

## THERMAL PROPERTIES OF HYDRAZINE IN NITRIC ACID SOLUTION

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Since some combustible, oxidative and reductive chemicals are used in the extracting process in the nuclear reprocessing plant the process has potential hazards of a fire and explosion due to the undesired reaction.

In this study to obtain a better understanding of the thermal properties of hydrazine in nitric acid solution which is used for preventing the oxidation of extracted plutonium, thermal analysis was carried out for the mixtures in various conditions. From the results of DSC it was revealed that the vessel material has an influence on the thermal decomposition of hydrazine. It was also found that hydrazine reacted with nitric acid in an autocatalytic manner, and concentration of nitric acid has a strong influence on the thermal hazard of hydrazine and nitric acid mixtures.

**Keywords:** DSC, hydrazine, kinetics, nitric acid, thermal analysis

### Introduction

Some chemicals, which are classified into the reactive chemicals, have hazards to bring an explosion and fire by an overheating, shock and contact with other chemicals. Hydrazine hydrate, which is known as one of them, is colorless liquid, base and reducer, and has been widely used as polymerization catalyst, intermediate of medicine, raw material of agrochemical and deoxidizer in the industry due to its high reactivity. Moreover, its dehydrate, which has high combustibility, is used as fuel of rocket by being reacted to the oxidizer.

In addition, in the nuclear fuel reprocessing plant, hydrazine and nitric acid mixture is used as the solution for reprocessing spent nuclear fuel in PUREX (Plutonium and Uranium Recovery by EXtraction) method which is the main current of wet reprocessing method in industrial scale. In this method, the spent nuclear fuel is dissolved by nitric acid and extracted using tri-*n*-butyl phosphate ( $C_{13}H_{27}PO_4$ ) as an organic solvent with *n*-dodecane ( $C_{12}H_{26}$ ) as a diluent. In a purification process after separation nitrate solution of Uranus ( $U(NO_3)$ ) or hydroxylamine ( $NH_2OH$ ) are used as a reducing agent with hydrazine ( $N_2H_4$ ) as an inhibitor of decomposition of hydroxylamine or hydroxylamine nitrate. However, some accidents occurred in the nuclear fuel reprocessing plant in the past. According to the reference [1, 2], in 1993, at Tomsk-7 in Russia, the oxidation reaction of extracting solvents by nitric acid occurred and the vessel which contained them was destroyed by generated gases which were degradation and oxidation products. In 1997, at Hanford site in

America, a tank that was used to prepare a nitric acid and hydroxyl amine solution exploded due to the chemical reaction of hydroxyl amine and nitric acid accelerated by dissolved metal ion (such as iron or nickel ion) [3]. Since hydrazine has reactivity resembled hydroxylamine, nuclear reprocess has a hazard of an explosion due to the abnormal reaction of hydrazine. It is necessary to investigate the thermal properties of hydrazine in nitric acid solution.

In this study to obtain a better understanding of the thermal properties of hydrazine in nitric acid solution, thermal analysis was carried out for the mixtures in various conditions. Differential scanning calorimetry (DSC) was carried out for the hydrazine with the SUS303 stainless steel closed crucible and gold plated crucible, the influence of the cell material on the decomposition scheme of hydrazine were studied by calculating activation energy, comparing  $Q_{DSC}$  with calculated heat of decomposition and isothermal decomposition behavior. Moreover the thermal property of hydrazine in nitric acid with various concentrations was evaluated by DSC.

### Experimental

#### Materials and methods

Materials used in this study were hydrazine monohydrate ( $N_2H_4 \cdot H_2O$ ; HH) and nitric acid ( $HNO_3$ ; NA). Both were reagents from Wako Chemicals Co. Ltd., and were used without further purification and prepared as desired concentration with deionized water.

As a preliminary study thermochemical calculation of hydrazine hydrate and fuming nitric acid

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mixture was performed with REITP-3 program and the maximum heat of reaction and its composition were estimated as 272 kJ mol<sup>-1</sup>-reactants (=5.900 J g<sup>-1</sup>-reactants) and 38 mass% of hydrazine hydrate, respectively.

#### Thermal decomposition scheme of hydrazine hydrate with DSC

Thermal behavior of hydrazine hydrate during heating was determined with pressure DSC 827° of Mettler Toledo. 1.0 to 2.0 mg of the sample was heated up from room temperature to 773 K and a heating rate was varied from 0.3 to 0.7 K min<sup>-1</sup>. The SUS303 stainless steel closed crucible and gold plated closed crucible were used to investigate the influence of the cell material under 0.1 MPa air atmosphere.

#### Thermal property of hydrazine hydrate in nitric acid with DSC

The thermal behavior of hydrazine hydrate in nitric acid solutions was evaluated by DSC Q200 of TA Instruments. At first the non-isothermal measurement method was the hydrazine and nitric acid mixtures of 1.0 mg injected into the SUS303 stainless steel closed crucible, and the temperature was raised at 473 from 323 K, the heating rate was 1.0 K min<sup>-1</sup>. Next the isothermal measurements were carried out, and the hydrazine and nitric acid of 5 M solutions of 1.0 mg were kept at 338 to 353 K. Data analysis was performed using the software provided by Mettler Toledo and TA Instruments for respective instruments.

## Results and discussion

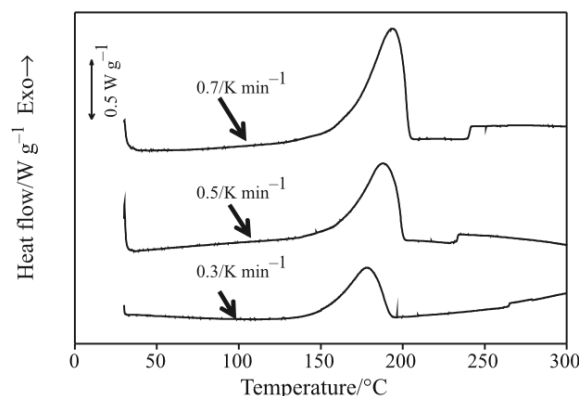
#### Thermal decomposition scheme of hydrazine hydrate with DSC

Figures 1 and 2 show the DSC curves of hydrazine hydrate in SUS303 closed crucible and gold plated crucible and Table 1 shows the summary of DSC measurement. The heats of reaction were 2.1 kJ g<sup>-1</sup> with SUS303 closed crucible and 1.8 kJ g<sup>-1</sup> with gold plated crucible.

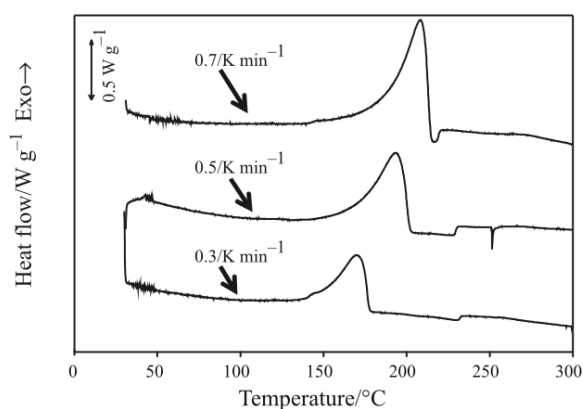
Figure 3 shows the Ozawa plot at conversion ( $\alpha$ )=0.5 and Table 2 shows the activation energy calculated from the result with Ozawa equation as follows [4].

$$\log\phi_1 + 0.4567\frac{E_a}{RT_1} = \log\phi_2 + 0.4567\frac{E_a}{RT_2} = \dots$$

where  $T$ ,  $\phi$ ,  $E_a$  and  $R$  are temperature (K), heating rate (K min<sup>-1</sup>), apparent activation energy (J mol<sup>-1</sup>) and gas constant (J mol<sup>-1</sup> K<sup>-1</sup>), respectively.



**Fig. 1** The DSC curves of hydrazine hydrate with SUS303 closed crucible



**Fig. 2** The DSC curves of hydrazine hydrate with gold plated closed crucible

**Table 1** Heat of decomposition of hydrazine hydrate

Heating rate/ K min <sup>-1</sup>	Heat of reaction/J g <sup>-1</sup>	
	SUS303	Gold plated
0.7	2195	1852
0.5	2167	1833
0.3	2170	1839

The apparent activation energy were determined as 105 kJ mol<sup>-1</sup> in SUS303 crucible at conversion ( $\alpha$ )=0.5 and 39 kJ mol<sup>-1</sup> in gold plated crucible at  $\alpha$ =0.5. According to the Kowhakul [5], the activation energy of decomposition of hydrazine calculated by Ozawa equation were determined as 41.0 kJ mol<sup>-1</sup> in gold pan and 140.7 kJ mol<sup>-1</sup> in glass capillary. Comparison of the result in this study with the reported data indicated a good agreement and it was revealed that gold has influence on the thermal decomposition of hydrazine.

According to Schmidt [6], the reaction scheme of thermal decomposition of hydrazine hydrate is following reactions



Reaction [b] can be expressed as 0.5·(reactions [a] and [c]). The heat of decomposition of hydrazine hydrate ( $Q_{\text{calculate}}$ ) is expressed as following formula in which  $X$  is defined the reaction [c] ratio.

$$Q_{\text{calculate}} = (1-X) \cdot \text{heat of reaction [a]} + X \cdot \text{heat of reaction [c]} \quad [\text{kJ g}^{-1}]$$

Heat of reactions [a] and [c], determined by calculation with ASTM CHETAH program version 7.3, were 2.39 and 1.08  $\text{kJ g}^{-1}$ , respectively, at 473 K. From the comparison of  $Q_{\text{DSC}}$  and  $Q_{\text{calculate}}$ , the ratio of reaction [c] is estimated about 15% with SUS303 closed crucible and almost of hydrazine decomposed with reaction [a]. On the other hand, with gold plated closed crucible, the reaction [c] was promoted about 43%. Figure 4 shows the reaction scheme of decomposition reaction of hydrazine.

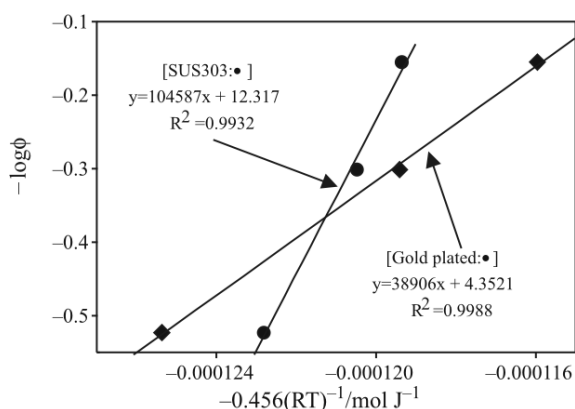


Fig. 3 Ozawa plot at conversion ( $\alpha$ )=0.5

Table 2 Calculated activation energy of thermal decomposition of hydrazine

Conversion, $\alpha$	Activation energy/ $\text{kJ mol}^{-1}$	
	SUS303	Gold plated
0.1	146	44
0.2	120	41
0.3	111	40
0.4	107	39
0.5	105	39
0.6	103	39
0.7	103	39
0.8	104	39
0.9	107	39

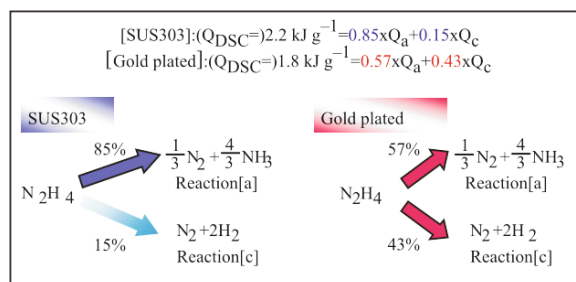


Fig. 4 Decomposition scheme of hydrazine

From these assumptions, it was concluded that activation energy of the reaction [c] was fallen out by catalysis effect of gold and the reaction [c] was progressed dominantly than the condition with SUS303 crucible.

*Thermal property of hydrazine in nitric acid solution with DSC*

Figure 5 shows the thermal behavior of 0.28 M hydrazine and nitric acid of 1 to 5 M concentration mixtures with DSC. Decreasing the onset temperature by the nitric acid concentration rose expected the difference of the thermal behavior between high concentration and low concentration of nitric acid. The reaction of the peak [p] was the same as one in the past report [7, 8] and the reaction of hydrazine and nitric acid. The reaction of the peak [q] was a violent exothermic reaction and according to the report [9], it is a thermal decomposition of hydrazine nitrate (HN). HN is known for its explosive nature and is used as rocket propellant or energetic material.

Figure 6 shows the thermal behavior of 0.28 M hydrazine in nitric acid of 5 M on the isothermal condition and Fig. 7 is enlargement of DSC curve at 348 K. In the several conditions of temperature, exothermic reactions of first peak began after induction time. An autocatalytic reaction usually begins after

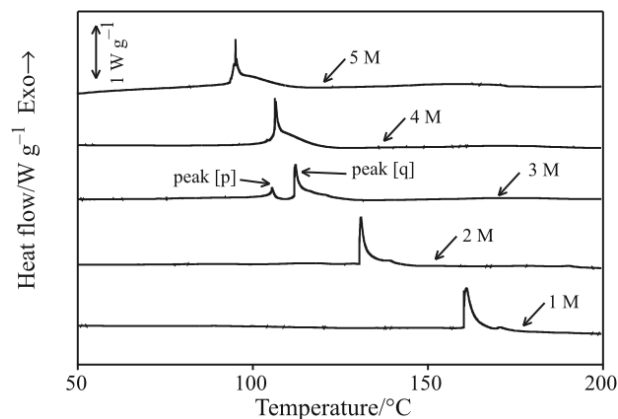
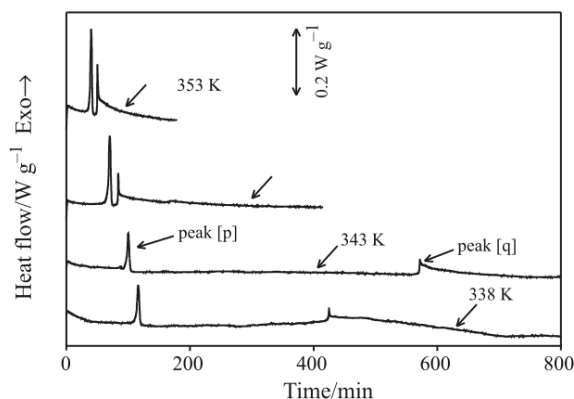
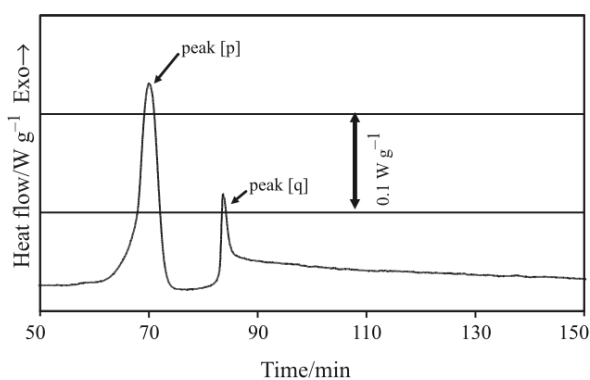


Fig. 5 DSC curves of hydrazine and nitric acid solutions



**Fig. 6** Thermal behavior of hydrazine in nitric acid of 5 M solution on the isothermal condition



**Fig. 7** DSC curve of hydrazine in nitric acid of 5 M solution at 348 K

**Table 3** Summary of temperature and induction time of isothermal test

Temperature, T/K	Induction time, t/min
338.15	105
343.15	68
348.15	50
353.15	31

induction time. The rate of an autocatalytic reaction is accelerated by the product of an initial reaction. Table 3 shows a summary of temperature and induction time in the isothermal test. Kinetics of the initial reaction is expressed as follows,

$$\frac{dq}{dt} = \Delta H \frac{dC}{dt} = \Delta H k f(C)$$

where,  $dq/dt$ ,  $\Delta H$ ,  $C$ ,  $t$ ,  $k$  and  $f(C)$  are a heat flow, heat of reaction, concentration, time, rate constant and function of concentration. An initial reaction is regarded to zero order reaction ( $f(C)=C^0$ ) [10],

$$\frac{dC}{dt} = kC^0$$

(Following equation is given by integration)

$$C = kt + \text{const.}$$

(const. is determined as an initial concentration  $C_0$ )

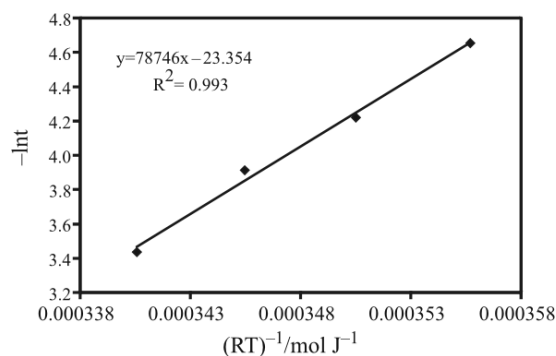
$$\ln t = \ln \frac{(C - C_0)}{A} + \frac{E_a}{RT}$$

(Rate constant of  $k$  is given Arrhenius equation)

As shown in the equation, there is a liner relationship between natural logarithm of an induction time and inverse of temperature. Figure 8 shows Arrhenius plot of  $\ln t$  vs.  $(RT)^{-1}$  and it was obtained a good liner relationship. The apparent activation energy of the initial reaction was determined as  $78.7 \text{ kJ mol}^{-1}$  from slope of the regression line.

Comparing with the result of 3 M nitric acid and hydrazine in non isothermal test which is shown in Fig. 5, it was determined that the peak [p] was the reaction of hydrazine with nitric acid and peak [q] was the decomposition of hydrazine nitrate.

It was concluded that hydrazine reacted with nitric acid in autocatalytic manner in SUS303 crucible and the apparent activation energy of the initial reaction was determined as  $78.8 \text{ kJ mol}^{-1}$ .



**Fig. 8** Arrhenius plot of  $\ln t$  vs.  $(RT)^{-1}$  on the initial reaction

## Conclusions

From the experimental investigation of DSC it was concluded as follows:

- Gold has a strong influence on the decomposition scheme of hydrazine.
- Concentration of nitric acid was important in the thermal stability of hydrazine/nitric acid mixture.
- Hydrazine reacted with nitric acid in autocatalytic manner in SUS303 crucible and apparent activation energy of initial reaction was determined as  $78.7 \text{ kJ mol}^{-1}$ .

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