



Hydroxylamine nitrate self-catalytic kinetics study with adiabatic calorimetry

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ARTICLE INFO

Article history:

Received 21 April 2008

Received in revised form 1 June 2008

Accepted 3 June 2008

Available online 11 June 2008

Keywords:

Hydroxylamine nitrate

Adiabatic calorimetry

Thermal explosion

Critical condition

ABSTRACT

Hydroxylamine nitrate (HAN) is an important member of the hydroxylamine compound family with applications that include equipment decontamination in the nuclear industry and aqueous or solid propellants. Due to its instability and autocatalytic behavior, HAN has been involved in several incidents at the Hanford and Savannah River Site (SRS) [Technical Report on Hydroxylamine Nitrate, US Department of Energy, 1998]. Much research has been conducted on HAN in different areas, such as combustion mechanism, decomposition mechanism, and runaway behavior. However, the autocatalytic decomposition behavior of HAN at runaway stage has not been fully addressed due to its highly exothermic and rapid decomposition behavior. This work is focused on extracting HAN autocatalytic kinetics and analyzing HAN critical behavior from adiabatic calorimetry measurements. A lumped autocatalytic kinetic model for HAN and associated model parameters are determined. Also the storage and handling critical conditions of diluted HAN solution without metal presence are quantified.

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1. Introduction

Runaway reaction in industrial reactors is a crucial research topic for chemical process safety. Due to thermal runaway characteristics, pseudo-adiabatic reaction conditions provide the most valuable information for reactive chemical hazards management and assessment. Adiabatic calorimetry has proved to be the most suitable method for identifying chemical hazards and is widely used in reactive chemical studies [2–4]. The great sensitivity of calorimetric measurements makes it possible to obtain thermodynamic and kinetic information simultaneously. Thermodynamic data, such as heat of reaction, maximum pressure, and pressure increase rate, can be easily evaluated and applied in pressure relief design and development of operating procedures. However it is a nontrivial task to extract kinetic parameters from data obtained with adiabatic calorimetry for complex reactions. Furthermore, the critical conditions, where the system exhibits thermal runaway behavior, for reactive chemicals have not been systematically studied. Critical parameters or conditions include some thermo-kinetic parameters (such as temperature, concentration, and heat transfer coefficients), for which small variations can significantly change system behavior, and can be identified with thermal explosion theory. To adhere

to the original work of Semenov, the term “explosion” in thermal explosion theory means reaction kinetics and not gas dynamics. Furthermore, the explosion regime is defined as the process of rapid conversion of reactants into final products.

Hydroxylamine nitrate ($\text{NH}_2\text{OH}\cdot\text{HNO}_3$), HAN, is commercially available as a clear and colorless aqueous solution. It has been used as a reductant in the nuclear industry and also considered for use as a liquid propellant or oxidizer for hybrid rockets. Its main advantages are a high energy density and environmental friendliness. Due to its instability, HAN has been involved in incidents especially at the Hanford and Savannah River Site (SRS) [1]. The Mary Kay O'Connor Process Safety Center (MKOPSC) and other research institutions and groups have conducted extensive research on its thermal stability, decomposition mechanism, and metal ion catalysis by using various techniques under different conditions [3–9]. These works accumulated significant knowledge of HAN and data to improve HAN processing safety. However more information for safe HAN storage and operations is needed.

Previous research investigated HAN self-catalytic behavior, decomposition pathways, and the effect of pH and metal ions. However these investigations attempted to correlate the self-catalytic kinetic parameters with n th order reaction model even though the self-catalytic behavior of HAN had been confirmed by adiabatic decomposition tests and modeling. So the work reported here aims to explore HAN autocatalytic parameters using adiabatic calorimetry data. Several authors proposed to explore the decomposition reaction network of reactive chemicals by measurements, such as IR spectroscopy, GC, and HPLC, on the final products at different

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Nomenclature

A	frequency factor
B	exothermicity of reaction, $QC_0R/\rho C_V E$
C	concentration (mol m^{-3})
C_0	initial concentration (mol m^{-3})
C_V	specific heat ($\text{kJ kg}^{-1} \text{K}^{-1}$)
E_a	activation energy (J mol^{-1})
h	heat transfer coefficient ($\text{JK}^{-1} \text{m}^{-2} \text{s}^{-1}$)
m	reaction order of catalyzed reaction step
n	reaction order of initiation reaction step
p	autocatalytic reaction parameter
Q	heat of reaction (J mol^{-1})
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
s	reaction cell interior surface area (m^2)
t	time (s)
T	temperature (K)
T_0	initial temperature (K)
ΔT_{AB}	adiabatic temperature rise (K)
T_s	surrounding temperature (K)
V	reaction cell volume (m^3)

Greek letters

α	fractional degree of conversion $(C_0 - C)/C_0$
θ	dimensionless temperature (RT/E_a)
θ_s	dimensionless surrounding temperature (RT_s/E_a)
τ	dimensionless time, $QRAC_0^n t / \rho C_V E_a$
ϕ	thermal inertia
ψ	modified Semenov number $QVAC_0^n R / hsE_a$

Table 1

HWS mode experimental parameters for HAN thermal decomposition

Experimental parameters	Experiment 1	Experiment 2
Start temperature ($^{\circ}\text{C}$)	120	110
Limit temperature ($^{\circ}\text{C}$)	200	200
Temperature increment ($^{\circ}\text{C}$)	10	10
Exothermic threshold ($^{\circ}\text{C}$)	0.05	0.05
Heat rate ($^{\circ}\text{C}/\text{min}$)	2	2
Sample mass (g)	4.12	2.01
Glass cell mass (g)	48.61	49.80
ϕ	3.30	5.81

search (HWS) operation mode was used to perform a thermal decomposition study on HAN. The APTAC calorimeter can be operated in a variety of test modes, such as heat-wait-search, and isothermal mode with temperatures up to 500°C and pressures ranging from vacuum to 2000 psia. It can detect the exotherms with heat generation rates from 0.04 to $400^{\circ}\text{C}/\text{min}$. It can also produce low thermal inertia data with the DIERS pressure compensation technique, in which the pressure outside the sample cell is controlled to match the pressure inside the sample cell. In HWS mode, the reactant in the reaction vessel will first be heated to the start temperature, such as 110°C , with heating rate $2^{\circ}\text{C}/\text{min}$. Then the reactant system will be stabilized for about 15 min and then the APTAC goes to search mode to see whether there is an exotherm. If not, the reactant will be heated to the next target temperature, 120°C , which is 10°C higher than previous target temperature. This procedure is repeated until an exotherm is detected and the APTAC then enters adiabatic operation mode. Details of APTAC equipment and its HWS mode are available in previous publications [4,13]. Glass sample cells and Teflon coated thermocouples were used to reduce the catalytic effect of metals. Experimental parameters are summarized in Table 1.

3. Mathematical analysis

3.1. Autocatalytic reaction model

A lumped overall reaction model can be represented in terms of Eq. (1),

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where t is the time, T is the temperature, and $\alpha = (C_0 - C)/C_0$ is the fractional degree of conversion for reactants ($0 \leq \alpha \leq 1$). Another generally accepted assumption is that the rate constant $k(T)$, which is temperature dependent and described by the Arrhenius equation, can be separated from the reaction model $f(\alpha)$ and represented by the Arrhenius equation as follows:

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where A is the frequency factor, E_a is the activation energy, and R is the universal gas constant. The objective of this work was to determine the most appropriate frequency factor, activation energy, and self-catalytic reaction model that could describe and reproduce the observed temperature changing profile of HAN thermal decomposition.

From a kinetic evaluation procedure developed for adiabatic calorimeters [14], the fractional conversion can be related to the system temperature change in the energy conservation equation. Although the specific heat of a reacting system changes with the solution composition and temperature during the decomposition process, the specific heat of diluted HAN solution was assumed to be constant ($4.3 \text{ kJ}/(\text{kg K})$) in the analysis for the similarity of

time [5,7–9]. The drawback of this approach is the concentrations of decomposition intermediates, such as HNO and HNO_2 , still cannot be accurately determined. The obtained reaction pathway and associated kinetic parameters are not easy to apply to the thermal runaway/explosion stages study. Although the decomposition process of HAN consists of many consecutive and competitive reaction steps, the work reported here proves that the observed thermal behavior could still be modeled well with a traditionally lumped single overall reaction.

Previous research on HAN has not fully analyzed the transition behavior from thermal decomposition to the thermal explosion/runaway state. Thermal explosion is generally characterized by self-heating or thermal runaway before larger amounts of explosion energy is released [10–12]. Once the heat removal rate is less than the self-heating rate, the accumulated heat will exponentially accelerate the reaction rate. This higher rate represents an explosion hazard for gasified chemicals, such as HAN and hydroxylamine (HA), the products of which are mainly gases. An explosion can occur when the vent sizing is not sufficient to protect the reactors or vessels.

2. Experimental

Hydroxylamine nitrate (24 mass%, Aldrich catalog number 438,235) aqueous solution was used without further purification. Although this product purchased from Aldrich contains some ions, such as iron ions, their catalytic effect could be omitted because their concentrations are fairly low. Therefore, the critical temperature for practical HAN storage in industrial tanks, which are normally made with stainless steel, may be lower than that obtained here for the contamination of iron ions. The automatic pressure tracking adiabatic calorimeter (APTAC) and its heat-wait-

diluted aqueous HAN solution to water [4,7]. The energy conservation equation for an adiabatic reactor is as follows:

$$\frac{dT}{dt} = \frac{Q}{C_V} \frac{d\alpha}{dt} \quad (3)$$

Integrating the above equation gives

$$\alpha = \frac{C_V}{Q}(T - T_0) = \frac{T - T_0}{\Delta T_{AB}} \quad \text{or} \quad \frac{d\alpha}{dt} = \frac{1}{\Delta T_{AB}} \frac{dT}{dt} \quad (4)$$

where ΔT_{AB} is the adiabatic temperature rise.

The first step of HAN decomposition process is generally agreed to be the disassociation of HAN to hydroxylamine and nitric acid. This dissociation step has been confirmed to be very rapid above 175 °C [7,9] so that the main process of HAN decomposition becomes the hydroxylamine oxidation by nitric acid and nitrous acid at the experimental conditions. Nitrous acid is both a product and a catalyst in this process. Although some work proposed that HNO could also generate and oxidize hydroxylamine, its effect was neglected because of the extreme instability of HNO. Although several lumped autocatalytic models have been developed to describe autocatalytic reaction behavior [15–17], the model developed at the Technical University of Berlin was adopted in the analysis for its better regression and prediction capability compared to the other models. With this model the conversion rate can be expressed as follows:

$$\frac{d\alpha}{dt} = AC_0^{n-1} \exp\left(-\frac{E_a}{RT}\right) (1 - \alpha)^n (1 + p\alpha^m) \quad (5)$$

where p and m are the parameters used to describe the catalytic effect of HNO_2 .

3.2. HAN critical behavior analysis

The fundamental principles of thermal explosion theory are energy conservation and mass reaction, which are represented as follows for the autocatalytic reaction discussed here.

$$\rho VC_V \frac{dT}{dt} = QVAC_0^n (1 - \alpha)^n (1 + p\alpha^m) e^{-E_a/RT} - hs(T - T_s) \quad (6)$$

$$\frac{dC}{dt} = -A e^{-E_a/RT} C_0^n (1 - \alpha)^n (1 + p\alpha^m) \quad (7)$$

where T_s is the surrounding temperature. One most important concept of thermal explosion theory is the determination of a critical condition. Other valuable information, such as induction time, can also be obtained following the determination of critical condition. The critical condition of the original thermal explosion theory is the tangency between the heat generation curve and the heat loss curve. One assumption of the original thermal explosion theory is that no reactant will be consumed during the reaction. However this assumption is not applicable for most practical cases, so the influence of reactant consumption must be included in the determination of critical conditions. Many efforts have been invested in this topic and much progress has been achieved [18–20]. Most recently Shouman and El-Sayed proposed to use an inflection point to define the critical condition for reactive chemicals and proved that their results are consistent with the results of previous work [21]. Compared with other methods, the inflection point concept is much easier to use and includes other criticality definitions. So the inflection point concept was used to determine critical condition for diluted HAN solutions. Furthermore, the critical condition not only is a function of temperature but also is a function of reactant concentration considering reactant consumption. So a rigorous critical condition should be defined on the temperature–concentration plane.

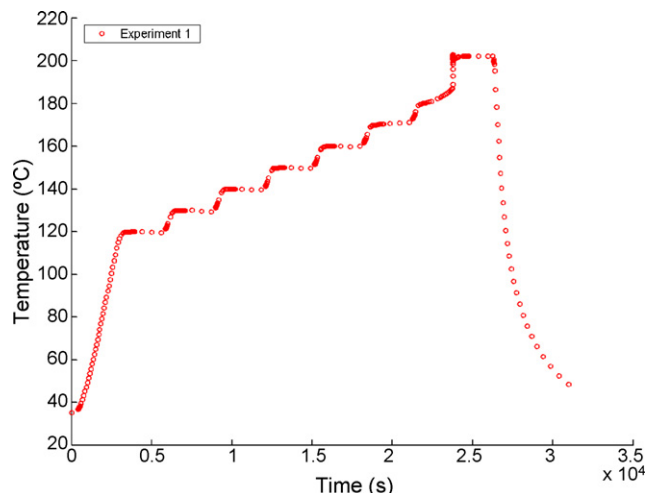


Fig. 1. HWS mode thermal decomposition of HAN in a glass cell.

With dimensionless variables $\theta = RT/E_a$, $\theta_s = RT_s/E_a$, $\alpha = (C_0 - C)/C_0$, $B = QC_0R/(\rho C_V E)$, $\psi = (QVAC_0^n R)/(hsE_a)$, and $\tau = (QRAC_0^n t)/(\rho C_V E_a)$, Eqs. (6) and (7) can be written in dimensionless form as follows:

$$\frac{d\theta}{d\tau} = (1 - \alpha)^n (1 + p\alpha^m) e^{-1/\theta} - \frac{\theta - \theta_s}{\psi} \quad (8)$$

$$\frac{d\alpha}{d\tau} = \frac{(1 - \alpha)^n (1 + p\alpha^m) e^{-1/\theta}}{B} \quad (9)$$

Eqs. (8) and (9) were combined to study the critical condition in the temperature–concentration plane and give Eq. (10). In the work of Shouman and El-Sayed, the critical condition is defined by setting $(d^2\theta/d\alpha^2 = 0)$ and $(d^3\theta/d\alpha^3 = 0)$ [21–23]. However, the sufficient condition of an inflection point existence is where the second derivative of the curve changes sign and the curve tangent exists [24]. Therefore, setting the third derivative to zero may neglect some solutions. This analysis used the rigorous definition of an inflection point to study the critical behavior of HAN.

$$\frac{d\theta}{d\alpha} = B \left[1 - \frac{\theta - \theta_s/\psi}{(1 - \alpha)^n (1 + p\alpha^m) e^{-1/\theta}} \right] \quad (10)$$

4. Results and discussion

4.1. Autocatalytic reaction model and parameter determination

A typical temperature profile of HAN decomposition under the HWS mode of the APTAC is shown in Fig. 1. The autocatalytic reaction model, Eq. (5), was used to regress the five parameters used in this model. Another experiment was carried out to validate the model and its parameters. Both temperature profiles of these two experiments are shown in Fig. 2. Most of the data points recorded by APTAC are in the heat-wait-search stage. Only data points following the detection of an appreciable exothermic reaction rate are kept to show the HAN self-heating behavior and are displayed in Fig. 3. The heat of reaction of HAN measured by the APTAC is about 118 ± 20 kJ/mol.

With the Matlab® ODE solver and optimization toolbox as well as the autocatalytic reaction model for HAN, the nominal reaction parameters of HAN self-heating stage were obtained by regressing experiment 1 data and summarized as follows, frequency factor $7E5 \pm 2E3$, apparent activation energy 82 ± 0.4 kJ/mol, reaction order n is 0.55 ± 0.06 , and the catalytic reaction parameters p and m are 165 ± 22 and 3.3 ± 0.2 , respectively. To validate the model and

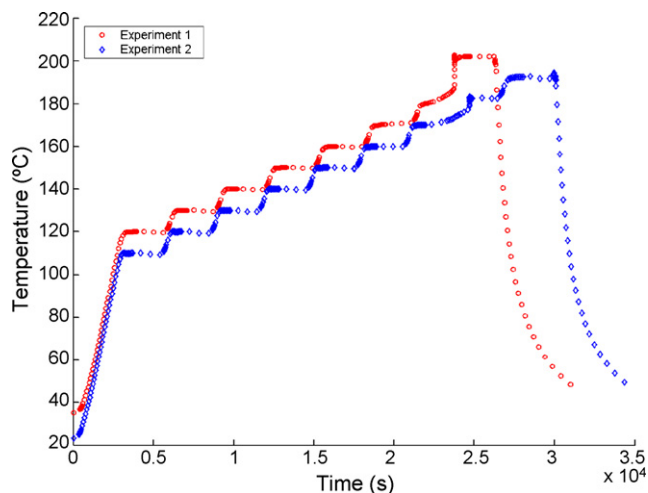


Fig. 2. HAN thermal decomposition with two different start temperatures of the HWS mode.

its parameters, these parameters were used to predict the temperature profile for experiment 2, which is shown in Fig. 3. The prediction quality is acceptable considering the complexity of the HAN decomposition process and the limited available information.

Pembridge and Stedman reported that the activation energy for oxidation of hydroxylamine (HA) by nitric acid and nitrous acid are 107 and 65 kJ/mol, respectively [25]. In addition, Shaw and Williams concluded that the activation energy of dissociation of HAN is between 61 and 71 kJ/mol [26]. Furthermore, Schoppelrei et al. [7] and Schoppelrei and Brill [8] used lumped first order reaction model to simulate the decomposition of HAN under similar conditions. Also they proposed that the apparent activation energy of HAN decomposition depends on the aqueous solution concentration. They reported that the activation energies for 0.92–1.52 M and 1.58–1.74 M HAN are 129 and 66 kJ/mol, respectively [7]. However Lee et al. reported much smaller activation energies for the apparent elementary reactions of the HAN decomposition process for highly concentrated HAN solutions and solid HAN [9]. The apparent activation energy reported here has the same magnitude as those for diluted HAN solution. The obtained apparent activation energy lies between the activation energies of oxidation of HA by nitric acid and by nitrous acid. This indicates that the self-heating stage

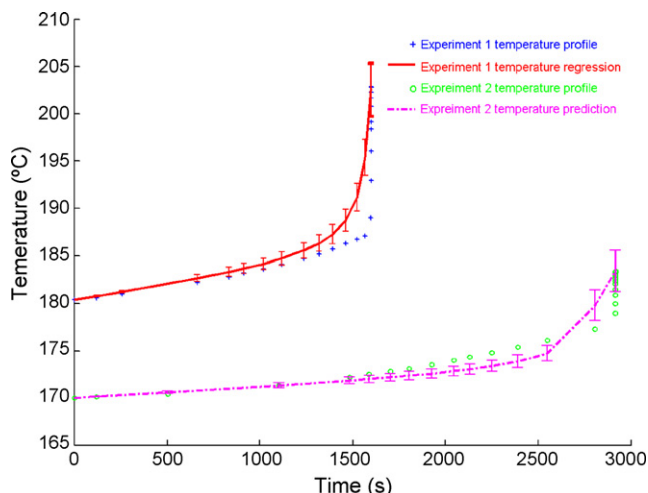


Fig. 3. Self-heating curve of HAN at different experimental conditions.

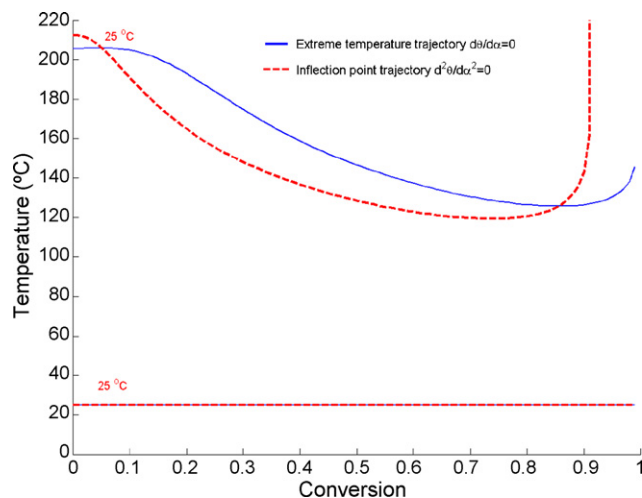


Fig. 4. Critical points demonstration on the temperature–concentration plane.

of HAN may consist of oxidation of HA by nitric acid and nitrous acid.

4.2. Critical behavior analysis

Following the determination of a HAN autocatalytic reaction model, the critical behavior of HAN was studied with this validated model. To find a meaningful inflection point, appropriate parameters for thermal explosion model must be chosen. So far the undetermined model parameters are the overall heat transfer coefficient, h , and the vessel dimension R (a spherical vessel was used in this analysis). To obtain a conservative estimate, the overall heat transfer coefficient, h , of 15–75 W/(m² K) [27], was used, and the vessel radius was 0.05 m.

Because the critical region is determined by inflection points as the previous work [21], the critical behavior analysis is equivalent to the determination of inflection points. The inflection points on the temperature–concentration plane are determined by searching the roots of the second order derivative $d^2\theta/d\alpha^2 = 0$ and checking whether the first non-zero higher order derivative has an odd order. The second derivative on the temperature–concentration plane is written as Eq. (11).

$$\frac{d^2\theta}{d\alpha^2} = B \left[\frac{n(\theta - \theta_s)}{\psi(1 - \alpha)^{n+1}(1 + p\alpha^m) e^{-1/\theta}(1 - \alpha)} + \frac{mp(\theta - \theta_s)\alpha^{m-1}}{\psi(1 - \alpha)^n(1 + p\alpha^m)^2 e^{-1/\theta}} + \frac{\theta - \theta^2 - \theta_s}{\psi(1 - \alpha)^n(1 + p\alpha^m)\theta^2 e^{-1/\theta}} \frac{d\theta}{d\alpha} \right] \quad (11)$$

The roots of the second order derivative $d^2\theta/d\alpha^2 = 0$ and the first order derivative $d\theta/d\alpha = 0$ for surrounding temperature, 25 °C, were superimposed on the temperature–concentration plane as illustrated in Fig. 4, where there are two roots for the first and second order derivatives, respectively. The roots of the first order derivative $d\theta/d\alpha = 0$ define the extreme temperature trajectory in Fig. 4. Because the third order derivatives at both roots of the second order derivative $d^2\theta/d\alpha^2 = 0$ are nonzero, both of these two roots are inflection points on the temperature–concentration plane and define the inflection point trajectories shown in Fig. 4. The temperature changing profiles with different initial reactant temperature were also superimposed on the temperature–concentration plane as illustrated in Fig. 5 to study the system critical behavior. Fig. 5

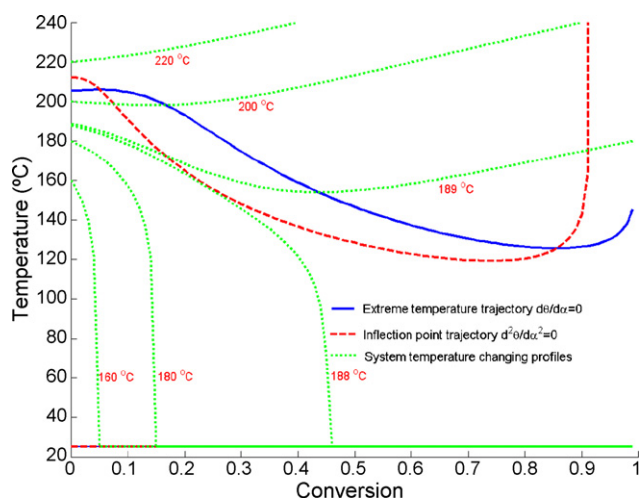


Fig. 5. Temperature changing profile for different initial reactant temperatures.

indicates the system temperature will continually increase and enter the non-return state, once the system temperature trajectory is above or intersects with the upper trajectory of the inflection points. So the upper trajectory of inflection points defines the critical behavior for diluted HAN solution, and the temperature-concentration plane is separated into subcritical, critical, and supercritical regions by the upper trajectory of inflection points. The small root of extreme temperature defines a stable status for the system, which is determined by the surrounding temperature. The system temperature eventually develops to this stable status if it is in the subcritical region.

The influence of the surrounding temperature was also analyzed and is shown in Fig. 6. To clearly show the result, the large roots of the second order derivative $d^2\theta/d\alpha^2=0$ and the first order derivative $d\theta/d\alpha=0$ for the 45 and 65 °C cases were not shown in Fig. 6, but they exhibit similar behavior to those of 25 °C. As illustrated in Fig. 6, the two roots for the second order derivative $d^2\theta/d\alpha^2=0$ merge together for the high temperature cases, which defines the lowest critical temperature. For high temperature cases, the subcritical region is the part below the large roots of the inflection point trajectories. The other regimes are the critical or supercritical regions, where the system temperature will continuously increase until the reactant is consumed. This fact demonstrates that the

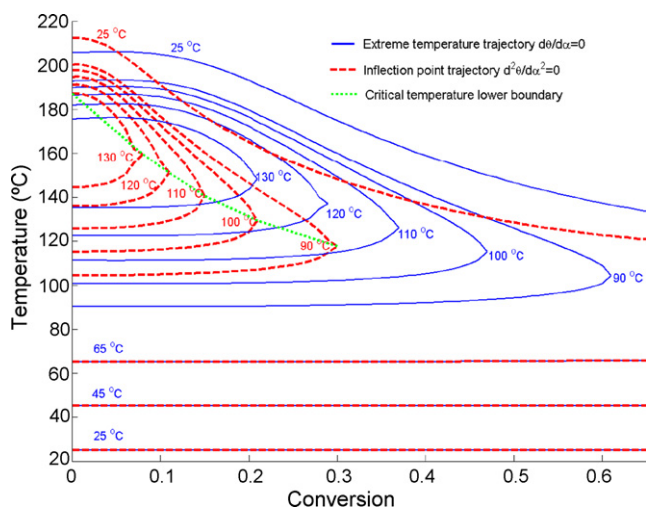


Fig. 6. Surrounding temperature influence on the temperature-concentration plane critical points.

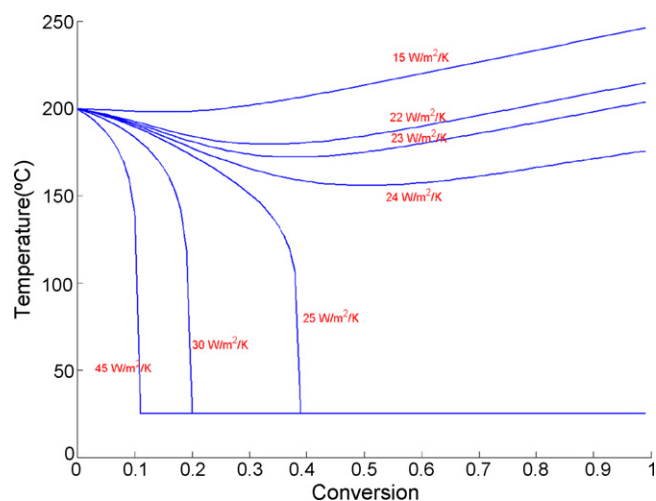


Fig. 7. The influence of the overall heat transfer coefficient.

feasible storage regime becomes smaller with the increase of temperature. An estimate of 187 °C for the critical temperature of fresh diluted HAN solution was obtained by connecting these intersections and extrapolating to zero conversion. This prediction result is consistent with the adiabatic test results as well as the results of other researchers [7].

As shown in Fig. 6, the critical trajectory is a function of both temperature and concentration, and it could enter the low temperature regime for the non-zero conversion system. The critical temperature is higher at the beginning of the reaction, where the catalysts have not accumulated significantly in the solution, but becomes smaller with the continuation of reaction and the accumulation of catalysts. This fact confirms that thermal explosion/runaway reactions can occur at low temperature. However, this important behavior of autocatalytic reactions may not be known or identified.

So far all analysis has been conducted with an overall heat transfer coefficient of 15 W/(m² K). Fig. 7 shows the influence of the overall heat transfer coefficient on the temperature changing profile with surrounding temperature of 25 °C and initial reactant temperature of 200 °C. Fig. 7 demonstrates that effective heat transfer can significantly reduce the thermal runaway risk of HAN. However for certain operations, such as storage, the heat transfer condition is comparably harder to improve. An easier and cost-effective solution may be to maintain the reactive chemical surrounding temperature well below its critical conditions. However, a thermal runaway reaction may occur at low temperatures for autocatalytic chemical systems due to the generation and accumulation of catalytic intermediates. Therefore autocatalytic reactive chemicals must be inspected periodically to insure that catalytic intermediate accumulation is sufficiently below critical conditions within the low temperature region.

For a fresh reactive chemical, its critical conditions are determined by the surrounding temperature and heat transfer conditions. As long as the initial temperature remains below its critical temperature, its temperature will eventually equilibrate with the surroundings. For autocatalytic reactive chemicals, the effect of conversion must be taken into account to avoid thermal explosion within the low temperature region. The safe storage and handling for reactive chemicals could be achieved by conducting all activities in the subcritical condition regions. However, the critical condition identified here has some uncertainties due to several reasons. First, HAN solution properties at high temperatures, such as heat capacity, are not available for its reactivity. Water heat capacity was used here and may lead to some uncertainties in

the final result. Second, this analysis does not consider the temperature gradient and natural convection, which may be developed for larger scale system. Normally, natural convection improves the heat transfer and removes more heat from the system. Therefore, the results obtained here are conservative. Finally, this discussion did not include the effect of gas generation because traditional thermal explosion does not integrate gas dynamics. With the advances in computers and mathematical algorithm, integration of gas dynamics into thermal explosion will become more practical and could significantly improve chemical safety.

5. Conclusions

With an appropriate autocatalytic model, the autocatalytic decomposition behavior of HAN in an adiabatic calorimeter is quantified, and the model parameters are validated. Fresh 24 mass% HAN solution without metal presence can be safely stored and used in room temperature. And this result is consistent with NFPA 704, in which the stated reactivity hazard of 24 mass% HAN is 0. The critical conditions of diluted HAN solution were further analyzed using thermal explosion theory on the temperature–concentration plane. Because the model obtained here is based on measurements from accelerated adiabatic experiments, in which all model parameters are conservative, the critical conditions identified here are also conservative and could be safely applied for small-scale dilute HAN storage and transportation practices.

Acknowledgements

This research was supported by the Mary Kay O'Connor Process Safety Center at Texas A&M University. The authors would like to thank the Supercomputer Lab Workstations at Texas A&M University for computer time, software, and support.

References

- [1] Technical Report on Hydroxylamine Nitrate, US Department of Energy, 1998.
- [2] L.O. Cisneros, W.J. Rogers, M.S. Mannan, Effect of air in the thermal decomposition of 50 mass% hydroxylamine/water, *Journal of Hazardous Materials* 95 (1/2) (2002) 13–25.
- [3] C. Wei, W.J. Rogers, M.S. Mannan, Thermal decomposition hazard evaluation of hydroxylamine nitrate, *Journal of Hazardous Materials* 130 (1/2) (2006) 163–168.
- [4] C. Wei, W. Rogers, M.S. Mannan, Detection of autocatalytic decomposition behavior of energetic materials using APTAC, *Journal of Thermal Analysis and Calorimetry* 83 (1) (2006) 125–130.
- [5] D. Amariei, L. Courtheoux, S. Rossignol, C. Kappenstein, Catalytic and thermal decomposition of ionic liquid monopropellants using a dynamic reactor. Comparison of powder and sphere-shaped catalysts, *Chemical Engineering and Processing* 46 (2) (2007) 165–174.
- [6] J.B. Wei, B.D. Shaw, Influences of pressure on reduced-gravity combustion of HAN–methanol–water droplets in air, *Combustion and Flame* 146 (3) (2006) 484–492.
- [7] J.W. Schoppelrei, M.L. Kieke, T.B. Brill, Spectroscopy of hydrothermal reactions. 2. Reactions and kinetic parameters of $[\text{NH}_3\text{OH}]\text{NO}_3$ and equilibria of $(\text{NH}_4)_2\text{CO}_3$ determined with a flow cell and FT Raman spectroscopy, *Journal of Physical Chemistry* 100 (18) (1996) 7463–7470.
- [8] J.W. Schoppelrei, T.B. Brill, Spectroscopy of hydrothermal reactions. 7. Kinetics of aqueous $[\text{NH}_3\text{OH}]\text{NO}_3$ at 463–523 K and 27.5 MPa by infrared spectroscopy, *Journal of Physical Chemistry A* 101 (46) (1997) 8593–8596.
- [9] H. Lee, T.A. Litzinger, Chemical kinetic study of HAN decomposition, *Combustion and Flame* 135 (1/2) (2003) 151–169.
- [10] A.G. Merzhanov, V.V. Barzykin, V.G. Abramov, Theory of thermal explosion: from N.N. Semenov to present day, *Chemical Physics Reports* 15 (6) (1996) 793–837.
- [11] A.A. Kossov, A.I. Benin, P.Y. Smykalov, A.N. Kasakov, A computerized system for research into the thermal safety of chemical processes, *Thermochimica Acta* 203 (1992) 77–92.
- [12] P. Misharev, A. Kossov, A. Benin, Methodology and software for numerical simulation of thermal explosion, *Process Safety and Environmental Protection* 74 (B1) (1996) 17–24.
- [13] S. Chippett, P. Ralbovsky, R. Granville, The APTAC: a high pressure, low thermal inertia, adiabatic calorimeter, in: *Proceedings of the International Symposium on Runaway Reactions, Pressure Relief Design, and Effluent Handling*, New Orleans, March 11–13, 1998, pp. 81–108.
- [14] D.I. Townsend, J.C. Tou, Thermal hazard evaluation by an accelerating rate calorimeter, *Thermochimica Acta* 37 (1) (1980) 1–30.
- [15] M.A. Bohn, Determination of the kinetic data of the thermal decomposition of energetic plasticizers and binders by adiabatic selfheating, in: *Proceedings of the Workshop on the Microcalorimetry of Energetic Materials*, Leeds, UK, May 17–19, 2nd., 1999, pp. F1–F25.
- [16] J. Steinbach, O. Klais, Prediction of self-reactive properties from DTA-measurements, *Institution of Chemical Engineers Symposium Series* 141 (1997) 261–272.
- [17] E. Wilcock, R.L. Rogers, A review of the phi factor during runaway conditions, *Journal of Loss Prevention in the Process Industries* 10 (5/6) (1997) 289–302.
- [18] B.F. Gray, J.C. Jones, Critical conditions in chemically reacting systems, *Combustion and Flame* 40 (3) (1981) 331–332.
- [19] T. Boddington, P. Gray, W. Kordylewski, S.K. Scott, Thermal explosions with extensive reactant consumption: a new criterion for criticality, *Proceedings of The Royal Society of London, Series A: Mathematical and Physical Sciences* 390 (1983) 13–30.
- [20] M. Morbidelli, A. Varma, Generalized criterion for parametric sensitivity: application to thermal explosion, *Chemical Engineering Science* 43 (1) (1988) 91–102.
- [21] A.R. Shouman, S.A. El-Sayed, Accounting for reactant consumption in the thermal explosion problem. Part I. Mathematical foundation, *Combustion and Flame* 88 (3/4) (1992) 321–344.
- [22] S.A. El-Sayed, Thermal explosion of autocatalytic reaction, *Journal of Loss Prevention in the Process Industries* 16 (4) (2003) 249–257.
- [23] S.A. El-Sayed, Explosion characteristics of autocatalytic reaction, *Combustion and Flame* 133 (3) (2003) 375–378.
- [24] I.N. Bronshtein, K.A. Semendyayev, G. Musiol, H. Muehlig, *Handbook of Mathematics*, 4th ed., Springer, Berlin/Heidelberg/New York, 2007.
- [25] J.R. Pembbridge, G. Stedman, Kinetics, mechanism, and stoichiometry of the oxidation of hydroxylamine by nitric acid, *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972–1999)* 11 (1979) 1657–1663.
- [26] B.D. Shaw, F.A. Williams, A model for the deflagration of aqueous solutions of hydroxyl ammonium nitrate, in: *Proceedings of the conference on 24th Combustion Institute*, Sydney, Australia, July 5–10, 1992, pp. 1923–1930.
- [27] E.U. Schlünder, *VDI Heat Atlas*, Woodhead Publishing Limited, Düsseldorf, 1993.