

Calculating Apparent Activation Energy of Adiabatic Decomposition Process Using Pressure Data *

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Abstract Considering the limitation of now available adiabatic kinetic analysis, a method to calculate activation energy by dealing with pressure data obtained from the adiabatic measurement is proposed. New kinetic equation is established and the apparent activation energies for the thermal decomposition of di-tert-butyl peroxide and 2-methyl-4-nitrobenzenesulfonic acid are calculated. The obtained apparent activation energies are compared with the values in the literature and the values obtained from other methods, and the difference between them and the underlying reasons are discussed.

Keywords: Activation energy, Adiabatic decomposition, Pressure, Accelerating Rate Calorimeter

Adiabatic measurement is now widely used to evaluate the thermal stability of reactive materials due to the advantage that the decomposition of sample is related only to the properties of materials themselves and independent of the external factors^[1-5]. So the study of adiabatic kinetic is becoming more and more important in simulating the behavior of the system.

The activation energy is always determined from the conventional adiabatic kinetic equation, which was given by Townsend and Tou in 1980^[1]. However, those calculation methods have not satisfied the usage of adiabatic calorimetry, especially when endothermic processes are encountered or/and when the adiabatic calorimetry system, such as Accelerating Rate Calorimeter (ARC), cannot provide the necessary response or data of temperature that would allow an acceptable analysis.

In this paper, we propose a kinetic equation expressed by pressure through establishing the relation between the reaction degree and pressure. Then the activation energy can be deduced by using the pressure data of an adiabatic test and the application fields of the adiabatic test may be extended.

1 Establishment of kinetic model

1.1 Conventional temperature equation

Under adiabatic condition, the simple n th-order decomposition reaction rate is expressed as

$$-\frac{dc}{dt} = kc^n \quad (1)$$

where c is the concentration of the reactant at temperature T (or time t); n is the reaction order; k is the rate constant of the reaction at temperature T , which can be expressed according the Arrhenius law $k = A \exp \left(-\frac{E_a}{RT} \right)$, where A and E_a are the apparent pre-exponential factor and the apparent activation energy respectively, R is the universal gas constant.

With the assumption that the heat capacity of the system remains constant throughout the reaction, the energy conservation law gives the reaction degree α as follows^[2]

$$\alpha = \frac{c_0 - c}{c_0} = \frac{T - T_0}{\Delta T_{ad}} \quad (2)$$

where c_0 is the initial concentration; $\Delta T_{ad} = T_f - T_0$ is the adiabatic temperature rise, T_0 and T_f are the initial and final temperatures of the reaction, respectively.

The self-heating rate, m_T , is obtained by differentiating eqn(2) with respect to t and substituting it into eqn(1),

$$m_T = \frac{dT}{dt} = k \left(\frac{T_f - T}{\Delta T_{ad}} \right)^n \Delta T_{ad} c_0^{n-1} \quad (3)$$

Rearranging eqn(3), the pseudo rate constant at temperature T , k_T^* , may be defined as

$$k_T^* = kc_0^{n-1} = \frac{m_T}{\left(\frac{T_f - T}{\Delta T_{ad}} \right)^n \Delta T_{ad}} \quad (4)$$

According to the relation $\ln k_T^* = \ln \left(c_0^{n-1} \cdot A \right) - \frac{E_a}{R} \left(\frac{1}{T} \right)$, the plot of $\ln k_T^*$ vs $1/T$ is, therefore, expected to be a straight line

providing the order of the reaction n is correctly chosen. Then the apparent activation energy E_a can be calculated from the slope of the plot ultimately.

1.2 Establishment of a new pressure equation

For a simple system under adiabatic condition, assuming the product is stable and do not go a further decomposition, there are relations as following

$$\frac{dp}{dt} \equiv \frac{dT}{dc} \equiv -\frac{dc}{dt}$$

and the relation between c_0 and c is

$$c \propto p_t - p$$

$$c_0 \propto \Delta p$$

where p_t is the final pressure of the system; p is the pressure at t ; $\Delta p = p_t - p_0$ is the pressure rise; and p_0 is the initial pressure.

For a gassy system, if the ideal gas law is obeyed, then

$$\frac{c}{c_0} = \frac{p_t - p}{\Delta p} \quad (5)$$

or
$$c = c_0 \cdot \frac{p_t - p}{\Delta p} \quad (6)$$

Differentiating and rearranging eqn(5), the rate of the change of the concentration c with pressure p is given by

$$\frac{dc}{dp} = -\frac{c_0}{\Delta p} \quad (7)$$

According to $\frac{dp}{dt} \equiv \frac{dp}{dc} \cdot \frac{dc}{dt}$, it is clear that

$$\frac{dp}{dt} = \left(-\frac{c_0}{\Delta p}\right)^{-1} (-kc^n) \quad (8)$$

By substituting eqn(6) into eqn(8), the pressure rise rate can be defined as

$$m_p = \frac{dp}{dt} = k \left(\frac{p_t - p}{\Delta p}\right)^n \Delta p c_0^{n-1} \quad (9)$$

k_p^* can be written as

$$k_p^* = kc_0^{n-1} \frac{m_p}{\left(\frac{p_t - p}{\Delta p}\right)^n \Delta p} \quad (10)$$

The apparent activation energy can be calculated using the same procedure mentioned above. Here the ideal gas law is just used to simplify the deduction. Through making corrections to real gas, this method should be suitable to real gas equally.

By using eqn(10), the kinetic parameter may be calculated easily. But for the decomposition reactions of solid materials, the kinetic aspects are complex. The concentration is very difficult to be measured, because it is not a defined property and the characteristic of the solid may change during the course of the reaction.

So replacing c with α , the reaction rate can be expressed as

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (11)$$

where $f(\alpha)$ symbolizes the kinetic model.

Substituting eqn(6) into eqn(2), α can be given as

$$\alpha = \frac{p - p_0}{\Delta p} \quad (12)$$

Differentiating eqn(12) with respect to t and comparing with eqn(11), it is obtained

$$m_p = \frac{dp}{dt} = \Delta p \cdot A e^{(-E_a/RT)} f\left(\frac{p - p_0}{\Delta p}\right) \quad (13)$$

then the following equation can be deduced

$$\ln \frac{m_p}{f\left(\frac{p - p_0}{\Delta p}\right)} = \ln(A \cdot \Delta p) - \frac{E_a}{R} \cdot \frac{1}{T} \quad (14)$$

The plot of $\ln \frac{m_p}{f\left(\frac{p - p_0}{\Delta p}\right)}$ vs T^{-1} should give a straight line with

a slope $-E_a/R$ providing the kinetic model is correctly chosen. Different kinetic models are used to try to find the best linearity of the linear regression, from which the activation energy can be calculated^[6].

2 Experimental

In order to check the validity of the method, the thermal decomposition of di-tert-butyl peroxide (DTBP) and 2-methyl-4-nitrobenzenesulfonic acid (MNBS) were studied.

2.1 Instrument and samples

Accelerating Rate Calorimeter (ARC) used is a product of the Columbia Scientific Industries, Austin, TX, USA.

DTBP (b. p. : 111 °C) is produced by Beijing Guohua Chemical New Material Co., C. R. ; 2-methyl-4-nitrobenzenesulfonic acid is purchased from Beijing Chemical Industry, laboratorial reagent.

2.2 Experimental principle

ARC is an adiabatic calorimeter that can track the process of the reactive materials' decomposition and record their pressure and temperature data. The detailed description of the ARC has been published elsewhere^[1,7-8].

The sample of known mass in a suitable bomb is heated to a preset start temperature. The external heater then tracks the sample temperature to ensure adiabaticity. Heat-wait-search mode is employed in all of the tests. Measurement conditions are listed in Table 1.

2.3 Experimental results and discussion

ARC curves of DTBP and MNBS are given in Fig. 1 and

Table 1 Measurement conditions of ARC

Parameters	DTBP	MNBS
Bomb type	Ti	Ti
Start temperature (°C)	50	100
Slope sensitivity (°C · min ⁻¹)	0.02	0.02
Heat step (°C)	5	5
Wait time (min)	10	10

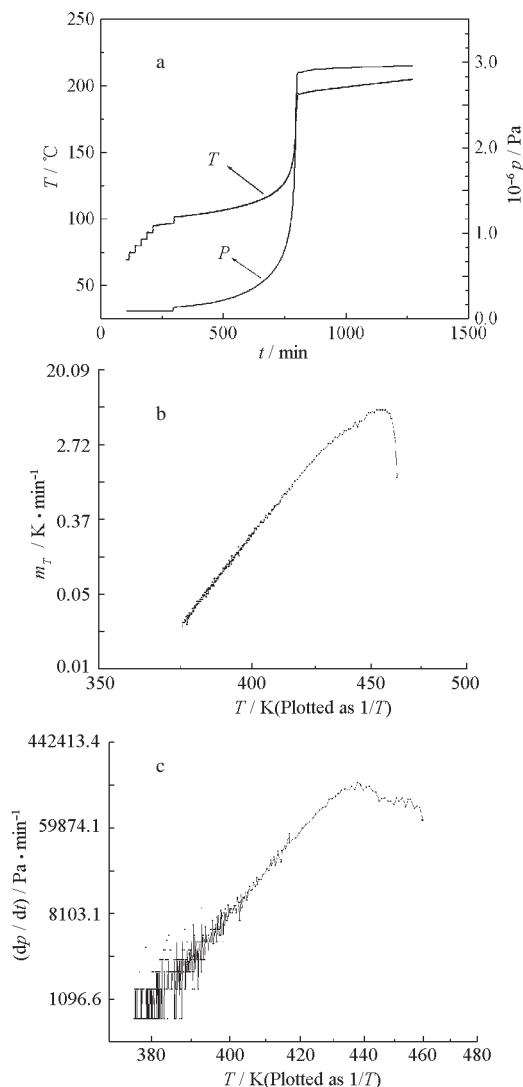


Fig. 1 Adiabatic decomposition curves of DTBP measured by ARC

(a) $T-t$, $p-t$; (b) m_T-T ; (c) $dp/dt-T$

Fig. 2. From Fig. 1(a), it is seen that the decomposition of DTBP starts at 102.5 °C. With the increase of the temperature, a large amount of gases generate and the pressure rises sharply. The pressure rise rate changes with the temperature rise rate linearly at early reaction stage, and then the linearity is lost as the reactant is depleted, the curves of the temperature rise rate and the pressure rise rate *vs* temperature are all decreased (see Fig. 1(b) and (c)). There is a small rise at the back of the curve (see Fig. 1(c)), it may be due to the decomposition of impurity or product. So this part is excluded during the follow-

Table 2 The influence of thermal inertia on the value of activation energy

Sample mass(g)	thermal inertia (ϕ)	$E_a/\text{kJ} \cdot \text{mol}^{-1}$
4.1910	1.42	165.32
2.8822	1.60	167.22
1.1511	2.16	168.53

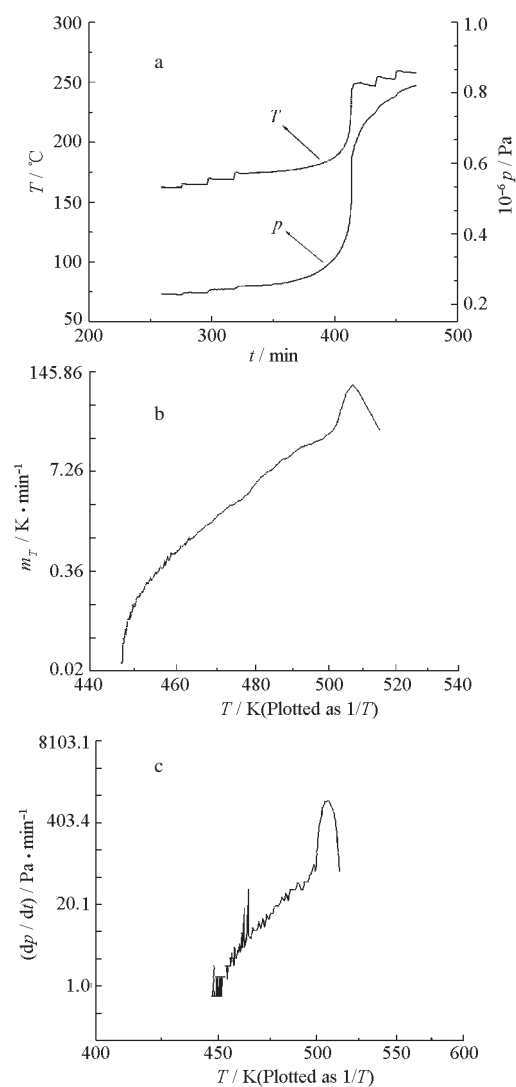


Fig. 2 Adiabatic decomposition curves of MNBS measured by ARC

(a) $T-t$, $p-t$; (b) m_T-T ; (c) $dp/dt-T$

ing treatment.

Fig. 2(a) shows that the pressure rise sharply after 2-methyl-4-nitrobenzenesulfonic acid starts to decompose at 175.04 °C. The linearity displayed in Fig. 2(c) explains the relation between the pressure rise rate and temperature.

The thermal decomposition of DTBP is a typical first-order reaction. The plot of pseudo rate constant calculated according to eqn(10) at any pressure *vs* temperature is shown in Fig. 3.

In this case, dispersive points are observed, which might be caused by the low sensitivity of ARC. The sensitivity of ARC for the heating-rate is $0.02 \text{ } ^\circ\text{C} \cdot \text{min}^{-1}$. That is to say, ARC regards the case as the beginning of an exothermic reaction when the heating-rate of a system is larger than $0.02 \text{ } ^\circ\text{C} \cdot \text{min}^{-1}$. To avoid the influence of these occasional factors in calculating the activation energy, several data at the beginning of the reaction should not be used.

Table 3 Regression results of kinetic parameters for MNBS

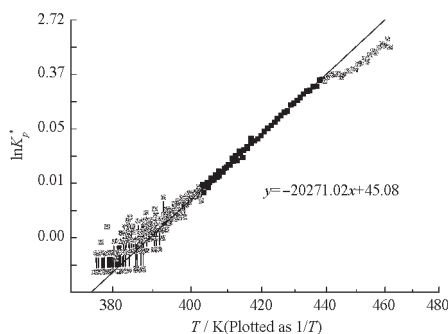
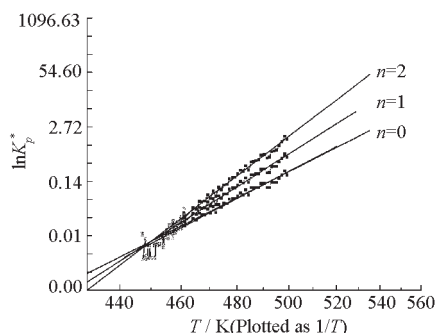
Reaction order	ln A	R*	$E_a/kJ \cdot mol^{-1}$
$n = 0$	34. 14	0. 9797	148. 05
$n = 1$	42. 76	0. 9870	179. 86
$n = 2$	52. 48	0. 9971	216. 25

R*: correlation coefficient for linear regression

Linear regression of the middle part of the data gives a reasonably straight line, which leads to the apparent activation energy 168. 53 $kJ \cdot mol^{-1}$. This result is in good agreement with that of in literature[9] ((167 \pm 6) $kJ \cdot mol^{-1}$).

Volatilization of samples should be considered in terms of pressure. In addition, for any adiabatic measurement, the thermal inertia(ϕ) cannot be neglected owing to some heat and pressure loss to the sample bomb^[1]. In order to reinforce the validity of the procedure, three experiments with different amounts of sample are carried out to demonstrate the behavior of the method on vapor pressure and ϕ factor. The calculated results are listed in Table 2.

From Table 2, it can be seen that little difference exists in the apparent activation energy obtained from three experiments. Combining with the onset temperature of DTBP which is prior to the boiling point, we think that though vapor pressure and thermal inertia may have some influence on this calculated method, it still can give satisfied results within the range of measurement.


Fig. 3 The pseudo-order rate constant k_p^* vs T for the adiabatic decomposition of DTBP

Fig. 4 The pseudo-order rate constant k_p^* vs temperature for the adiabatic decomposition of MNBS

Because the order of the decomposition reaction of 2-methyl-4-nitrobenzenesulfonic acid is not defined, three different values 0, 1 and 2 are selected to fit the experiment data according to eqn(10). The curves of the fitting lines are shown in Fig. 4, and the results of the linear regression are listed in Table 3.

The data shown in Table 3 present that the linearity is the best when the reaction order is two. The corresponding value of the apparent activation energy is 216. 25 $kJ \cdot mol^{-1}$.

According to eqn(14), linear regression is carried out by substituting 16 kinds of kinetic models^[10]. The fitting results and the estimated kinetic parameters are listed in Table 4.

It is shown that the form of $(1 - \alpha)^2$ may be the most probable kinetic model of the decomposition reaction of 2-methyl-4-nitrobenzenesulfonic acid by comparing the value of correlative coefficient given in Table 4, from which the activation energy calculated are 232. 12 $kJ \cdot mol^{-1}$. It is in agreement with the value calculated according to eqn(10).

In order to compare with other methods, the results obtained from different methods are listed in Table 5.

From Table 5, it can be seen that the activation energies obtained from methods 1, 2 and 4 are in good agreement, but there is a small different in the value obtain from method 3. This may be due to the many simplification processes^[1].

Table 4 Estimation of kinetic parameters for MNBS

$f(\alpha)$	R	$E_a/kJ \cdot mol^{-1}$	$f(\alpha)$	R	$E_a/kJ \cdot mol^{-1}$
$1/(2\alpha)$	0. 91785	64. 10	$3/2(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$	0. 98888	158. 59
$2\alpha^{1/2}$	0. 97710	208. 30	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	0. 97813	111. 61
$(1 - \alpha)$	0. 98831	196. 18	$3\alpha^{2/3}$	0. 97529	224. 32
$(1 - \alpha)^2$	0. 99184	232. 12	$3(1 - \alpha)^{2/3}$	0. 97509	136. 27
$2(1 - \alpha)^{3/2}$	0. 99030	214. 15	$2(1 - \alpha)^{1/2}$	0. 97718	142. 26
$[- \ln(1 - \alpha)]^{-1}$	0. 97508	272. 99	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	0. 98250	121. 00
$3/2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$	0. 72892	29. 34	$2(1 - \alpha)[1 - \ln(1 - \alpha)]^{1/2}$	0. 97446	136. 95
$3/2(1 + \alpha)^{2/3}[(1 + \alpha)^{1/3} - 1]^{-1}$	0. 95240	82. 38	$2/3[(1 - \alpha)^{-1/3} - 1]^{-1}$	0. 83097	41. 33

Table 5 Results of calculated kinetic parameters of MNBS using different methods

	Methods	$E_a/\text{kJ} \cdot \text{mol}^{-1}$
1	Eqn(4)	216.25
2	Eqn(10)	227.12
3	Time to maximum rate*	186.84
4	Eqn(14)	232.12

* Discussed in reference[1]

3 Conclusion

By establishing the kinetic equation expressed by the pressure, i. e., eqns(10) and (14), a reliable method to calculate the apparent activation energy of adiabatic decomposition reaction is proposed. It makes the best usage of the pressure data of adiabatic test and brings ARC into a wider thermoanalysis field where the ARC system cannot provide the necessary response or data of temperature. In addition, less assumption is required for calculation with the present method. However, the feasibility of this method is discussed tentatively in this paper, and further studies would be carried to solve the problem of the reproducibility of the pressure data and improve the precision of this method.

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用绝热测试的压力数据计算分解反应的表现活化能*

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摘要 绝热量热技术的广泛应用促进了绝热动力学研究的发展. 至今为止, 绝热动力学的研究仍是以 Townsend 和 Tou 在 1980 年提出的绝热动力学方程为基础. 他们利用反应物浓度与温度的关系建立动力学模型, 从而求得了反应的活化能. 但这种方法在反应体系的温度效应不明显时的应用, 就受到很大的限制. 因此, 本文通过建立用压力表示的动力学方程, 充分利用绝热量热中的压力数据, 提出了一种计算反应活化能的新方法. 同时用这种方法计算了过氧化二叔丁基和 2-甲基-5-硝基苯磺酸的绝热分解活化能值, 并与文献值和其他计算方法所得结果进行了比较.

关键词: 活化能, 绝热分解, 压力, 绝热加速量热仪(ARC)

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