

Catalytic effects of inorganic acids on the decomposition of ammonium nitrate

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Abstract

In order to evaluate the catalytic effects of inorganic acids on the decomposition of ammonium nitrate (AN), the heat releases of decomposition or reaction of pure AN and its mixtures with inorganic acids were analyzed by a heat flux calorimeter C80. Through the experiments, the different reaction mechanisms of AN and its mixtures were analyzed. The chemical reaction kinetic parameters such as reaction order, activation energy and frequency factor were calculated with the C80 experimental results for different samples. Based on these parameters and the thermal runaway models (Semenov and Frank-Kamenetskii model), the self-accelerating decomposition temperatures (SADTs) of AN and its mixtures were calculated and compared. The results show that the mixtures of AN with acid are more unsteady than pure AN. The AN decomposition reaction is catalyzed by acid. The calculated SADTs of AN mixtures with acid are much lower than that of pure AN. © 2005 Elsevier B.V. All rights reserved.

Keywords: Ammonium nitrate; Inorganic acid; Catalytic effect; Decomposition; Heat flux calorimeter

1. Introduction

Ammonium nitrate (AN) is a widely used chemical material in industry and agriculture, its structural formula is NH_4NO_3 . AN is used not only as a fertilizer, but also as an important raw material in the chemical industry, an AN is now widely used as cheap material of industrial explosives [1]. Pure AN is considered relatively safe in comparison with other reactants because of its high stability in the lower temperature range. However, in the process of its manufacture, storage, transport and use, AN is often contaminated by some impurities, such as inorganic acid, organic oil and others. Auto-ignition and explosion may take place because of the catalytic effects of the impurity on the decomposition of AN. There are a lot of fire and explosion accidents caused

by AN in the recent decade. Table 1 shows several serious accidents of AN and its mixtures. Along with the accidents of several explosions involving AN or AN mixtures, efforts have been devoted to study the thermal stabilization of AN and its mixtures [2–7].

In order to evaluate the catalytic effects of inorganic acids on the decomposition of AN, the relationships between heat release and temperature of pure AN and its mixtures with some inorganic acids were measured by a heat flux calorimeter C80. The catalytic effects of sulfuric acid and hydrochloric acid on the decomposition of AN were studied. The thermal kinetic and reaction dynamic parameters of AN and its mixtures were calculated based on heat flux data measured by C80 calorimeter. Furthermore, according to the Semenov and Frank-Kamenetskii thermal explosion models, the self-accelerating decomposition temperature (SADT) of AN and its mixtures were calculated to estimate their thermal stabilization.

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Nomenclature

a_0	reactant characteristic dimension, for cylinder, a_0 is its radius
A	frequency factor (s^{-1})
C_p	specific heat ($J g^{-1} K^{-1}$)
d	reactant diameter (m)
dH/dt	overall heat flow (W)
E	activation energy ($J mol^{-1}$)
ΔH	heat of reaction ($J g^{-1}$)
l	reactant height (m)
M	mass of reactant (g)
M_0	initial mass of reactant (g)
n	reaction order
q_G	heat generation (J)
q_L	heat loss (J)
R	universal gas constant ($J K^{-1} mol^{-1}$)
S	contact area between package surface and ambient (m^2)
t	time (s)
T	temperature of system (K)
T_{NR}	no return temperature (K)
T_0	ambient temperature (K)
U	overall heat transfer coefficient ($J m^{-2} K^{-1} s^{-1}$)

Greek letters

δ_c	Frank-Kamenetskii critical parameter
κ	heat transfer coefficient ($J m^{-1} K^{-1} s^{-1}$)
ρ	reactant density ($g m^{-3}$)

2. Experimental apparatus and sample preparation*2.1. Experiment apparatus*

In this study, a CALVET heat flux calorimeter (C80) manufactured by SETARAM in France was used. It has the merits of high sensitivity (with several μW at least), many functions and a quite wide testing temperature range from room temperature to 300 °C. By using different types of experiment vessel with sample mass up to about 10 g and different functions, a great number of measurements can be made with C80, such as heat capacity determination of substances; heat generation by a change of state, mixing or a chemical reac-

Table 2

Experimental samples

Sample no.	Crystalline AN (purity: 99%) (wt.%)	Sulfuric acid (purity: 98%) (wt.%)	Hydrochloric acid (HCl content: 36–38%) (wt.%)
1	100	0	0
2	95.23	4.77	0
3	80	20	0
4	97.56	0	2.44
5	95.24	0	4.76

tion; determination of reactivity and kinetic parameters of reactive substance; hazards evaluation of reactive substance and so on [8,9]. The sample is sealed in a stainless steel vessel, pressure-proof at 100 bar. The reference was filled with alumina, whose amount is identical to the sample mass. During an experimental process, heat flux and the pressure were detected.

2.2. Sample preparation

In this study pure AN powder, sulfuric acid and hydrochloric acid were used to prepare the samples. Table 2 shows the percentage of each element in the samples.

3. Experiment results and discussions*3.1. Experiment results*

Two kinds of experiments were selected in this study. An isothermal experiment was executed to confirm the reaction order of the decomposition reaction of AN and its mixtures with inorganic acid. Constant temperature rising-rate experiments were performed to study the heat behavior of the whole reaction or decomposition process, and the data were used to calculate the activation energy and pre-exponential factor of the reaction.

Fig. 1 shows the heat flux curves of pure AN and its mixtures with different mass of sulfuric acid. The curves of Fig. 1 demonstrate that there are three endothermic peaks on the curve of sample 1 (the heat flow curve of pure ammonium nitrate). The endothermic peaks at 86 and 127 °C are the first and second crystalloid change of ammonium nitrate respectively, and the endothermic peak at 167 °C is the melting of ammonium nitrate. In the exothermic peak, the heat flow increases very slowly and gradually with the temperature

Table 1

Accidents involving AN or AN mixtures

Sample no.	Time	Site	AN amount (kg)	Death
1	September 21, 1921	Stockpile of AN containing 45% ammonium sulfate, Oppau, Germany	4500000	600
2	April 16, 1947	Cargo ship, Texas Harbor, USA	7700000	600
3	July 28, 1947	Cargo ship, Brest, France	3300000	29
4	August 5, 1993	Warehouse, Shenzhen, China	210000	15
5	January 26, 1998	AN solution in manufacture system, Xingping Shanxi, China	–	22
6	September 21, 2001	Warehouse, between process parts, storage and packaging, Toulouse, France	390000–450000	30

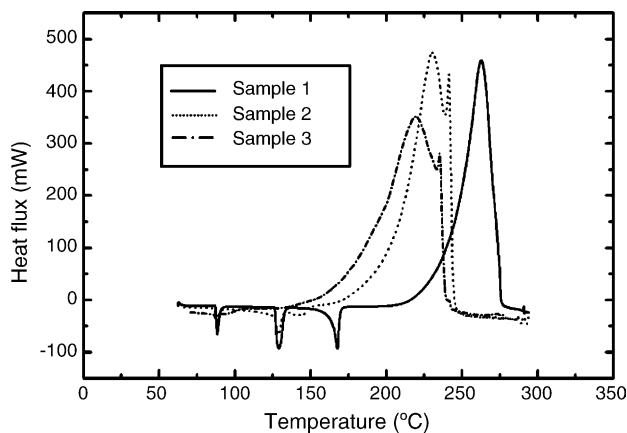


Fig. 1. Heat flux curves of pure AN and its mixture with sulfuric acid, heating rate: $0.2\text{ }^{\circ}\text{C}/\text{min}$, sample mass: 2.0 g.

increasing in the range of $190\text{--}232\text{ }^{\circ}\text{C}$, and increases sharply above $232\text{ }^{\circ}\text{C}$. For the heat flow curve of sample 2, the first two endothermic peaks are the same as those in sample 1. However, the decomposition reaction starts before the melting peak of pure AN. The heat flow increases gradually with the temperature increasing in the range of $145\text{--}207\text{ }^{\circ}\text{C}$, and increases sharply above $207\text{ }^{\circ}\text{C}$. For the heat flow curve of sample 3, only one endothermic peak exists on the curve at $86\text{ }^{\circ}\text{C}$. At the exothermic peak of decomposition, heat flow increases gradually with the temperature increasing in the range of $135\text{--}188\text{ }^{\circ}\text{C}$, and increases sharply above $188\text{ }^{\circ}\text{C}$. It is obvious that the decomposition of ammonium nitrate starts at lower temperature when sulfuric acid is present.

Fig. 2 shows the measured heat flux curves of pure AN and its mixtures with different mass of hydrochloric acid. It shows that the heat flux curve of sample 4 is similar to that of sample 5, but much different from that of pure AN. It is clear that the decomposition reaction of the mixtures starts at about $128\text{ }^{\circ}\text{C}$ when AN mixed with hydrochloric acid, not only much lower than that of pure AN, but also lower than

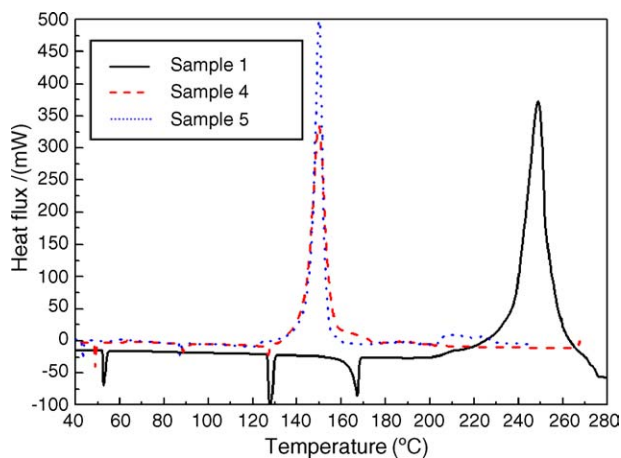


Fig. 2. Heat flux curves of pure AN and its mixture with hydrochloric acid, heating rate: $0.2\text{ }^{\circ}\text{C}/\text{min}$, sample mass: 1.0 g.

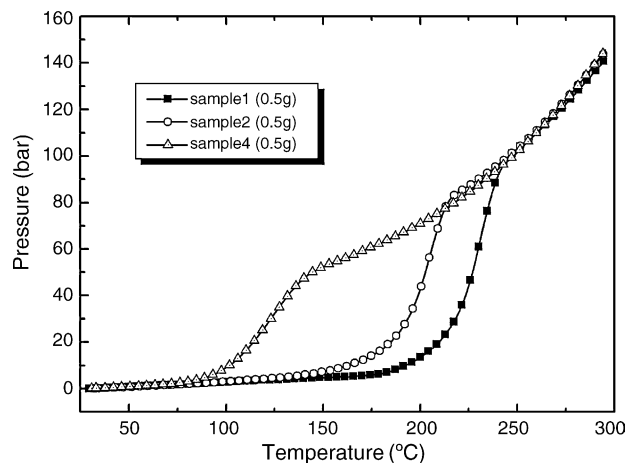


Fig. 3. Measured pressure curves of samples during their decomposition processes, heating rate: $0.1\text{ }^{\circ}\text{C}/\text{min}$, sample mass: 0.5 g.

that of the mixture of AN and sulfuric acid. It can be also found that the heat fluxes of the samples 4 and 5 increase very sharply with an increasing temperature, and their temperature range of decomposition reaction is much narrower than that of pure AN ($39.82\text{--}42.21\text{ K}$ versus 74.21), which means that when AN is mixed with hydrochloric acid, it will decompose more violently.

Fig. 3 shows the measured pressure curves of samples 1, 2 and 4 during the decomposition processes at a constant temperature rising rate of $0.1\text{ }^{\circ}\text{C}/\text{min}$ from room temperature to $300\text{ }^{\circ}\text{C}$. It is clear from the experimental results that the pressure rises when the temperature rises, and the pressure rise rates for each sample are much different, but the measured pressures for each sample are almost the same when the temperature is below $75\text{ }^{\circ}\text{C}$ or higher than $250\text{ }^{\circ}\text{C}$. Although the sulfuric and hydrochloric acid can catalyze the decomposition reaction of AN and decrease the onset temperature of AN decomposition, they cannot change the decomposition products of AN.

3.2. Discussions

3.2.1. Catalytic mechanisms

The above-mentioned results show that both sulfuric and hydrochloric acid can catalyze the AN decomposition reaction. However, the catalysis mechanisms of various substances are different.

Fig. 4 presents one conceivable explanation of the catalysis mechanism of sulfuric acid [5]. Sulfuric acid can replace the NO_3^- ion in AN, thus promote the buildup of nitric acid, which will increase the decomposition of AN. Because this process is the first step of AN decomposition which occurs at relatively low temperature, the heat release curve measured by C80 starts at a lower temperature than that of pure AN. This mechanism is also applicable to other strong acids such as nitric acid, etc. [5].

Fig. 5 presents the conceivable explanation of the catalysis mechanism of the Cl^- ion to the AN decomposition

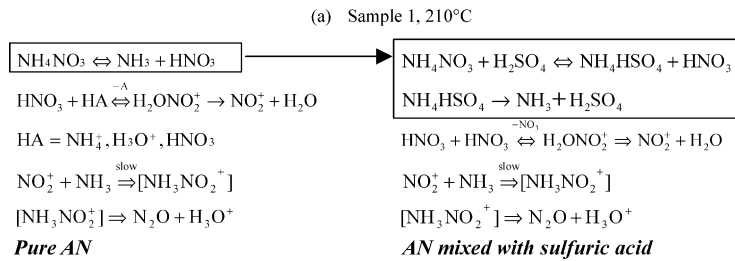


Fig. 4. The conceivable reaction mechanism of pure AN and AN mixed with sulfuric acid.

in acidic conditions [10]. During the process of pure AN decomposition, Eq. (*) is the controlling step because of its slow reaction rate. When mixed with hydrochloric acid, this step is substituted by the Eq. (*'), the ion Cl⁻ and H⁺ activate NO₂⁺ and NH₃, thus increasing the generation rate of with mediate product [NH₃NO₂⁺] at lower temperature. The activation energy of reaction (*) is decreased, priority the catalysis mechanism of Cl⁻ for the AN decomposition in acidic conditions [10].

3.2.2. Decomposition kinetic parameters of an and its mixtures

(1) Reaction order (n)

The rate of the mass consumption of reactant can be defined as Eq. (1)

$$-\frac{dM}{dt} = f(M)k(T) \quad (1)$$

where $f(M)$ is the model function and $k(t)$ is the reaction rate constant. A simple reaction mechanism is assumed to be dependent on the Arrhenius law:

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

Usually, $f(M)$ is presented as:

$$f(M) = M^n \quad (3)$$

Substituting Eqs. (1) and (3) into Eq. (1)

$$-\frac{dM}{dT} = A \exp\left(-\frac{E}{RT}\right) M^n \quad (4)$$

At the initial stage, the consumption of the reactant can be negligible. Therefore, M is approximately equal to M_0 . Multiplying Eq. (4) with the heat of reaction ΔH and coordinating, the heat generation of the reaction is obtained as:

$$q_G = \frac{dH}{dt} = \Delta H M_0^n A \exp\left(-\frac{E}{RT}\right) \quad (5)$$

At the same temperature, the sample mass is different, and Eq. (6) can be obtained:

$$\frac{(dH/dt)_1}{(dH/dt)_2} = \left(\frac{(M_0)_1}{(M_0)_2}\right)^n \quad (6)$$

The reaction order can be calculated by Eq. (7)

$$n = \frac{\ln(dH/dt)_1 - \ln(dH/dt)_2}{\ln(M_0)_1 - \ln(M_0)_2} \quad (7)$$

Fig. 6 shows the typical heat flux curves of three samples (samples 1, 2 and 4) during an isothermal experimental process. According to these experimental results and Eq. (7), the reaction orders can be obtained, and the reaction orders of all samples are equal to 1.

(2) Activation energy (E) and pre-exponential factor (A)

Substituting $n = 1$ into Eqs. (5) and (8) can be obtained:

$$\frac{dH/dt}{\Delta H M_0} = A \exp\left(-\frac{E}{RT}\right) \quad (8)$$

Taking the natural logarithm of Eq. (8)

$$\ln\left(\frac{dH/dt}{\Delta H M_0}\right) = -\frac{E}{R}\left(\frac{1}{T}\right) + \ln A \quad (9)$$

By plotting the curve of $\ln((dH/dt)/\Delta H M_0)$ versus $1/T$, the activation energy (E) and frequency factor (A) can be calcu-

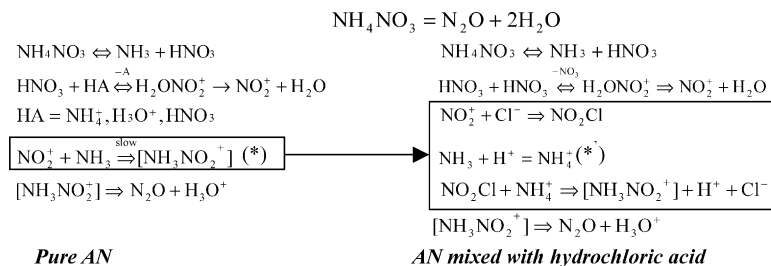
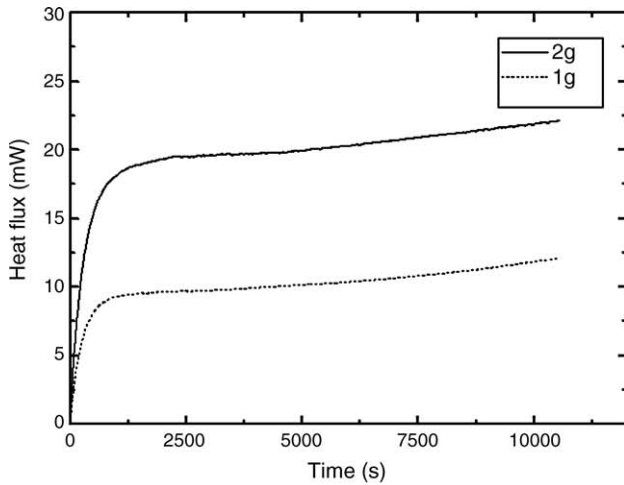
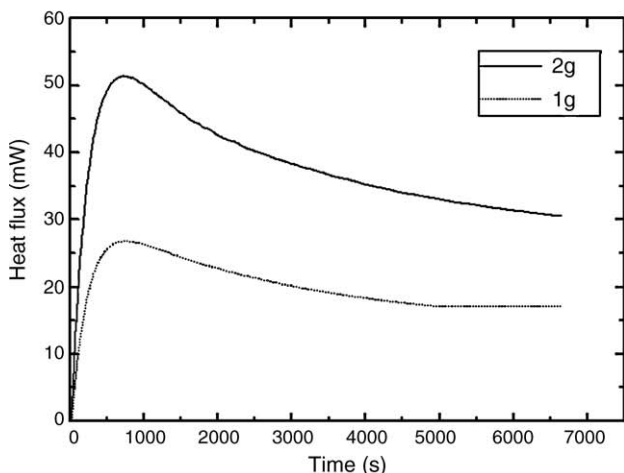


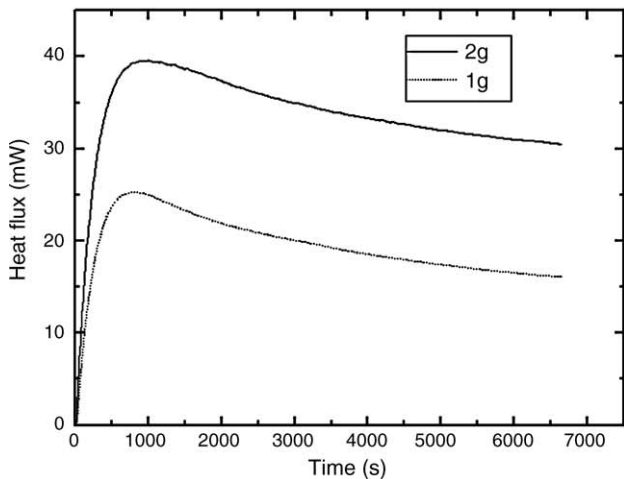
Fig. 5. The conceivable reaction mechanism of pure AN and AN mixed with hydrochloric acid.



(a) Sample 1, 210°C

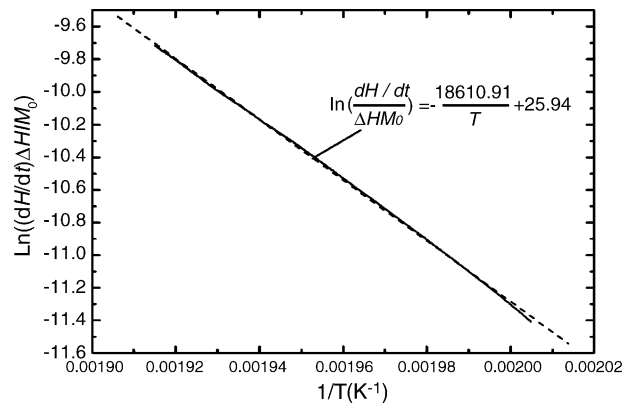


(b) Sample 2, 190°C

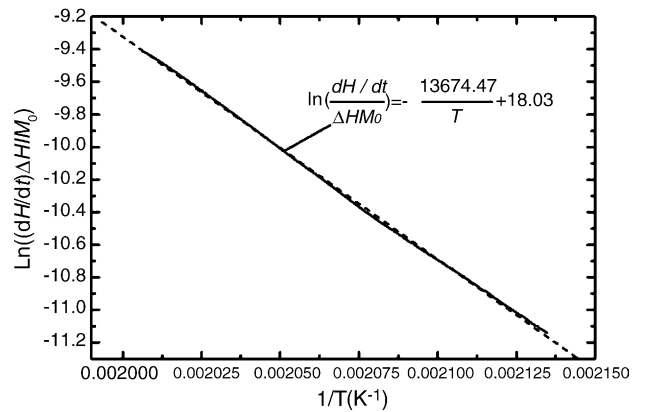


(c) Sample 2, 140°C

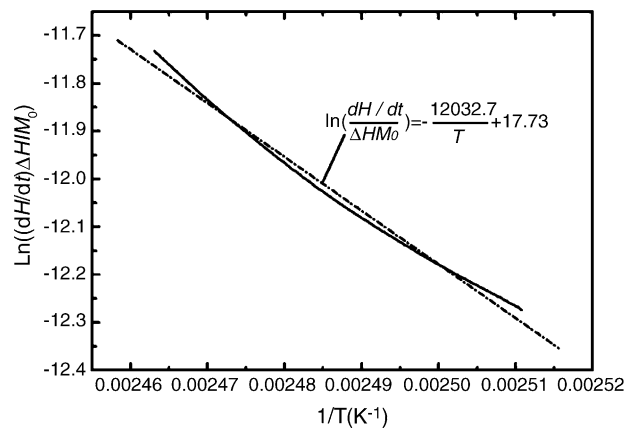
Fig. 6. Isothermal experimental results.



(a) sample 1



(b) sample 2



(c) sample 4

Fig. 7. Relationships between $\ln((dH/dt)/\Delta HM_0)$ and $1/T$ of three samples.

lated. Fig. 7 shows the process to estimate the thermal kinetic parameters. The calculated kinetic parameters of all samples are listed in Table 3.

According to above experimental results, the analysis of the decomposition kinetic parameters of AN and its mixtures, although both sulfuric and hydrochloric acid cannot change the decomposition products and the reaction order of AN, they can decrease the activation energy of the AN decom-

Table 3
Reaction kinetic parameters of samples

Sample no.	Reaction order (n)	Activation energy, E (kJ/mol) ^a	Frequency factor, A (s ⁻¹) ^a
1	1	154.7	1.8×10^{11}
2	1	113.7	6.7×10^7
3	1	74.4	3.8×10^3
4	1	110.7	1.8×10^8
5	1	100.0	5.0×10^7

^a Average value from two independent experimental results.

position, which facilitates the decomposition (or reaction) of AN mixtures with sulfuric and hydrochloric acid.

4. Evaluation of SADT

4.1. SADT of 25 kg standard package of samples based on the Semenov model

The purpose is to compare the SADT of the five samples based on the Semenov model, the packaging and the surface conditions are the same: 25 kg standard package, the wetted area $S = 4812.4 \text{ cm}^2$, the overall heat transfer coefficient $U = 2.8386 \times 10^{-4} \text{ J cm}^{-2} \text{ K}^{-1} \text{ s}^{-1}$ [11].

Based on the Semenov model, the heat balance equation is:

$$C_p M_0 \frac{dT}{dt} = \Delta H M_0^n A \exp\left(-\frac{E}{RT}\right) - US(T - T_0) = q_G - q_L \quad (10)$$

where $q_G = \Delta H M_0^n A \exp(-E/RT)$, $q_L = US(T - T_0)$, from the isothermal experiment results, the reaction order $n = 1$.

At the no return temperature (T_{NR}), both $dT/dt = 0$ and $d(dT/dt)/dT = 0$ must be held. Thus Eq. (11) is obtained as:

$$\frac{E}{R} = \frac{T_{NR}^2}{T_{NR} - T_0} \quad (11)$$

where T_0 is the surrounding temperature which is equal to the SADT, thus

$$\text{SADT} = T_0 = T_{NR} - \left(\frac{RT_{NR}^2}{E}\right) \quad (12)$$

Using this equation and the thermal-kinetic parameters estimated from the isothermal and non-isothermal experiment results, the SADT of the five samples feed in the 25 kg standard package were calculated. The results are listed and compared in Table 4.

The results show that when AN is mixed with sulfuric or hydrochloric acid, the activation energy of the decomposition reaction is lower than that of the pure AN decomposition reaction, the SADTs of AN mixtures calculated under the same packaging conditions are moreover much lower than that of the pure AN, when AN is mixed with sulfuric or hydrochloric

Table 4
SADTs for different sample mass

Sample no.	Reactant density, ρ (g/m ³)	SADT (°C, for 25 kg sample in standard package)	SADT (°C, for 300 ton sample in cylinder storehouse)
1	1.5×10^6	171.7	102.8
2	1.6×10^6	127.2	55.4
3	1.9×10^6	88.4	19.6
4	1.5×10^6	107.5	39.2
5	1.6×10^6	85.2	17.4

ric acid in storage or in production, much care should be taken.

4.2. SADT of 300 ton of samples based on the Frank-Kamenetskii model

In the accident occurred in France in September 2001, about 300 tons AN was stored. Reports showed that the contamination with the leaked sulfuric acid was one of the reasons that caused the accidents [12]. Because of the large amount of the AN stored, the Semenov model is no longer suitable for the calculation of SADT, and the Frank-Kamenetskii model is adopted.

Based on the Frank-Kamenetskii model [13], considering the internal heat transfer in the ammonium nitrate storage, the heat balance equation is:

$$\rho C_p \frac{\partial T}{\partial t} = \kappa \nabla^2 T + \Delta H \rho^n A \exp\left(-\frac{E}{RT}\right) \quad (13)$$

The Frank-Kamenetskii critical parameter is defined as [14]:

$$\delta_c = \frac{a_0^2 \Delta H E \rho^n A \exp(-E/RT_0)}{\kappa R T_0^2} \quad (14)$$

where T_0 is the surrounding temperature which is equal to the SADT:

$$\text{SADT} = T_0 \quad (15)$$

Assuming all AN is stored in a cylinder of height \times diameter 4 m \times 8 m. In such a finite cylinder, the Frank-Kamenetskii critical parameter $\delta_c = 2.78$ can be calculated by:

$$\delta_c = 2.0 + 0.195 \left(\frac{d}{l}\right)^2 \quad (16)$$

The heat transfer coefficient of AN mixtures (sample 2–5) can be considered equal to that of pure AN. By substituting into Eq. (14) of the reaction kinetic parameters of AN, AN mixtures with sulfuric and hydrochloric acid, heat transfer coefficient ($\kappa = 0.239 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$) of AN and characteristic dimension $a_0 = d/2 = 4 \text{ m}$, SADTs of all samples are calculated. The results are listed in Table 4.

Although the SADT of 300 tons of pure AN stored in a cylinder storehouse is 102.8 °C, when pure AN mixed with sulfuric or hydrochloric acid, the SADTs of 300 tons samples

become to very low, especially for samples 3 and 5, at 19.6 and 17.4 °C respectively. Auto-ignition and explosion may take place at room temperature when they are stored in large mass. Such materials are hazardous in their manufacture, storage, transportation, etc.

5. Conclusions

The decomposition reaction characteristics and the heat generation of pure AN and its mixtures with sulfuric and hydrochloric acid were researched using a C80 calorimeter. The catalysis mechanism of sulfuric and hydrochloric acid in the decomposition of AN were analyzed. The following results were obtained.

Both the contamination of sulfuric and hydrochloric acid have almost no influence on the decomposition products and the reaction order of AN, but they have significant influence on the activation energy of the AN decomposition; both of them decrease the activation energy, induce AN to decomposes (or react) more easily.

The catalysis mechanism of hydrochloric and sulfuric acid in the AN decomposition were analyzed. The activation effect of Cl^- and H^+ to NO_2^+ and NH_3 is the reason of hydrochloric acid catalysis. When pure AN is mixed with sulfuric acid, the HSO_4^- can replace the NO_3^- ion in AN, thus promoting the buildup of nitric acid, and enhancing the decomposition of AN.

Based on the Semenov model and the decomposition kinetic parameters of AN and its mixtures, the SADTs of the samples for 25 kg standard package were calculated and compared. The SADTs of AN mixtures (AN mixed with sulfuric acid and hydrochloric acid) were much lower than that of the pure AN.

The SADTs of 300 tons AN and its mixtures with sulfuric and hydrochloric acid stored in a cylinder were calculated based on the Frank-Kamenetskii model. When pure AN is mixed with sulfuric or hydrochloric acid, the results show that their SADTs are very low, especially for samples 3 and 5, at only 19.6 and 17.4 °C respectively. Auto-ignition and explosion may take place at ambient temperature for such materials during the process of storage, transportation, etc.

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