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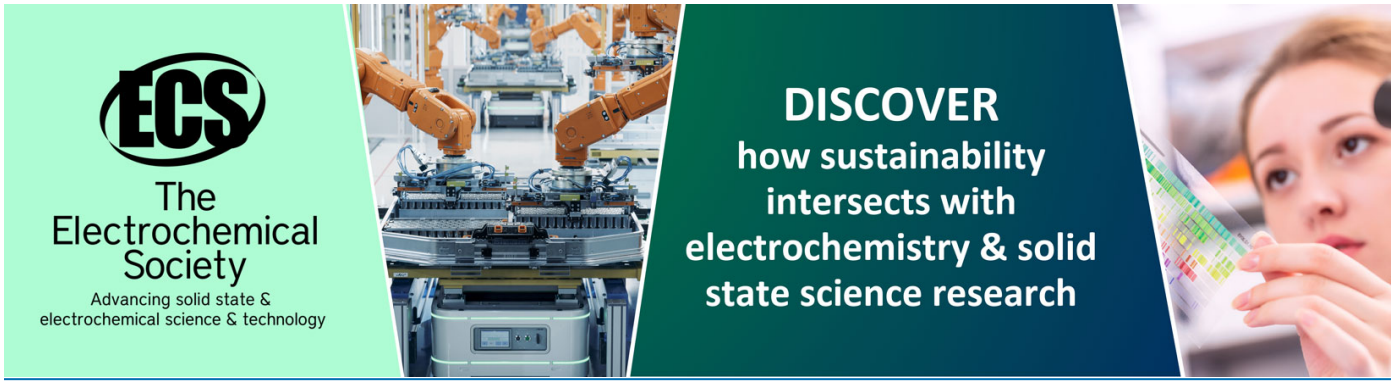

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Thermal Decomposition of GAP Studied by Dynamic Pressure-measuring Thermal Analysis

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Abstract: The thermal decomposition process of GAP in a vacuum confined space was measured by Dynamic Pressure-measuring Thermal Analysis(DPTA). In order to avoid the test error, the test process was improved: the method of liquid nitrogen condensation was used to prevent GAP volatilization in the process of vacuum pumping in the reaction test tube, and the vapor pressure at different temperatures was measured by thermogravimetric analysis. The results show that at 80℃ to 120℃, the mechanism function of GAP non-isothermal decomposition reaction is Jander equation, the apparent activation energy is 159.8kJ·mol-1, and the pre-exponential factor lnA is 25.8. At the GAP isothermal reaction stage, the mechanism function changes with the temperature. When the temperature increases, the thermal decomposition reaction changes from diffusion reaction to activation reaction. The decomposition rate constant K increases exponentially with increasing temperature. When T=80℃, K=1.27×10-6; when T=120℃, K=36.93×10-6. According to the data of the decomposition time of 0.1% in the temperature range of 80~120 ℃, the Semenov equation is lntT = 19039.90/T- 43.012. The storage life is 35.96 years at 25℃.

1. Introduction

As the current research hot spot, Polyglycidyl azide (GAP) has high generate heat, large density, low pollution, no corrosive gas, low characteristic signal, low combustion temperature, and low sensitivity, which often considered making high energy solid propellant [1]. Kubota and Brill [2] et al studied the initial stage of GAP by T-jump and FTIR, then made a detailed review of GAP thermal decomposition. Chen Zhiqun et al [3] studied the process of GAP thermal decomposition by DSC,TG-FTIR and other technologies, and proposed the possible decomposition mechanism. Liang Lei et al [4] analyzed the structure of GAP by infrared spectroscopy and tested its thermal decomposition characteristics. They believed that GAP's decomposition peak temperature was high and its thermal stability was good, so it could be selected as the material of high-energy low characteristic signal propellant.

Although the above method can obtain the kinetic parameters of GAP thermal decomposition process, it cannot accurately obtain the thermal decomposition process of GAP in vacuum environment, and cannot analyze the slow decomposition process of GAP at low temperature, which has little significance for practical application. Therefore, the research method should be improved. Based on the principle of vacuum stability (VST), Zhang Tonglai et al [5] establish the dynamic vacuum stability test (DVST) with pressure and temperature sensors, which provides a new method for studying the stability of energetic materials and predicting their storage life. In 2010, Rui Liu [6] et al studied the thermal decomposition process of HMX by using dynamic vacuum stability experiment, and obtained the thermal stability of decomposition mechanism and storage life of

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HMX In 2015. Liu Jianchao et al [7] studied the thermal decomposition mechanism of lead azide (LA) by DVST method, and analyzed the influence of crystalline controller on the thermal stability and thermodynamic parameters of LA. In 2015, Rui Liu [8] established and improved the Dynamic Pressure-measuring Thermal Analysis (DPTA) technology, which was used to study the thermal properties of various types of energetic materials. In this study, DPTA) method was used to study the thermal decomposition process of GAP, and the boiling volatilization problem was improved for GAP in the process of external vacuumization, focusing on GAP heating at low temperature with high vacuum degree Long time storage process caused by heat and low pressure double factors (thermal pyrolysis production of gas product and the process of gas production rate, the thermal decomposition kinetic parameters were obtained through the quantitative analysis of reaction mechanism of the thermal stability and storage life, and the test results for direct production using the safe operation of storage and transportation process control storage conditions have important application value.

2. Experiment

2.1. Experimental materials

GAP, which is from Xi 'an Modern Chemical Institute; Non-volatile at room temperature, brown-yellow viscous liquid, vitrification temperature of -67℃, number average molecular weight Mn=5013, weight average molecular weight M33=6617, hydroxyl value 40.21mgKOH/g dispersion index 1.32, molecular formula is CH3[CH2CH(CH2N3)O]nCH3.

2.2. Test device

DPTA test system [9]: DPTA instrument was developed by the State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology. The instrument is composed of three parts: thermal decomposition reaction unit, temperature control program, heating unit, data acquisition and processing unit. The instrument is used for dynamic real-time monitoring of the pressure and temperature changes during the thermal decomposition of materials at a certain vacuum and temperature. The volume of the test tube is 25mL.

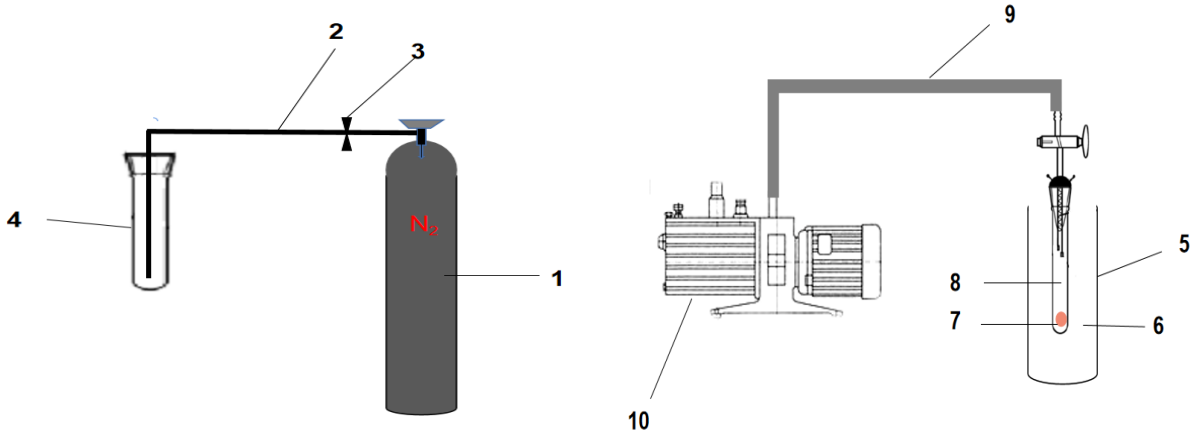
Thermogravimetric Analyzer: PerkinElmer Pyris type, the sample volume is about 1mg. Open platinum crucible, dynamic N_2 atmosphere flow rate 20mL/min.

2.3. Test process

The thermal decomposition test process includes two stages: the non-isothermal stage of uniform temperature rising to the set temperature and the isothermal process at the set temperature. In the process of vacuuming, the pressure in the sealed test tube is reduced, the boiling point of GAP is reduced, and volatilization is prone to increase in test error. Therefore, the reaction test tube is purged with nitrogen to dilute the air before the test, and the reaction test tube is cooled with liquid nitrogen in liquid nitrogen to cool down, which can prevent GAP boiling volatilization; When the sample is heated in the test tube, part of the sample will also volatilize and increase the dynamic pressure. Therefore, the vapor pressure should also be calibrated and deducted, The specific steps are as follows:

(1) The nitrogen replacement air process

As is shown in figure 1 first open the valve, then extend the rubber tube connected to the nitrogen gas tank into the bottom of the reaction test tube, and slowly inject nitrogen into the reaction test tube. After continuous 5 minutes, the air in the reaction test tube can be slowly removed.



1- High pressure nitrogen cylinder; 2-rubber hose; 3- valve; 4- Partial reaction test tube; 5- Dewar bottles; 6- Liquid nitrogen; 7- Volatile energetic materials; 8- Nitrogen; 9- Rubber hose; 10- Vacuum pump

Figure 1. Nitrogen replacement device and liquid nitrogen cooling unit.

(2) Sample loading

Weigh about 0.5g of sample and load it into a reaction test tube with good air tightness, the reaction test tube is built with a miniature pressure sensor and a miniature temperature sensor, GAP does not contact with the pressure sensor and temperature sensor; The internal temperature T and pressure P of the viscous liquid are different from the temperature and pressure of the gas in the reaction test tube.

(3) Sample condensation process of liquid nitrogen

The reaction test tube with GAP is placed in a dewar bottle filled with liquid nitrogen for condensation treatment. After the condensation, the reaction test tube is vacuumized to a pressure less than 10Pa. After the pressure in the reaction test tube is stabilized, the pressure and temperature in the reaction test tube are recorded. When the sample is condensed, the external temperature is lower than the freezing point of GAP.

Liquid nitrogen is colorless, tasteless, non-corrosive and very low temperature liquid. The temperature of liquid nitrogen is between -196℃ and -210℃, and the freezing point of nitrogen is -209.86℃, which can absorb a lot of heat during gasification. Put the test tube into liquid nitrogen, on the one hand, liquid nitrogen gasification will absorb the heat inside the test tube to reduce the temperature of GAP; On the other hand, as a result of the test tube inside and outside temperature difference will generate heat transfer, the temperature of the test pipe internal temperature is greater than the external cause heat transfer results in the decrease of internal temperature of the test tube. This methon is safe and simple, to solve the pressure in the closed container when volatile energetic materials volatilized caused by the reduction of quality affect DPTA test experimental data results.

(4) The dynamic stress test

The reaction test tube is removed from a low temperature environment and placed in a heating furnace for heating, Set the heating rate to 6 ℃/min, constant temperature time records for 48 h, Record the pressure and temperature in the reaction test tube in real time online; The pressure is normalized and then standardized, and the pressure value P_1 is obtained.

(5) The vapor pressure test process

It is also weighed about 1mg sample, using thermogravimetric analysis (TGA) method to test GAP evaporation process at different temperatures and calculate the corresponding vapor pressure value P_0.

(6) Thermal decomposition pressure analysis

The pressure value P_1 after treatment at the same temperature is subtracted from the vapor pressure value P_0 to obtain the pressure increase value P caused by the decomposition of the energetic material, and the data is used for thermal analysis of the energetic material.

3. Results and discussion

3.1. Relationship between GAP vapor pressure and temperature

Assuming that the free surface area is constant, both evaporation and sublimation reactions are zero-order reactions, so in TG test, the sample is as flat as possible on the platinum crucible.

Under constant temperature, the mass loss rate caused by evaporation is constant. Evaporation under vacuum is described by Langmuir equation [10]:

$$-\frac{dm}{dt} = p\alpha\sqrt{\frac{M}{2\pi RT}} \tag{1}$$

-dm/dt-Evaporation rate per unit area, P-vapor pressure, M-molecular weight of vaporized gas, R - ideal gas constant, *T* - thermodynamic temperature, M - molecular weight of gas, *T*- temperature of gas, K;

The vapor pressure *P* of a standard substance can be calculated from its known Antoine equation [11]:

$$\lg P = A - B/(C+T) \tag{2}$$

Langmuir equation and Antoine equation were combined:

$$\ln P = A\ln(dm/dt) + B \tag{3}$$

Through experiments, Rui Liu obtained the corrected Antoine equation of standard substance benzoic acid [12]:

$$\ln P = 1.0964\ln(dm/dt) + 1.5901 \tag{4}$$

The dm/dt value of GAP was measured by thermostatic TG method and substituted into equation (4). The corresponding relationship between dm/dt and temperature *T* is shown in the following table. The vapor pressure increases with the temperature.

Table 1. GAP vapor pressure at different temperatures.

T/℃	*T*/K	dm/d*t* /μg·min^{-1}	ln*P*	*P*
80	353.15	0.33	0.3745	1.454
90	363.15	0.81	1.345	3.838
100	373.15	3.50	2.964	19.37
110	383.15	9.01	3.999	54.54
120	393.15	12.1	4.314	74.74

3.2. Decomposing the corresponding relationship between pressure and time

Five test temperatures were set at 80, 90, 100, 110 and 120℃. respectively, to obtain the original curve of GAP thermal decomposition pressure measured with time in the temperature-programmed stage and isothermal stage, and to deduct the atmospheric pressure and initial value of the original curve. Due to the volatile nature of GAP, the vapor pressure of the material when heated to a set temperature in a vacuum is also subtracted. Then, the curve of standard pressure (P) of GAP thermal decomposition gas changing with time (t) is obtained, as shown in figure 2. Figure 2 shows that when the initial pressure is similar, the gas pressure of GAP thermal decomposition increases with the increase of heating time. GAP gas pressure at the same time and at different temperatures also increases with the increase of temperature. The results show that the storage temperature has a significant effect on the stability, storage safety and service life of GAP.

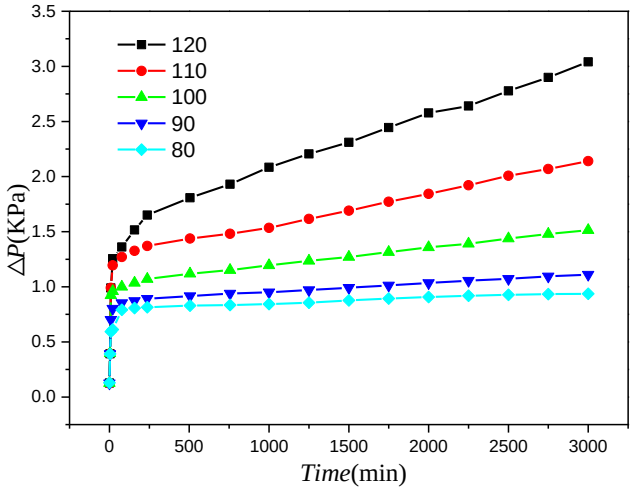


Figure 2. Variation of standard pressure of GAP net decomposed gas with time at different temperatures.

3.3. thermal decomposition kinetics research

Measured with the sample in a moment at the termination of the released gas volume V and test out the ratio of gas volume V_L said sample at the moment of conversion rate (or decomposition depth) alpha test the product gas pressure data manager wants to gas state equation transformation, said after the decomposition conversion for:

non-isothermal phase:

$$PT_L/P_LT=\alpha \quad (5)$$

Isothermal stage:

$$P/P_L=\alpha \quad (6)$$

P-the standard pressure of gas released at a certain measurement moment, kPa; P_L - the standard pressure of gas released at the time of test termination, KPa; *T*-the temperature at a measurement moment in the non-isothermal stage, K; T_L-the set test temperature, K.

3.3.1. Dynamic study at non-isothermal stage. The GAP was heated from 25 to 80,90,100,110,120℃. According to formula(5), the data of net separation liberated gas pressure (P) in five non-isothermal stages were converted to conversion rate (α), and the data of conversion rate (α) and its rate of change with temperature (dα/dT) were used for thermal analysis dynamics calculation. The general integral method [13]64 and differential equation method [13]80 were used to perform linear fitting for the known mechanism functions [13]151-160 of different types No.1-41. The optimal mechanism functions and corresponding dynamic parameters were screened by taking the highest linear correlation coefficient (R) as the criterion The results of dynamic parameters in the non-isothermal stage are shown in table 2. The results show that the thermal decomposition process in GAP non-isothermal stage at different test temperatures conforms to the No.6 mechanism function, namely Jander equation,n=2, which describes the three-dimensional diffusion, spherical symmetry and deceleration α -T curve. The activation energy of GAP at different temperatures is close to the pre-exponential factor value, which indicates that the activation energy of GAP thermal decomposition process is independent of heating temperature. The average E_a of GAP calculated by excluding errors generated by different test conditions is 159.8kJ·mol^{-1} and the average lnA is 25.8.

Table 2. Kinetic parameters of GAP thermal decomposition at non-isothermal stage.

T/°C	Function number	E_a/(kJ·mol^{-1})		ln(A·s^{-1})		standard deviation r	
		Universal integration	Differential equation method	Universal integration	Differential equation method	Universal integration	Differential equation method
80	6	158.9	159.1	25.15	24.14	-0.9938	-0.9927
90	6	159.3	160.2	26.35	25.13	-0.9945	-0.9819
100	6	157.8	160.0	25.18	27.12	-0.9967	-0.9925
110	6	158.2	161.2	24.95	26.17	-0.9939	-0.9945
120	6	160.2	163.2	26.45	27.19	-0.9956	-0.9813

As shown in figure 3,the thermal decomposition process of GAP is a complex process, it is generally believed that GAP first occurs the fracture rearrangement of azide group -CH_2-N_3,-CH_2-N_3 becomes -CH=NH, and then in the heating process, the main chain skeleton decomposes to generate CO、N_2、CO、HO_2、CH_4 and other substances. The GAP activation energy Ea measured in the experiment is close to the bond strength of RN=N_2 146~172, so it can be inferred that the GAP activation reaction is the fracture of azide group.

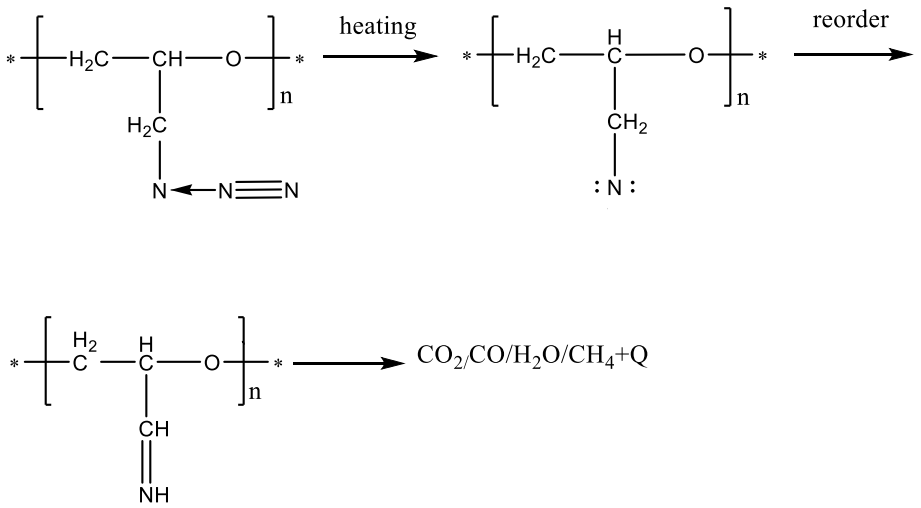


Figure 3. Thermal decomposition process of GAP under heating condition.

3.3.2. Kinetic study of thermal decomposition at isothermal stage. The GAP thermal decomposition gas pressure (*P*) at isothermal stage is converted into conversion rate (α) according to Formula (6). The data of conversion rate (α) and constant temperature time (t) are linearly fitted according to the kinetic equation of heterogeneous reaction G(α)= kt [14]. For different types of mechanism functions from 1 to 41, the least square method is used to make linear regression of G(α)-t relation y=Ax+B. The suitable mechanism function G(α) is selected with the maximum linear correlation coefficient R and the minimum intercept B as the comprehensive criterion. The optimal function is selected as the reaction mechanism function and the least square method is used to make linear regression y=Cx again The slope C of the fitted line is the reaction rate constant k at this temperature. The isothermal data of GAP at different temperatures from 80 to 120 are processed by this method. The results obtained are listed in table 3.

Table 3. Kinetic parameters of thermal decomposition at GAP isothermal stage.

T/℃	Function Number	Function name and mechanism	K/($10^{-6}S^{-1}$)	G(α)
80	9	Zhuralew-Lesokin-Tempelman Equation, three dimensional diffusion	1.27	$[(1-\alpha)^{-1/3}-1]^2$
90			2.79	
100	8	Anti-Jander Equation, three dimensional diffusion	6.45	$[(1+\alpha)^{1/3}-1]^2$
110			16.13	$[(1+\alpha)^{1/3}-1]^2$
120	5	Jander equation，n=1/2，three dimensional diffusion	36.93	$[1-(1-\alpha)^{1/3}]^{1/2}$

When the temperature increases, the intermolecular interaction of GAP is not enough to restrain the stronger intermolecular motion, and the intermolecular distance increases, and the internal friction decreases. For liquid viscosity mainly depends on intermolecular friction, when the temperature increases, the viscosity of GAP decreases, increasing the intermolecular diffusion For the GAP of single molecules, according to the lindemann monomolecular reaction activation mechanism: A molecular decomposition or isomerization reaction must go through with high-energy collisions among the molecules become activated molecules A*, if the energy is transferred to need breaking by impact the key of forming P, if A* internal energy is not fully transfer with low molecular collision energy, residual energy into A* will lost For ordinary molecule A, the reaction rate is the formation rate of product P. If the reaction activation energy is large, it is an activation controlled reaction. If the intermolecular viscosity of reactants is large, the reaction is mainly controlled by diffusion.

3.4. Study on thermal stability

The measured net decomposition standard pressure P data of GAP placed at five different temperatures at a constant temperature were converted into the gas discharge under standard condition by using the ideal gas equation according to the calculation method of gas discharge stipulated in military standard GJB772-97. The results are shown in table 4 below.

Table 4. Net gas emission of thermal decomposition obtained by DPTA at different temperatures.

t/℃	△*P*/KPa	*V*/（ml·g^{-1}）
80	0.941	0.2324
90	1.064	0.2620
100	1.509	0.3731
110	2.140	0.5280
120	3.030	0.7484

As can be seen from table 4, with the increase of heating temperature, the net liberated gas volume increases. According to GJB772-97, if the gas volume of 1 g sample is less than 2.00mL at 48 h under 100, it indicates that the vacuum stability and the gas volume released by each GAP at 100 is 0.3731mL /g, and the thermal stability is qualified.

3.5. Research on storage

Semenov equation is used when GAP storage life is estimated at different temperatures [6]. Semenov equation is:

$$\ln t_T = a + b_T \quad (7)$$

T-the test temperature, K; tT-Reaction time at a certain depth of decomposition, s; a and b are undetermined coefficients;

The decomposition depth (α) is defined as the ratio of the volume of gas released by the sample at a certain measurement moment to that released by the sample after complete decomposition. The end

point of the storage life of explosives is defined as the decomposition depth of 0.1% [15]. The pressure data of gas phase products are used to represent the complete decomposition depth:

$$Pa/P=\alpha \quad (8)$$

In the formula, P_a is the standard pressure KPa of gas released by thermal decomposition of the sample at a certain measurement moment; P is the standard pressure KPa of gas released by complete decomposition of the sample.

According to the law of mass conservation and the equation of state of ideal gas, the theoretical pressure of gas released when GAP is completely decomposed is 3465.5KPa. According to Equation(8), the decomposed gas pressure P of GAP at a measured moment in the temperature range of 80~120 is converted to the total decomposition depth α, and the time required for GAP decomposition depth to reach 0.1% at different temperatures can be calculated according to the relationship between α and *T*.

Table 5. Time t_T needed for GAP to decompose 0.1% at different temperature *T*.

T/℃	t_T/s
80	54295.7
90	12295.6
100	3016.9
110	797.1
120	224.9

The data in table 5 are substituted into the Semenov equation, and the linear fitting of lntT and 1/T is obtained as lntT = 19039.90/T- 43.012. The fitting curve of r=0.9916 is shown in figure 4. According to the equation, the effective storage life of GAP is 35.96 years when the storage temperature is 25℃.

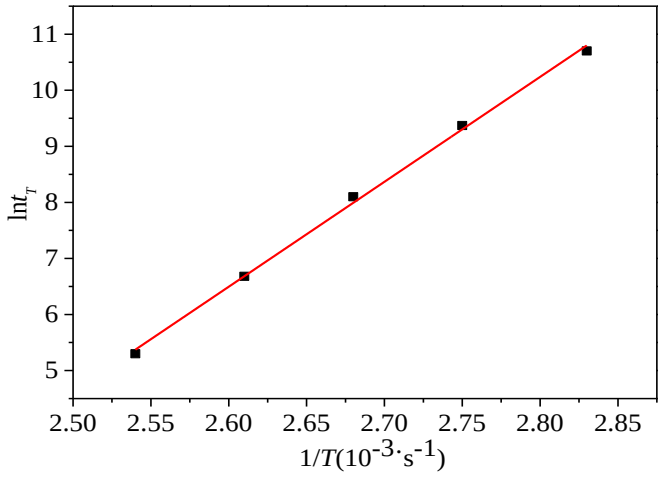


Figure 4. Correlation curve between lnt_T and 1/*T* of GAP.

4. Conclusion

(1) The thermal decomposition process of GAP at five different constant temperatures at 80~120 was studied by dynamic pressure measurement and thermal analysis. The thermal decomposition mechanism function and kinetic parameters of GAP were obtained according to the process of pressure and temperature changing with temperature.

(2) At these five set temperatures, the decomposition mechanism function of GAP at non-isothermal stage is Jander equation, n=2, and the integral form of the mechanism function is $G(\alpha)=[1-(1-\alpha)1/3]^2$. The activation energy E and pre-exponential factor A are close to each other at

different temperatures. The mechanism function of GAP is different at different test temperatures. The value of reaction rate constant K increases with the increase of test temperature.

(3) At five test temperatures, the net decomposed gas volume of GAP calculated by the net decomposition pressure is less than 1mL/g, which can be judged that GAP has good thermal stability.

(4) Semenov equation fitted by DPTA method is $\ln t_T = 19039.90/T - 43.012$, and storage life is 35.96A when extrinsic 25.

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