutions can produce NO_x at pH values below 6.0. (Braida and Ong).¹⁵

2. EXPERIMENTAL WORK

2.1. Materials. Sodium nitrite (NaNO₂) and ammonium chloride (NH₄Cl) used in this study were ACS reagent grade obtained from Honeywell and Thermo Fisher Scientific, respectively. Deionized water with a resistivity of 18.2 MΩ·cm was used in preparation of the salt solutions. Sodium hydroxide used to adjust pH of NaNO₂/NH₄Cl solutions was an ACS grade reagent obtained from Thermo Fisher Scientific.

2.2. Methodology of Gas Producing and Pressure Generating Reaction Tests. This study used a standard method for determining the kinetics of compounds that give gaseous products. The amount of gas that evolved at atmospheric pressure was measured as a function of time using the water displacement method.^{4,12} In a volumetric round flask, 5 mL of each salt solution at different equimolar and variable concentrations was added. Water in a volumetric

cylinder was displaced by gas produced, and the amount of gas that evolved was measured as a function of time. The vapor pressure reported at the examined temperature was detected from the gas-produced volume.

Also, a VINCI pressure–volume–temperature (PVT) cell with a total volume of 40 cm³ was used for the pressure generation tests. A 10 mL two-salt mixture at an equivalent volume was introduced into the preheated PVT cell at the designated temperature. The pressure generated due to the thermochemical reaction was monitored at a time interval of 2 s.

The pH measurements for ammonium chloride and sodium nitrite solutions at different concentrations were performed before and after gas production tests. From the generated data, initial and average reaction rates were determined using the typical methodology used (Figure 1). The initial reaction rates were determined from the slope of the tangent to the reaction curve and passing by the origin, while the average reaction rates were determined from the slope for the line going from origin to the time point of interest.

2.3. Experimental Setups. Figure 2 shows the water displacement setup used to measure evolved nitrogen gas due to the reaction of ammonium chloride and sodium nitrite. The closed system used to monitor generated pressure due to evolved nitrogen gas from the thermochemical reaction is shown in Figure 3. It consists of a VINCI Educational PVT cell

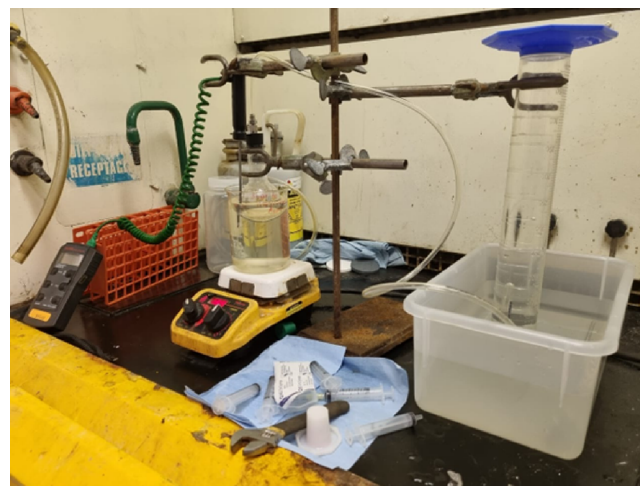


Figure 2. Water displacement setup.

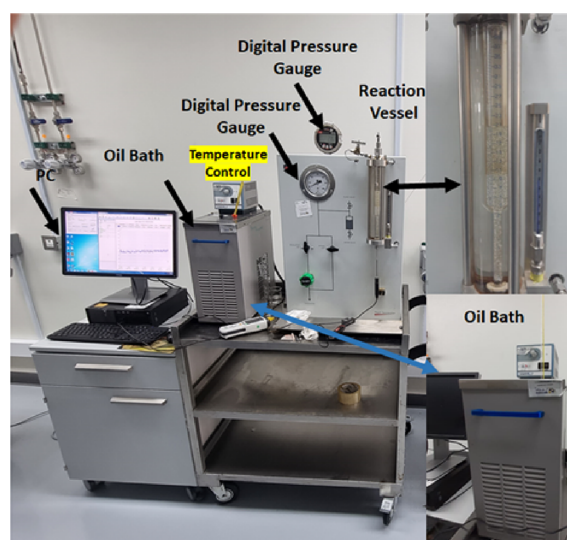


Figure 3. Closed system setup.

for phase behavior analysis connected to analog and digital pressure gauges. An oil bath was used to maintain the transparent PVT chamber temperature as required. The pressure generated by the reaction was monitored as a function time by a nearby PC.

The pH measurements were conducted using an Accumet AR-15 pH meter utilizing a microprobe, glass body single-junction Ag/AgCl reference with an auto temperature compensation.

2.4. Experimental Design. The experimental work conducted in this study involved the use of open and closed systems, as given in Table 1. The effect of the reactant

Table 1. Summary of the Experimental Plan

nitrogen production from the open system setup			
	effect of the concentration		purpose
first batch	equimolar 2, 3, 4, and 5 M	variable molarity 2 M NaNO ₂ , 4 M NH ₄ Cl, 4 M NaNO ₂ , and 2 M NH ₄ Cl	to study kinetic order of reaction and reaction rates
second batch	effect of temperature	70, 80, and 90 °C	to determine activation energy and frequency factor
pressure generation from the closed system setup			
	effect of the concentration		purpose
first batch	equimolar 2, 3, 4, and 5 M	variable molarity 2 M NaNO ₂ , 4 M NH ₄ Cl, 4 M NaNO ₂ , and 2 M NH ₄ Cl	to verify and support open system results
second batch	effect of temperature	50, 60 70, 80, and 90 °C	to verify and support open system results

concentration was investigated to study the reaction kinetics of the NaNO₂/NH₄Cl system, which involved measuring the reaction rate and determining the reactants' kinetic orders. The effect of temperature was addressed to determine the activation energy of the thermally activated NaNO₂/NH₄Cl reaction and frequency factor.

3. RESULTS AND DISCUSSION

3.1. Effect of the Reactant Concentration and Temperature. The reaction of sodium nitrite and ammonium chloride was assessed through the measurement of gas produced and pressure generated as a function of time. In addition, the effect of temperature and concentration was investigated to study the kinetics of this reaction. Figure 4 shows that nitrogen gas evolved, and pressure generated increased as the two-salt concentration was increased for the examined concentrations (1, 2, 3, 4, and 5 M). Similarly, increasing the temperature in the examined range (50, 60, 70, 80, and 90 °C) increased the gas-generated pressure, as shown in Figure 5. The low concentration (1 M) and low temperatures (50 and 60 °C) were examined using the closed system since the system can be run overnight at an automated mode.

From the pressure-obtained data and utilizing the ideal gas law, initial reaction rates can be determined as follows:

$$PV = nRT \quad (2)$$

where P is the pressure in Pascal, Pascal = J/m³, V is the volume in L, n is the number of moles, R is the gas constant (J·mol⁻¹·K⁻¹), and T is the temperature in Kelvin.

$$C = \frac{n}{V} = \frac{1}{RT}P \quad (3)$$

$$\frac{dC}{dt} = \frac{1}{RT} \frac{dP}{dt} \quad (4)$$

dP/dt can be obtained from generated pressure, and based on that, initial rates can be determined, as given in eq 4. Figure 6 shows that both the concentration and temperature had a significant impact on initial rates of NaNO₂/NH₄Cl reaction where an exponential reaction rate is observed for both. The effect of the thermochemical concentration and temperature on the average reaction obtained for a period of 15,000 s is illustrated in Figure 7. Unlike the initial reaction rate, there is a linear relation between the average reaction rate and the concentration; as the concentration was increased, the reaction rate increased. The impact of temperature on the average reaction rate was more than that for the concentration where a polynomial of second order was obtained for curve fitting. However, the impact after 70 °C was much less. Figure 8 shows that the reaction rate of the thermochemicals tended to increase significantly at the early time of the reaction and then decreased to reach a plateau. The initial rates received more attention in this study as a result of this reaction's behavior observed at the early time.

3.2. Effect of pH. The effect of pH on the reactivity of NaNO₂/NH₄Cl solutions at an equimolar concentration of 4 M and at 90 °C was investigated using the closed system. The pH values examined ranged from 6.5 to 8.5. Figure 9a shows the pressure generated, while Figure 9b shows the initial reaction rates for NaNO₂/NH₄Cl at 4 M/4 M solutions with different pH values. The results showed that the reactivity of nitrogen/heat generating reaction was significantly influenced by solution pH. As the solution's pH value was increased, the reactivity decreased where the initial reaction rate for a solution with a pH value of 6.54 was higher by more than 20 times than that for a solution with a pH value of 8.54. The initial rate for the equimolar (4 M) NaNO₂/NH₄Cl system at 90 °C and for the examined pH range is governed by a second-order polynomial equation as given below:

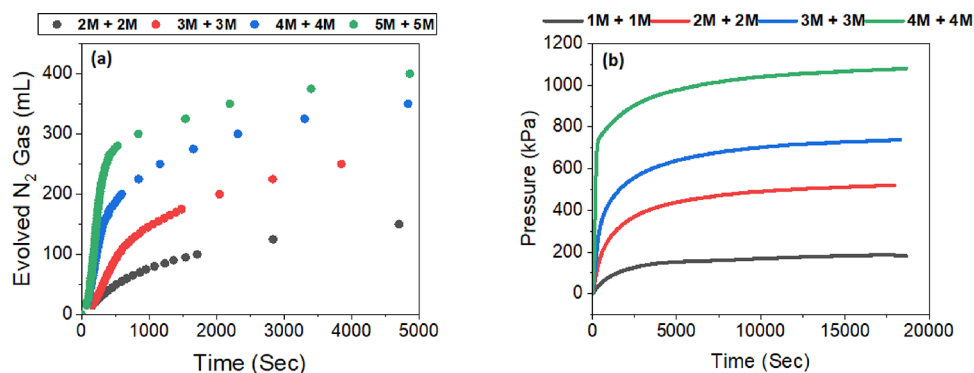


Figure 4. Effect of the concentration on (a) evolved nitrogen gas and (b) generated pressure.

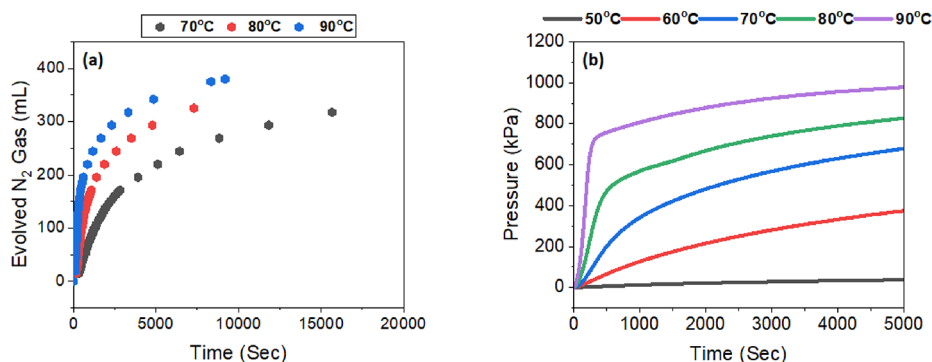


Figure 5. Effect of temperature on (a) evolved nitrogen gas and (b) generated pressure.

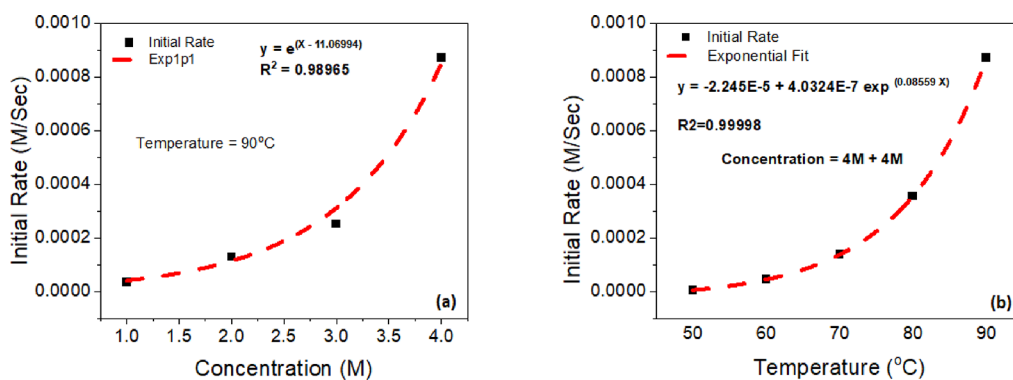


Figure 6. Effect on initial reaction rate: (a) concentration and (b) temperature.

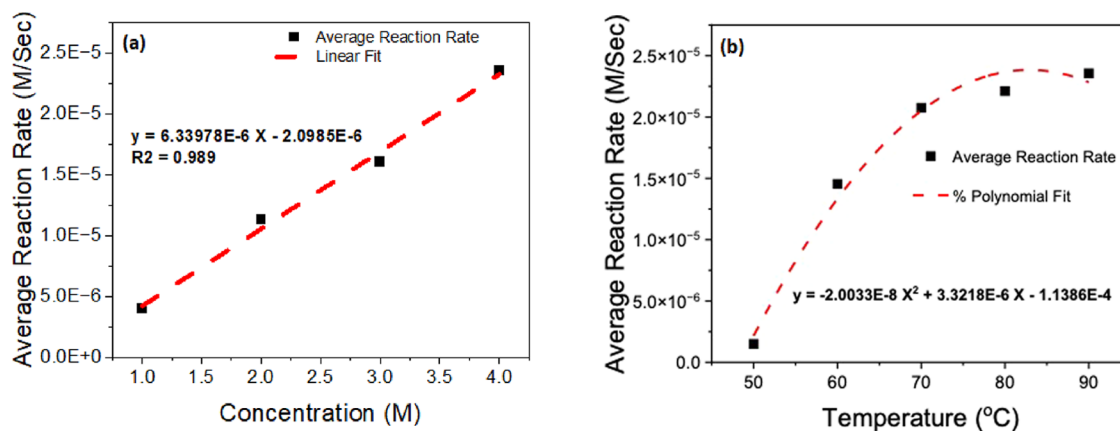


Figure 7. Effect on average reaction rate: (a) concentration and (b) temperature.

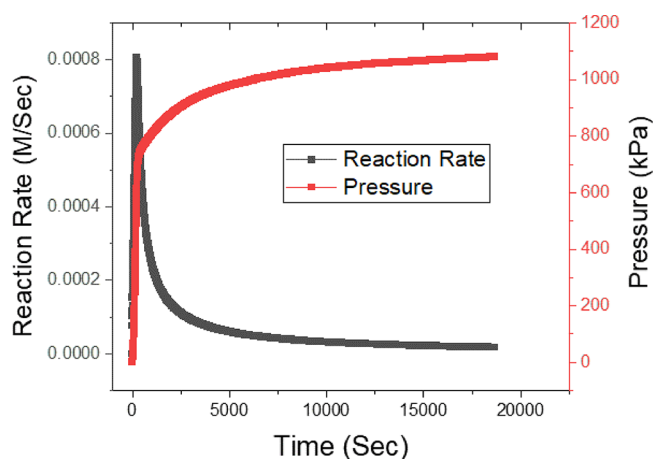


Figure 8. Pressure generated and reaction rate of 4 M NaNO_2 + 4 M NH_4Cl at 90 °C as a function of time.

$$\text{initial rate (Y)} = 1.559 \times 10^{-3}(\text{pH})^2 - 2.79 \times 10^{-3}(\text{pH}) + 1.248 \times 10^{-2} \quad (5)$$

3.3. Effect of Salinity. The effect of salinity on the reactivity of the thermochemicals of interest in this study was investigated. Application of thermochemicals in upstream operations will expose these chemicals to high salinity formation water (Table 2). In this study, formation water solutions at 5, 10, and 20% were used to prepare thermochemicals at an equimolar of 4 M/4 M and their reactivity was examined in comparison with that prepared using deionized water (DI) at 90 °C in the closed system. Figure 10 shows the buildup pressure in kPa due to generated nitrogen gas as a function of thermochemical system base-water salinity. The results showed that water salinity enhanced thermochemical fluid reactivity at the early time and had a minor impact at the end. It was observed that thermochemicals prepared in formation water (FW) showed foamability, which might contribute to relatively higher reactivity.

3.4. Kinetic Study. The kinetic study conducted in this work for the thermally activated $\text{NaNO}_2/\text{NH}_4\text{Cl}$ reaction was mainly based on the results obtained from the open system (evolved N_2), while the closed system results (generated pressure) were used as supportive evidence. The kinetic equation of the reaction between NaNO_2 and NH_4Cl in the absence of acid can be expressed as given in eq 6.

Table 2. Composition of Formation Water (FW)

ion	ion concentration (mg/L)	salt used	mass of salt (g/L)
$[\text{Ca}^{2+}]$	13,045.04	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	47.95
$[\text{Mg}^{2+}]$	3133.08	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	28.88
$[\text{Na}^+]$	65,658.12	NaCl	167.00
$[\text{K}^+]$	576.89	KCl	1.10
$[\text{HCO}_3^-]$	0		
$[\text{SO}_4^{2-}]$	0		
$[\text{Cl}^-]$	134,437.82		

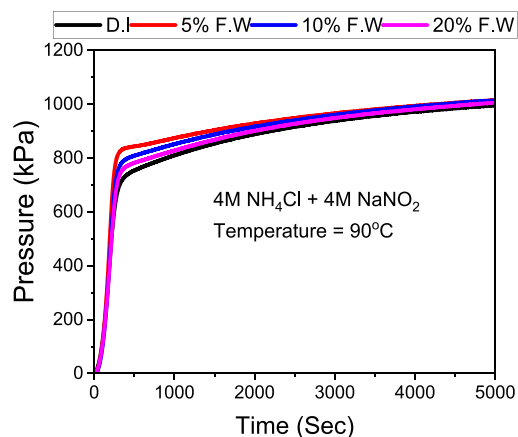


Figure 10. Effect of salinity (DI, 5, 10, and 20% FW) on the reactivity of the nitrogen/heat generating system.

$$\text{rate} = K[\text{NaNO}_2]^x [\text{NH}_4\text{Cl}]^y \rightarrow -\frac{dc}{dt} = K[\text{NO}_2]^x [\text{NH}_4\text{Cl}]^y \quad (6)$$

In the practical field application, the gas generating rate of the in situ N_2 generating systems can be predicted by the kinetic equation of the $\text{NaNO}_2/\text{NH}_4\text{Cl}$ mixture according to certain formation conditions.⁴ In situ nitrogen gas generation from this thermochemical reaction is proposed to be utilized in foam generation for different oilfield applications, including fracturing, well cleanout, and EOR operations, where down-hole geothermal heat is one of the suggested mechanisms to initiate this reaction.^{16–19} From the gas evolved measurements, initial reaction rates of NaNO_2 and NH_4Cl at different concentrations and at 90 °C were obtained, as given in Table 3.

Incorporating obtained data (Table 2) into eq 6 gives the reactant order as given below:

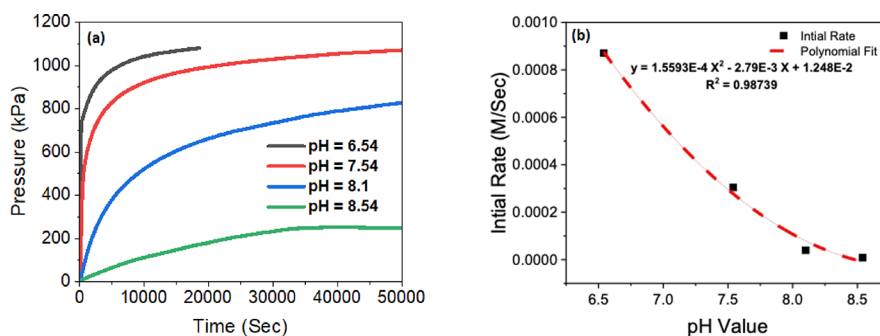


Figure 9. Effect of pH on (a) generated pressure and (b) initial reaction rates of 4 M/4 M solutions at 90 °C in the closed system.

Table 3. Initial Reaction Rates of NaNO₂ and NH₄Cl at Different Concentrations and at 90 °C

trial	NaNO ₂ (M)	[NH ₄ Cl] (M)	initial rate (mL/s)
1	4	4	0.4566
2	4	2	0.1638
3	2	4	0.2336

$$\left(\frac{4}{2}\right)^x = \left(\frac{0.4566}{0.2336}\right) = 1.955 \rightarrow x = 0.967; \left(\frac{4}{2}\right)^y = \left(\frac{0.4566}{0.1638}\right) = 2.78 \rightarrow y = 1.479$$

Based on obtained x and y , eq 6 becomes:

$$-\frac{dc}{dt} = K[\text{NaNO}_2]^{0.967}[\text{NH}_4\text{Cl}]^{1.479}$$

The results revealed that the thermally activated reaction kinetics at 90 °C was nearly first order for NaNO₂ and nearly 1.5 for NH₄Cl. Figure 11 supports these findings and showed that the gas evolved, and the pressure generated was more at a higher concentration of NH₄Cl. This can be explained by the fact that the excess amount of NH₄Cl, a weak acid, tends to drop the pH value of the NaNO₂/NH₄Cl mixture (Table 4), which makes the reaction trigger by two mechanisms, heat and acid, and thus, higher reaction rate is observed compared with the case of excess NaNO₂.

Ammonium chloride is very soluble in water with a reported solubility at 25 °C of 383.0 g/L²⁰ where the ammonium ion and chloride ion are formed as given below:



The ammonium ion dissociates in water to give an acidic proton (H⁺) and ammonia (eq 4), and the dissociation constant (K_d) at 25 °C in dilute solution is 5.01×10^{-10} .^{21,22}



As a result of higher dissociation at a higher temperature, a drop in pH values of NH₄Cl solutions was observed at 50 °C compared to that at ambient temperature (Table 5). These results indicate that thermochemical mixtures with excess NH₄Cl are expected to have lower pH values and higher associated reaction rates.

In another attempt to study the reaction kinetics, K in eq 6 was replaced by the Arrhenius equation to give the following equation:

Table 4. pH Value of Different NaNO₂ and NH₄Cl Solutions at Ambient Temperature before Testing

salt type and concentration	pH	salt type and concentration	pH
2 M NaNO ₂	7.84	2 M NaNO ₂ + 2 M NH ₄ Cl (11)	6.13
3 M NaNO ₂	7.93	4 M NaNO ₂ + 2 M NH ₄ Cl (11)	6.41
4 M NaNO ₂	8.10	2 M NaNO ₂ + 4 M NH ₄ Cl (11)	5.94
2 M NH ₄ Cl	4.58	2 M NaNO ₂ + 2 M NH ₄ Cl (11)	6.13
3 M NH ₄ Cl	4.61	3 M NaNO ₂ + 3 M NH ₄ Cl (11)	6.34
4 M NH ₄ Cl	4.44	4 M NaNO ₂ + 4 M NH ₄ Cl (11)	6.32

Table 5. pH Values of Ammonium Chloride Solutions Measured at Ambient Temperature and at 50 °C

concentration of NH ₄ Cl (M)	2	3	4
pH at ambient temperature	4.58	4.61	4.44
pH at 50 °C	4.34	4.26	4.05

$$\frac{dc}{dt} = Ae^{-\Delta E/RT} [\text{NaNO}_2]^x [\text{NH}_4\text{Cl}]^y \quad (9)$$

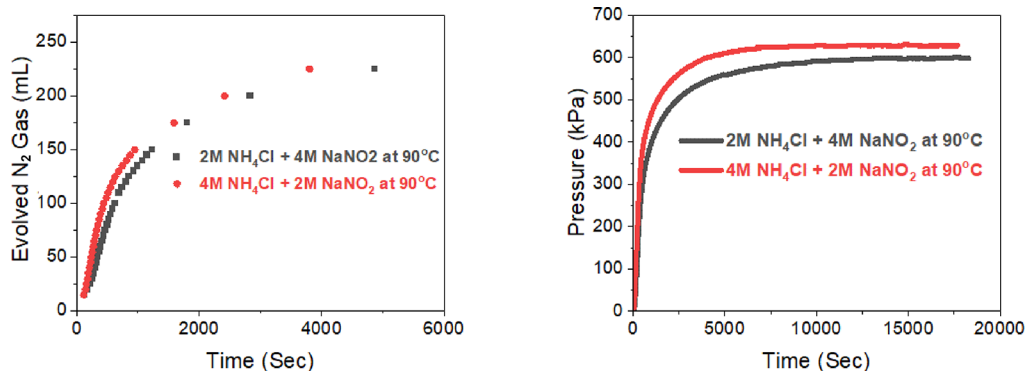
where A and ΔE (kJ mol⁻¹) are the frequency factor and the apparent Arrhenius activation energy, respectively, x and y are reaction orders of NaNO₂ and NH₄Cl, respectively, $[\text{NaNO}_2]$ and $[\text{NH}_4\text{Cl}]$ are the concentrations of NaNO₂ and NH₄Cl in molar, respectively, R is the ideal gas constant (8.314 J·mol⁻¹·K⁻¹), and T (K) is the absolute temperature. When an equimolar concentration is considered for the two salts, ($[\text{NaNO}_2] = [\text{NH}_4\text{Cl}] = C$), and $x + y = n$, then eq 3 becomes

$$\frac{dc}{dt} = Ae^{(-\Delta E/RT)} C^n \quad (10)$$

We followed the same method of Qian et al.⁴ where transposing and integrating eq 10 as given in the Appendix yields eq 11:

$$t = \frac{k^{n-1} - 1}{1 - n} A^{-1} e^{\Delta E/RT} C_0^{n-1} \quad (11)$$

where k is the ratio of the initial concentration and the current concentration of each reactant (theoretical GPV/(theoretical – real-time), C_0 (M) is the initial concentration of NaNO₂ and NH₄Cl, and t (s) is the time consumed for collecting a certain gas volume. Note that GPV stands for the gas production volume, which was measured at 1 atm. Taking the common and natural logarithms of both sides results in the following equations:

**Figure 11. Effect of the excess concentration of NaNO₂ versus the excess concentration of NH₄Cl on the reaction rate.**

$$\log t = \log \left(\frac{k^{n-1} - 1}{n - 1} \right) - \log A + (1 - n) \log C_0 + \frac{\Delta E}{2.303RT} \quad (12)$$

$$\ln t = \ln \left(\frac{k^{n-1} - 1}{n - 1} \right) - \ln A + (1 - n) \ln C_0 + \frac{\Delta E}{RT} \quad (13)$$

The activation energy for the thermally activated reaction of 4 M NaNO₂ with 4 M NH₄Cl was determined using two methods. In the first method, the time that the reaction produced a certain gas volume (50, 100, 150, 200, 250, and 300 mL) was recorded at various temperatures (343, 348, 353, 358, and 363 K) with the presence of 4 M of each reactant. Then, plotting of $\ln t$ versus $1/T$ gives linear relation for the examined produced volumes of nitrogen gas (Figure 12). From the average slope of the six lines, a calculated apparent Arrhenius activation energy of 90.55 KJ/mol was obtained.

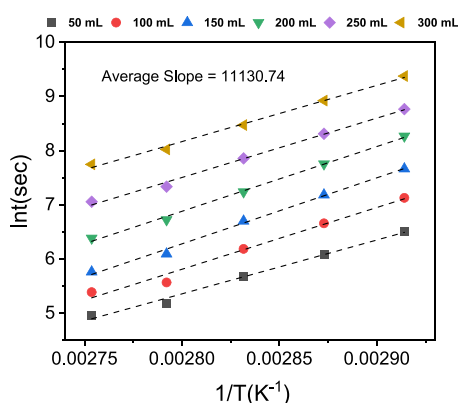


Figure 12. Linear relation graph of $\ln t - 1/T$.

In the second method, the apparent Arrhenius activation energy was determined from the linear relation between the reaction constant, $\ln K$, and $1/T$, as given by the Arrhenius equation.

The reaction constants calculated from initial rates and kinetic reaction orders (Table 1) were used to determine the apparent Arrhenius activation energy. Figure 13 shows a linear relationship between the $\ln K$ and $1/T$. The calculated activation energy based on the slope obtained was found to be 90.353 KJ/mol, which is comparable to that obtained from

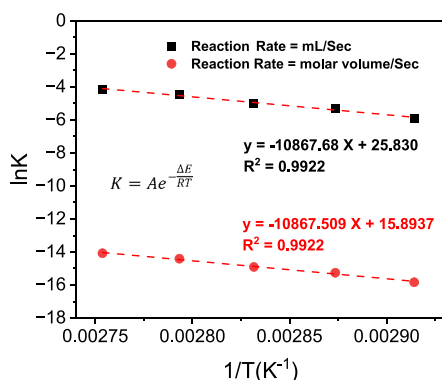


Figure 13. Linear relation graph of $\ln K - 1/T$.

plotting $\ln t$ versus $1/T$ (92.54 KJ/mol). The average activation energy based on the two methods is 91.44 KJ/mol. The activation energy obtained by Qian et al. is lower (51.28 KJ/mol) than the one obtained in this study due to the catalyst (authigenic acid) used in their study. It is well addressed that a catalyst tends to lower the activation energy. Based on intercepts of linear relation in Figures 11 and 12, the calculated average frequency factor (A) based on eqs 14 and 15 is 7.66×10^{11} .

$$A = \log \left(\frac{k^{n-1} - 1}{n - 1} \right) - \log A + (1 - n) \log C_0 \quad (14)$$

$$B = \ln A \quad (15)$$

where A and B are the intercepts of eqs 12 and 13, respectively.

The reaction rate order was obtained from plotting $\log t$ versus $\log C_0$ (Figure 14), which gives a linear relation for four

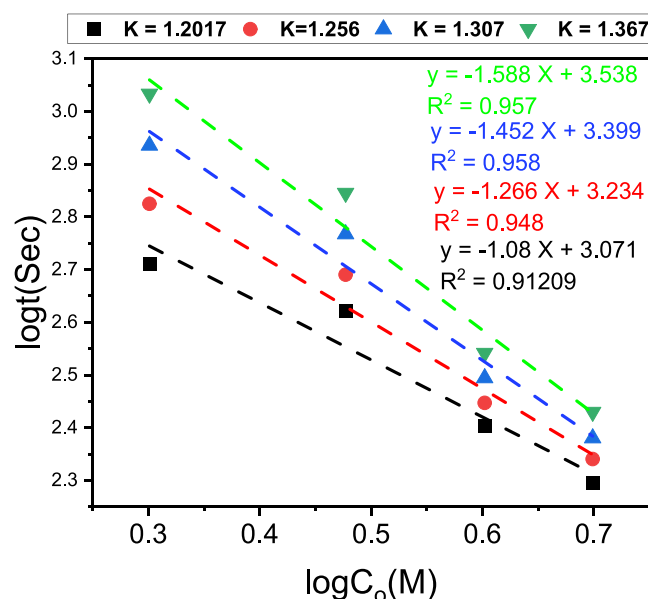


Figure 14. Linear relation graph of $\log t - \log C_0$.

lines generated at three different k (the ratio of the theoretical produced gas volume to (theoretical volume - real-time volume)). The average slope of the four lines is equal to $(1 - n)$, as given in eq 12, where n is the order of reactants. The calculated reactant order is 2.346, comparable to that obtained from the initial reaction rate result (2.45).

4. CONCLUSIONS

The kinetics of the reaction between NH₄Cl and NaNO₂ activated thermally was studied, and the rate of the reaction was monitored by measuring the volume of nitrogen gas evolved as a function of time. The effect of the reactant concentration and temperature was investigated.

- Nitrogen gas production and associated buildup pressure were found to increase as the NaNO₂ and NH₄Cl concentration and temperature were increased.
- The reactivity of the nitrogen/heat generating system is strongly influenced by pH values and reaction temperature.
- The water salinity had negligible impact on the reactivity of the nitrogen/heat generating system.

- The excess concentration of NH_4Cl with respect to the NaNO_2 concentration tended to have a higher reaction rate compared with the same excess concentration of NaNO_2 with respect to the NH_4Cl concentration.
- The kinetic order of NH_4Cl was higher than that of NaNO_2 , as revealed from evolved gas results and supported by generated pressure data.
- The kinetics of thermally activated nitrogen generating reaction of $\text{NH}_4\text{Cl}/\text{NaNO}_2$ is given as $\frac{dc}{dt} = K[\text{NaNO}_2]^{0.97}[\text{NH}_4\text{Cl}]^{1.48} = -7.66 \times 10^{11} C_0^{2.45} e^{(-91.44 \text{ kJ/mol})/RT}$.

A. APPENDIX

$$\text{rate} = K[\text{NaNO}_2]^x[\text{NH}_4\text{Cl}]^y \rightarrow -\frac{dc}{dt} = K[\text{NO}_2]^x [\text{NH}_4\text{Cl}]^y \quad (\text{A1})$$

$$\text{At equal concentration } [\text{NO}_2] = [\text{NH}_4\text{Cl}] = C \quad (\text{A2})$$

$$n = x + y; \frac{dc}{dt} = kC^n \quad (\text{A3})$$

$$K = Ae^{-\Delta E/RT}; \frac{dc}{dt} = C^n Ae^{-\Delta E/RT} \quad (\text{A4})$$

$$\frac{dc}{C^n} A^{-1} e^{\Delta E/RT} = dt \rightarrow A^{-1} e^{\Delta E/RT} \int_0^t \frac{dc}{C^n} = \int_0^t dt \quad (\text{A5})$$

$$A^{-1} e^{\Delta E/RT} \int_0^t \frac{dc}{C^n} = \int_0^t dt \rightarrow t = \frac{1}{1-n} (c_t^{1-n} - c_0^{1-n}) A^{-1} e^{\Delta E/RT} \quad (\text{A6})$$

$$t = \frac{1}{1-n} (c_t^{1-n} - c_0^{1-n}) A^{-1} e^{\Delta E/RT} \rightarrow t = \frac{1}{1-n} \left(\frac{c_t^{1-n}}{c_0^{1-n}} - 1 \right) A^{-1} e^{\Delta E/RT} c_0^{1-n} \quad (\text{A7})$$

$$t = \frac{1}{1-n} \left(\frac{c_t^{1-n}}{c_0^{1-n}} - 1 \right) A^{-1} e^{\Delta E/RT} c_0^{n-1} \rightarrow t = \frac{1}{1-n} \left[\left(\frac{c_t}{c_0} \right)^{1-n} - 1 \right] A^{-1} e^{\Delta E/RT} c_0^{1-n} \quad (\text{A8})$$

C_0 is the theoretical gas produced volume (T_v) and C_t is the theoretical gas produced volume – real-time produced volume (R_v).

$$\left(\frac{c_t}{c_0} \right)^{1-n} = \left(\frac{T_v - R_v}{T_v} \right)^{1-n} \text{ and } k = \frac{T}{T - R_v} \left(\frac{c_t}{c_0} \right)^{1-n} = (k^{-1})^{1-n} \quad (\text{A9})$$

$$t = \frac{k^{n-1} - 1}{1-n} A^{-1} e^{\Delta E/RT} c_0^{n-1} \quad (\text{A10})$$

$$\log t = \log \left(\frac{k^{n-1} - 1}{n-1} \right) - \log A + (1-n) \log C_0 + \frac{\Delta E}{2.303RT} \quad (\text{A11})$$

$$\ln t = \ln \left(\frac{k^{n-1} - 1}{n-1} \right) - \ln A + (1-n) \ln C_0 + \frac{\Delta E}{2.303RT} \quad (\text{A12})$$

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Author Contributions

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Notes

The authors declare no competing financial interest.

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