

# The criteria of critical runaway and stable temperatures of catalytic decomposition of hydrogen peroxide in the presence of hydrochloric acid

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## Abstract

The hydrogen peroxide and hydrochloric acid are used in close proximity in the computer chip manufacture. The hydrochloric acid catalyzes an exothermic decomposition of hydrogen peroxide into oxygen and water. The accumulation of heat and non-condensable gas increases temperature and pressure in this reaction process always lead to runaway reaction and accident owing to inadvertent mixing. Thus, the chemical reaction hazard has to be clearly identified. Its critical runaway temperatures and unstable reaction criteria in this reaction process have to be determined urgently. In this investigation, we estimated its kinetic parameters at various volumetric ratios of the hydrogen peroxide to hydrochloric acid. Then, used these kinetic parameters to evaluate their critical temperatures and stable criteria in each reaction processes. The analytic results are important and useful for the design of safety system in the computer chip manufacture.

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**Keywords:** Hydrogen peroxide; Hydrochloric acid; Computer chip manufacture; Runaway reaction; Critical temperature; Stable criteria

## 1. Introduction

In chemical industries catastrophes, so many thermal runaway incidents were caused by the organic peroxides owing to the peroxy function group,  $-O-O-$ , which is essentially unstable and active. The peroxide group is sensitive to heat and incompatible with many materials such as acids, bases, metals, ions, etc. The hydrogen peroxide is used widely in chemical industry. Its thermal instability or reactive incompatibility has caused so many incidents in the past [1]. In computer chip manufacture, the hydrogen peroxide and hydrochloric acid are commonly used to wash computer chips in process. Since these two chemicals are present in close proximity, a situation of inadvertent mixing is not only possible, but also likely. Inadvertent mixing of these chemicals had been documented in over 12 instances, which has been mentioned on a previous literature [2]. Finally, the hydrochloric acid catalyzes an exothermic decomposition of hydrogen peroxide. This violent reaction always leads to runaway reaction and hazardous situation. Unfortunately, its critical

runaway temperatures and unstable criteria of reaction are still unknown so far.

The runaway reaction systems can be classified as tempered and non-tempered systems [3,4]. A tempered system is one in which the reaction heat can be removed by latent heat of vaporization. Either the reactant or the solvent can provide the latent heat. For this reason these systems essentially possess high vapor pressure even the ambient temperature is not very high. Note that a tempered reaction can accommodate a gassy reaction as long as the reaction temperature can be controlled. On the other hand, non-tempered system exhibits minor latent heat of cooling, which is a typical low vapor pressure system. The heat release is largely retained in the reaction system that can lead to peak temperature rise rate. Most of the publications on runaway reactions had dealt with the tempered and vapor systems only [5–9]. Leung have developed emergency venting requirements of a runaway reaction system with gas generation using an aqueous hydrogen peroxide decomposition example [10]. We have previously evaluated the critical condition and stability criterion in decomposition reaction of hydrogen peroxide with its initial concentrations as 7.5, 15 and 30 wt.%, respectively [11]. In this paper, we found that the decomposition reaction of hydrogen peroxide with low concentration is a tempered hybrid system,

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### Nomenclature

$A$	pre-exponential factor of Arrhenius's equation ( $\text{min}^{-1}$ )
$C$	concentration of hydrogen peroxide (mol/l)
$C_P$	heat capacity (J/g K)
$C_0$	initial concentration of hydrogen peroxide (mol/l)
$E$	activation energy (kJ/mol)
$h$	overall heat transfer coefficient of ambient cooling medium ( $\text{kJ}/\text{min m}^2 \text{K}$ )
$hS_{(\text{tr})}$	value of $hS$ at transition point ( $\text{kJ}/\text{min K}$ )
$\Delta H$	the measured exothermic heats of hydrogen peroxide reaction (J/g)
$\Delta H_t$	the transient released heat of reaction at reaction time $t$ (J)
$\Delta H_{\text{total}}$	the overall released heat (J)
$k$	reaction rate constant ( $\text{M}^{1-n} \text{min}^{-1}$ )
$n$	reaction order
$q$	molar exothermic heat of hydrogen peroxide (kJ/mol)
$Q_g$	heat generation rate (kJ/min)
$Q_r$	heat removal rate by cooling medium (kJ/min)
$-r_b$	chemical reaction rate (mol/l min)
$R$	universal constant (J/g mol K)
$S$	external surface area of reactor ( $\text{m}^2$ )
$t$	reaction time (min)
$T$	temperature of reactant (K)
$T_a$	ambient temperature at cooling medium (K)
$T_{a,\text{tr}}$	ambient temperatures at the transition point (K)
$T_C$	critical ignition or extinction temperature (K)
$T_{C,E}$	critical extinction temperature (K)
$T_{C,I}$	critical ignition temperature (K)
$T_{C,\text{tr}}$	transition point of critical ignition and extinction temperatures (K)
$T_{\text{max}}$	final temperature of hydrogen peroxide reaction (K)
$\Delta T_{\text{max}}$	the temperature difference between $T_0$ and $T_{\text{max}}$ (K)
$T_M$	intermediate temperature of intersection point of curves $Q_g$ and $Q_r$ (K)
$T_S$	temperature at the steady state is the intersection point of curves $Q_g$ and $Q_r$ (K)
$T_{S,E}$	final stable point of extinction temperature (K)
$T_{S,H}$	high stable temperature at steady state (K)
$T_{S,I}$	final stable point of ignition temperature (K)
$T_{S,L}$	low stable temperature at steady state (K)
$T_0$	initial heating temperature of hydrogen peroxide reaction (K)
$V$	volume of reactant ( $\text{m}^3$ )
$V_{\text{HCl}}$	volume of hydrochloric acid (ml)
$V_{\text{H}_2\text{O}_2}$	volume of hydrogen peroxide (ml)
$x_A$	fractional conversion of hydrogen peroxide
<i>Greek letter</i>	
$\rho$	density of reactant ( $\text{g}/\text{cm}^3$ )

but it is a non-tempered hybrid system in high concentration hydrogen peroxide.

The batch reactor is a dynamic system whose trajectory depends on various parameters. Parametric sensitivity signifies large changes in the reactor trajectory induced by small changes in parameters across threshold values. This is a form of critical behavior and can lead to runaway conditions, resulting in unsafe reactor operation. Most investigations of parametric sensitivity have been theoretical or based on numerical simulations. Semenov's classical theory of thermal explosions is concerned with evaluating the critical temperature above which the temperature rise in the reactor is very fast [12]. He analyzed the zeroth-order reaction. This approximation is applicable for reactions going to low conversion or reactions occurring slowly where the change in concentration can be neglected over the progress of the reaction or when the reactants are present in excess. Morbidelli and Varma have determined a generalized criterion for parametric sensitivity for batch and tubular reactors [13,14]. They determined the variation in the maximum temperature of the non-adiabatic reactor with respect to different parameters. Eigenberger and Schuler have discussed the concepts of stability and safety in the context of batch and continuous systems [15]. Villiermaux and Georgakis discuss runaway criteria in terms of time constants for reactions and cooling [16]. Most of the works on parametric sensitivity performed has been of a theoretical nature. However, the various criteria existing in the literatures have been seldom verified.

In this investigation, the kinetic parameters of decomposition reaction of hydrogen peroxide in the presence of hydrochloric acid as catalyst can be measured and estimated from reactive system screening tool (RSST) apparatus. The evaluations of kinetic parameters were incorporated with Semenov's sufficient and necessary conditions of thermal explosion to determine the critical runaway reaction temperatures and stable criteria [7–19]. The requirements of heat transfer coefficient in the critical conditions can also be estimated. Then, these stable criteria and critical temperatures can be expressed as function of kinetic parameters and chemical properties.

## 2. The kinetic parameters of decomposition reaction of hydrogen peroxide with the hydrochloric acid as catalyst

### 2.1. Experimental

The decomposition reaction of hydrogen peroxide using the hydrochloric acid as catalyst is expressed as



The experimental chemicals of hydrogen peroxide with 30 wt.% concentration and hydrochloric acid with 37 wt.% concentration from Merck Co. were used without further purification. Their densities were 1.11 and 1.2 kg/l, respectively. The thermo-kinetic parameters were measured and estimated using RSST adiabatic calorimeter. The RSST (Fauske & Associates Inc.) is a commercial version of the Design Institute for Emer-

gency Relief Systems (DIERS) in bench-scale apparatus, which was designed to operate under almost true adiabatic conditions. The RSST can be used to characterize a runaway chemical reaction, which includes a single heater element is controlled by feedback from the sample temperature measurement to allow enough heater power to overcome heat losses.

A series of measurements were made using the volumetric ratios 15:1, 7:1 and 13:3 of hydrogen peroxide to hydrochloric acid with a total sample volume of 8 ml, respectively. Reagents were added with the sample container positioned inside the calorimeter and adiabatic conditions were established from ambient temperature using the ‘heat-wait-search’ mode of operation. The experimental information obtained from RSST includes the transient temperature profile, the transient pressure profile, the transient temperature variation profile, the transient pressure variation profile, etc.

## 2.2. Analysis of the experimental results

RSST is a reaction calorimeter system, which is capable of measuring reaction temperature and pressure variation for very fast exothermic reaction systems in adiabatic condition. Figs. 1 and 2 show the transient temperature and pressure profiles of hydrogen peroxide decomposition reaction in the presence of hydrochloric acid catalyst at volumetric ratios 15:1 and 13:3 of hydrogen peroxide to hydrochloric acid, respectively. The maximal temperatures  $T_{\max}$  and pressures  $P_{\max}$  corresponding to these three volumetric ratios are equal to 194.2, 185.0, 179.5 °C and 5.17, 4.55, 4.13 bar, respectively. The values of  $T_{\max}$  are higher than the boiling point temperature of water. The temperature of reaction cannot be tempered by vapor stripping. Therefore, the released heat is largely retained in the reaction system that leads to abrupt temperature rising. Furthermore, the pressure of reaction system contributed from the non-condensable gas and vapor pressure. Therefore, the catalytic decomposition of high concentration hydrogen peroxide by hydrochloric acid is a typical non-tempered hybrid system.

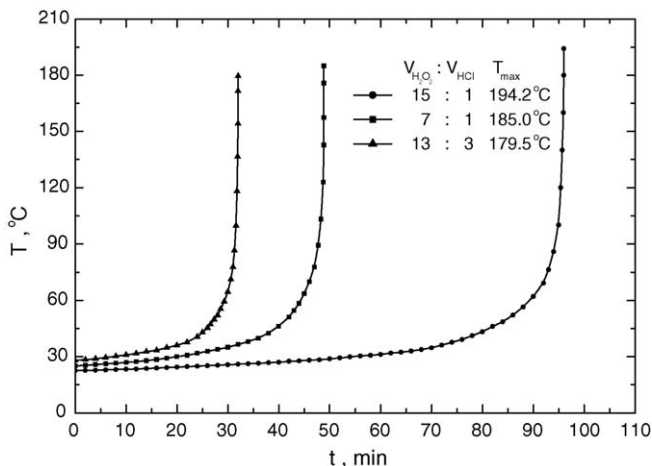


Fig. 1. Measured transient temperature of the catalytic decomposition reaction of hydrogen peroxide at various volumetric ratios by means of RSST.

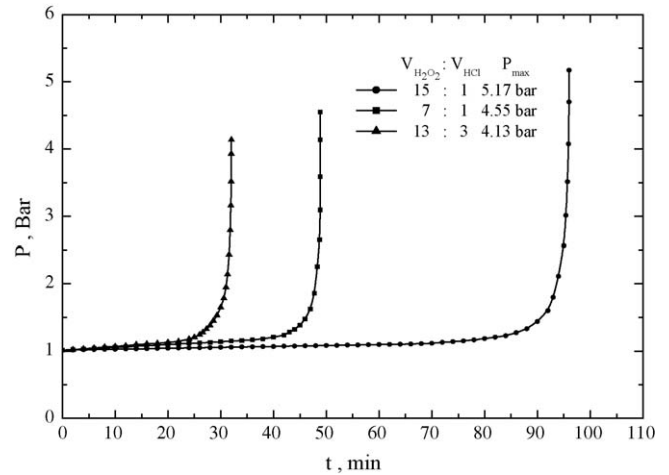


Fig. 2. Measured transient pressure of the catalytic decomposition reaction of hydrogen peroxide at various volumetric ratios by means of RSST.

## 2.3. Evaluation of the kinetic parameters

In an adiabatic reaction system, the fractional conversion  $X_A$  and reaction temperature  $T$  at any reaction time  $t$  can be correlated by the ratio value of transient heat release  $\Delta H_t$  at any reaction time  $t$  to the overall heat release  $\Delta H_{\text{total}}$  as

$$X_A = \frac{\Delta H_t}{\Delta H_{\text{total}}} = \frac{mC_p(T - T_0)}{mC_p(T_{\max} - T_0)} = \frac{T - T_0}{T_{\max} - T_0} \quad (2)$$

where  $T_0$  and  $T_{\max}$  are the initial and final temperatures in the catalytic decomposition reaction of hydrogen peroxide, respectively. The reaction concentration in an adiabatic reactor therefore can be correlated as

$$C = C_0(1 - X_A) = C_0 \frac{T_{\max} - T}{T_{\max} - T_0} = C_0 \frac{T_{\max} - T}{\Delta T_{\max}} \quad (3)$$

where  $C_0$  is the initial concentration of hydrogen peroxide and  $\Delta T_{\max}$  is equal to  $T_{\max} - T_0$ . An  $n$ th-order rate equation of hydrogen peroxide decomposition is expressed as

$$-r_b = -\frac{dC}{dt} = kC^n \quad (4)$$

Substituting Eq. (3) into Eq. (4) and combining with the Arrhenius's equation yields

$$k^* = C_0^{n-1} A \exp\left(-\frac{E}{RT}\right) = \frac{dT/dt}{[(T_{\max} - T)/\Delta T_{\max}]^n \Delta T_{\max}} \quad (5)$$

Taking natural logarithms on both sides of Eq. (5) we obtain

$$\begin{aligned} \ln k^* &= \ln\left(\frac{dT/dt}{[(T_{\max} - T)/\Delta T_{\max}]^n \Delta T_{\max}}\right) \\ &= \ln(C_0^{n-1} A) - \frac{E}{RT} \end{aligned} \quad (6)$$

where  $dT/dt$  is the temperature increasing rate between the initial temperature  $T_0$  and the maximum temperature  $T_{\max}$  in an adiabatic reaction system. We can determine the kinetic parameters  $E$  and  $A$  from Eq. (6).

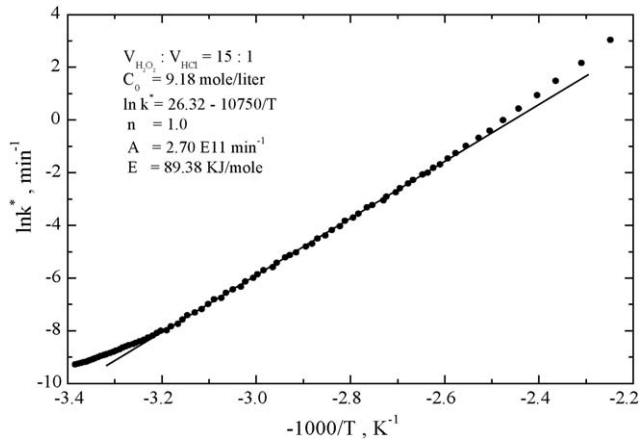


Fig. 3. The correlation of overall rate constant  $k^*$  and temperature  $T$  for the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=15:1$ .

Substituting the experimental data which are measured from RSST into Eq. (6) and assuming that  $n = 1$ , we can plot  $\ln k$  versus  $-1000/T$  and obtain a fairly good linear correlations as shown in Figs. 3–5. Therefore, the assumption of  $n = 1$  for reaction order is reasonable. The activation energy  $E$  and pre-frequency  $A$  can be obtained from the values of slope and intersection point at the vertical axis. These measured and evaluated kinetic parameters of catalytic decomposition reaction of hydrogen peroxide are listed in Table 1.

### 3. The stable criteria and critical runaway temperatures for the catalytic decomposition reaction of hydrogen peroxide in a non-isothermal reaction system

Semenov [12] assumed a uniform temperature distribution within a reaction system. This assumption is very close to the case of a homogeneous system in a stirred tank reactor. The general formula of heat generation rate owing to the reaction in a control volume  $V$  is expressed as

$$Q_g = qV(-r_b) \quad (7)$$

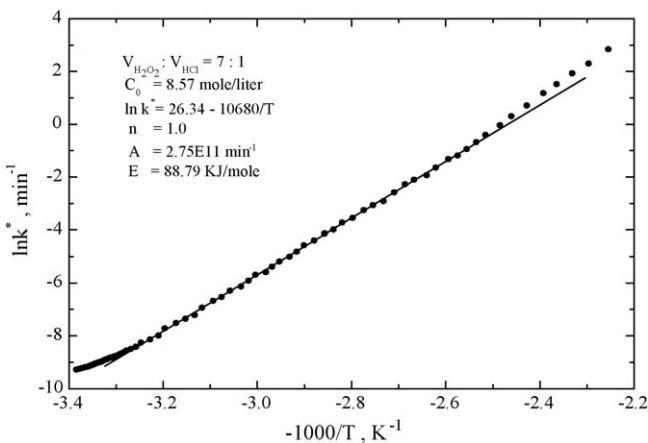


Fig. 4. The correlation of overall rate constant  $k^*$  and temperature  $T$  for the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=7:1$ .

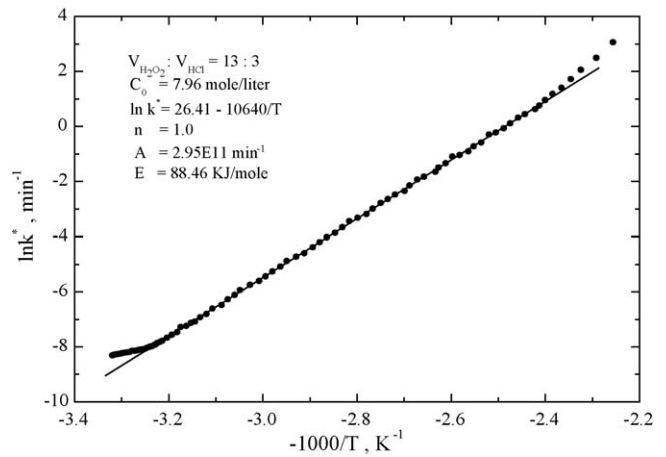


Fig. 5. The correlation of overall rate constant  $k^*$  and temperature  $T$  for the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=13:3$ .

where  $q$  is the molar exothermic heat of reaction. The heat removal rate from the reactor to the ambient cooling medium is expressed as

$$Q_r = hS(T - T_a) \quad (8)$$

where  $h$  is the heat transfer coefficient of the cooling medium and  $S$  is the external surface area of the reactor. The  $T$  and  $T_a$  are the temperatures in the reactor and ambient cooling medium, respectively. Expressing the reaction rate in Arrhenius's form and substituting Eq. (4) into Eq. (7), hence the heat generation rate can be expressed as

$$Q_g = qVAC^n e^{-E/RT} \quad (9)$$

The overall energy balance in the control volume is that the heat accumulation rate is equal to the heat generation rate subtracts the heat removal rate, which is

$$\rho VC_P \frac{dT}{dt} = Q_g - Q_r \quad (10)$$

combining Eqs. (8)–(10) to express this overall energy balance as

$$\rho VC_P \frac{dT}{dt} = qVAC^n e^{-E/RT} - hS(T - T_a) \quad (11)$$

Table 1

The kinetic parameters of the hydrogen peroxide catalytic decomposition reaction

Items	Values
$V_{H_2O_2}:V_{HCl}$	15:1, 7:1, 13:3
$C_0$ (mol/l)	9.18, 8.57, 7.96
$T_0$ ( $^{\circ}C$ )	22.50, 25.00, 28.00
$T_{max}$ ( $^{\circ}C$ )	194.22, 185.01, 179.50
$\Delta T_{max}$ (K)	171.72, 160.01, 151.50
$(dT/dt)_{max}$ (K/min)	1842, 1311, 667
$q$ (kJ/mol)	98.05, 98.05, 98.05
$C_P$ (J/g K)	3.922, 3.894, 3.867
$n$	1.0, 1.0, 1.0
$A$ ( $min^{-1}$ )	$2.70 \times 10^{11}$ , $2.75 \times 10^{11}$ , $2.95 \times 10^{11}$
$E$ (kJ/mol)	89.38, 88.79, 88.46

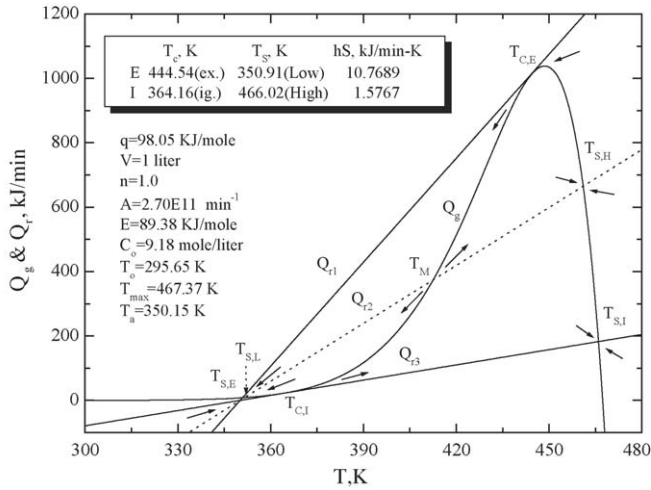


Fig. 6. The balance of generation heat  $Q_g$  and removal heat  $Q_r$  in the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=15:1$ .

We have assumed that the reaction order  $n$  is equal to unity. Thus, substituting Eq. (3) into Eq. (11) with  $n = 1$ , we can rewrite this equation as

$$\rho V C_P \frac{dT}{dt} = q V A C_0 \left( \frac{T_{max} - T}{T_{max} - T_0} \right) e^{-E/RT} - hS(T - T_a) \quad (12)$$

At steady state, i.e.  $(dT/dt)=0$ , the Semenov's sufficient and necessary conditions for critical runaway reaction in a control volume are

$$Q_g|_{T=T_C} = Q_r|_{T=T_C} \quad (13)$$

and

$$\left. \frac{dQ_g}{dT} \right|_{T=T_C} = \left. \frac{dQ_r}{dT} \right|_{T=T_C} \quad (14)$$

Eq. (13) also represents the heat generation rate of the system is equal to the heat removal rate. If the value of  $Q_g$  is greater than the value of  $Q_r$ , then  $(dT/dt) > 0$ . Finally, this heat accumulation should lead to runaway of the system. From Eq. (13), we can obtain

$$q V A C_0 \left( \frac{T_{max} - T_C}{T_{max} - T_0} \right) e^{-E/RT_C} = hS(T_C - T_a) \quad (15)$$

From Eq. (14) we can obtain

$$\frac{q V A C_0}{T_{max} - T_0} e^{-E/RT_C} \left( -1 + (T_{max} - T_C) \frac{E}{RT_C^2} \right) = hS \quad (16)$$

After Eq. (16) divided by Eq. (15) and rearranging, we can obtain the critical runaway temperature in this reaction system as the

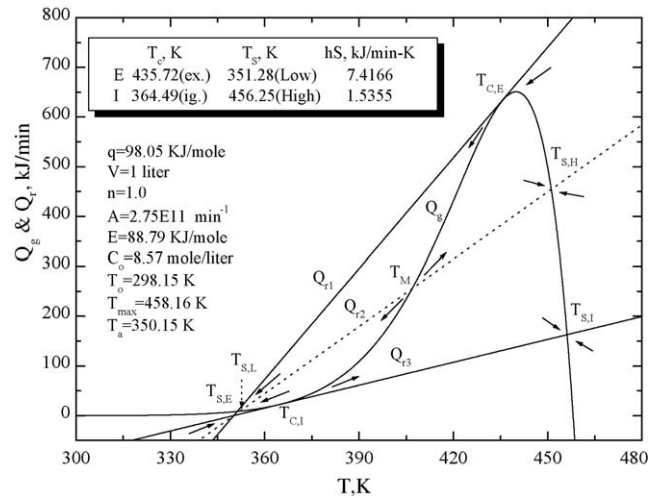


Fig. 7. The balance of generation heat  $Q_g$  and removal heat  $Q_r$  in the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=7:1$ .

following equation:

$$\frac{E}{RT_C^2} = \frac{1}{T_C - T_a} + \frac{1}{T_{max} - T_C} \quad (17)$$

Solving this quadratic equation for  $T_C$ , we can express the critical runaway temperature as

$$T_C = \frac{(T_{max} + T_a) \pm \sqrt{(T_{max} + T_a)^2 - 4[1 + R(T_{max} - T_a)/E]T_{max}T_a}}{2[1 + R(T_{max} - T_a)/E]} \quad (18)$$

Eq. (18) expresses the critical runaway temperature as a function of the activation energy ( $E$ ), the temperature of the cooling medium ( $T_a$ ) and final temperature of the reaction system ( $T_{max}$ ). This equation is a quadratic form of  $T_C$ . There are three typical heat balances between the generation rate and removal rate versus reaction temperature in the catalytic decomposition reaction of hydrogen peroxide, which are calculated using Eqs. (8) and (9) with volumetric ratios 15:1, 7:1 and 13:3 of hydrogen peroxide to hydrochloric acid shown in Figs. 6–8, respectively. The reaction rates are affected by the initial concentrations of hydrogen peroxide in these figures. The trajectory of the curve  $Q_g$  is not same as locus of the curve  $Q_r$  as a straight line owing to the exponential term. The ambient temperature  $T_a$  is set as 350.15 K in these three plots of heat balance. We found that there are two tangent points at  $T_{C,E}$  and  $T_{C,I}$ , two intersection points at  $T_{S,E}$  and  $T_{S,I}$  between the curves  $Q_g$ ,  $Q_{r1}$  and  $Q_{r3}$ . In Fig. 6, two tangent points  $T_{C,E}=444.54$  K and  $T_{C,I}=364.16$  K can be calculated from Eq. (18) denote the critical extinction and ignition temperatures, respectively. Substituting these two values of critical temperature into Eq. (16) to evaluate the values of  $hS$  which is the heat transfer coefficient multiplied by the external surface of the reactor. The calculated values of  $hS$  are equal to 10.7689 and 1.5767 kJ/min K at critical temperatures  $T_{C,E}$  and  $T_{C,I}$ , respectively. By substituting the above values of  $hS$  into Eq. (15) and calculating by iterating we can obtain other roots of temperature  $T_C$ , which are denoted as  $T_{S,E}$  and  $T_{S,I}$ . These calculated values



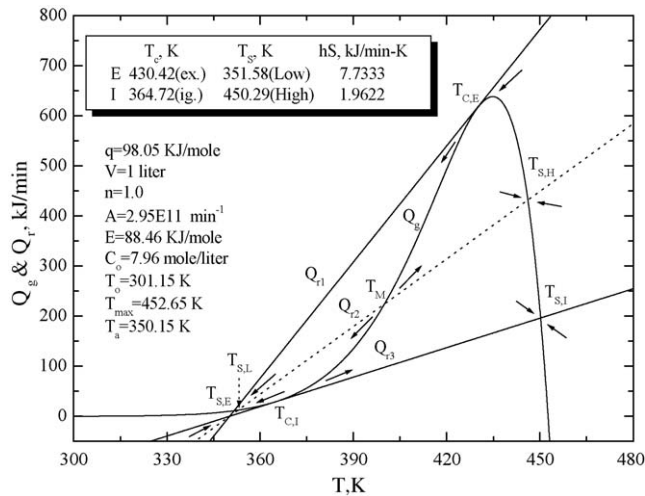


Fig. 8. The balance of generation heat  $Q_g$  and removal heat  $Q_r$  in the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=13:3$ .

of  $T_{S,E}$  and  $T_{S,I}$  are not tangent points but the intersection points between the curves  $Q_g$ ,  $Q_{r1}$  and  $Q_{r3}$ . The values of  $T_{S,E}$  and  $T_{S,I}$  can also be obtained directly by a graphical method from Figs. 6–8 at various values of  $hS$ , respectively. Consequently, we found that the value of  $T_{S,I}$  is equal to 466.02 K and the value of  $T_{S,E}$  is equal to 350.91 K as in Fig. 6. In this figure, when  $hS=10.7689$  kJ/min K and the temperature of reaction system is greater than 444.54 K, i.e.  $T > T_{C,E}$ , then the heat removal rate  $Q_{r1}$  is greater than the heat generation rate  $Q_g$ . Therefore, the temperature of the reaction system decreases continually and moves toward the temperature of the point  $T_{C,E}$ . Finally, it terminates at this point. When the temperatures of the reaction system are in the ranges of  $T_{S,E} < T < T_{C,E}$ , similarly the heat removal rate  $Q_{r1}$  is again greater than the heat generation rate  $Q_g$  and leads to the temperature of the reaction system decreasing and finally moves toward the temperature of the point  $T_{S,E}$ . Once the temperature of the reaction system is lower than the temperature of the point  $T_{S,E}$ , i.e.  $T < T_{S,E}$ , the heat removal rate  $Q_{r1}$  now is smaller than the heat generation rate  $Q_g$ . Thus the temperature of the reaction system increases and finally goes back to the temperature of the point  $T_{S,E}$ . The points  $T_{C,E}$  and  $T_{S,E}$  are called the critical extinction temperature and the final stable extinction temperature, respectively. These two points also stand for the temperature that never goes up and the temperature that never

drops down at  $hS=10.7689$  kJ/min K, respectively. Other calculated results using Eqs. (16) and (17) obtain the values of  $T_{C,I}$  and  $hS$  equal to 364.16 K and 1.5767 kJ/min K, respectively. The intersection point  $T_{S,I}$  of curves  $Q_g$  and  $Q_{r3}$  for this calculation is equal to 466.02 K. When the temperatures of the reaction system are lower than 364.16 K, i.e.  $T < T_{C,I}$ , then the heat removal rate  $Q_{r3}$  is smaller than heat generation rate  $Q_g$ . Therefore, the temperature of the reaction system increases and moves towards the temperature of the point  $T_{C,I}$ . When the temperatures of the reaction system are in the ranges of  $T_{C,I} < T < T_{S,I}$ , the heat removal rate  $Q_{r3}$  is again smaller than the heat generation rate  $Q_g$ . This situation leads to the temperature of the reaction system increasing and moves from the point  $T_{C,I}$  to the point  $T_{S,I}$  and finally stops at this point. Once the temperature inside the reactor is higher than the temperature of the point  $T_{S,I}$ , i.e.  $T > T_{S,I}$ , the heat removal rate  $Q_{r3}$  now is larger than the heat generation rate  $Q_g$  which leads to the temperature of the reaction system decreasing and returning to the temperature of the point  $T_{S,I}$ . The points  $T_{C,I}$  and  $T_{S,I}$  are called the critical ignition temperature and the final stable ignition temperature, respectively. Thus, at the condition of  $hS=1.5767$  kJ/min K, these two points also stand for the temperature of no return and the temperature that never drops down, respectively. When the values of  $hS$  are in the ranges of  $1.5767$  kJ/min K  $< hS < 10.7689$  kJ/min K, we can obtain three intersection points between the curves  $Q_{r2}$  and  $Q_g$ . These three points are denoted as  $T_{S,L}$ ,  $T_M$  and  $T_{S,H}$  which represent the steady state at low, intermediate and high temperatures, respectively. The curve  $Q_{r2}$  is expressed as a dashed line. As in the previous analysis, it is difficult to reach the intermediate point  $T_M$  owing to this point being unstable. Suppose it is possible to start this reaction system exactly at the temperature of the point  $T_M$ ; then if some slight upset in the operating conditions is to take it away from this steady state, it will not go back to it but will finish up either at the low or high temperature at steady state points  $T_{S,L}$  or  $T_{S,H}$ , respectively. Hence a slight increase of temperature produces a net heat generation, which will tend to drive the temperature even higher. Conversely, a slight drop of temperature induces a net heat removal, which will cause the temperature to fall even more. In this sense, we say that the intermediate steady state temperature of the point  $T_M$  is unstable. By contrast, these state temperatures of the points  $T_{S,L}$  and  $T_{S,H}$  are stable and if the state is perturbed away from one of them it will return there naturally. In Figs. 7 and 8, we have different operating conditions in this reaction system. The values of  $hS$ ,  $T_{C,I}$ ,  $T_{C,E}$ ,  $T_{S,I}$  and  $T_{S,E}$  are listed in Table 2.

Table 2

The stable temperatures and values of  $hS$  at the critical conditions for various volumetric ratios of hydrogen peroxide to hydrochloric acid

$V_{H_2O_2}:V_{HCl}$	$T_a$ (K)	$hS$ (kJ/min K)	$T_{C,I}$ (K)	$T_{C,E}$ (K)	$T_{S,I}$ (K)	$T_{S,E}$ (K)
15:1	350.15	10.7689	364.16	444.54	466.02	350.91
		1.5767				
7:1	350.15	7.4166	364.49	435.72	456.25	351.28
		1.5355				
		7.7333				
13:3	350.15	7.7333	364.72	430.42	450.29	351.58
		1.9622				

To obtain the stable and unstable criteria in the reaction system, the heat generation and removal diagram does not allow us to conclude stability when

$$\frac{dQ_g}{dT} < \frac{dQ_r}{dT} \quad (19)$$

This equation is only a *necessary*, but *not sufficient* condition for *stability*. However, it does allow us to say the state will be *unstable* when

$$\frac{dQ_r}{dT} < \frac{dQ_g}{dT} \quad (20)$$

If we define  $T_S$  as a stable temperature in a reactor at the state of  $Q_g = Q_r$  and a small temperature perturbation as  $\delta T = T - T_S$  at this state, the reaction system is *stable* under the following conditions:

$$\text{If } \delta T \begin{cases} > 0, & Q_g < Q_r \\ < 0, & Q_g > Q_r \end{cases} \quad (21)$$

Eq. (21) is the *sufficient* and *necessary* conditions for a stable reaction system. These criteria of stability had been analyzed by Luo et al. [17–19].

From the above definitions and energy–mass balance equations, the stable and unstable criteria in this catalytic decomposition reaction of hydrogen peroxide can be determined. Let us choose an arbitrary value of temperature as 350.15 K for the ambient temperature  $T_a$  in Figs. 6–8. These three figures reveal the equilibrium of the heat generation rate  $Q_g$  and the heat removal rate  $Q_r$  versus the temperature of the reaction system. When the values of temperature  $T$  in the reaction system at steady state are greater than the value of the temperature  $T_{C,E}$ , i.e.  $T > T_{C,E}$ , its temperature perturbations satisfy the conditions of Eq. (21). Therefore, the system is stable in this area.

If the temperatures of the reaction system at steady state are in the ranges of  $T_{C,I} < T < T_{C,E}$ , this means that  $T = T_S = T_M$  and heat transfer coefficients are in the ranges of  $1.5767 \text{ kJ/min K} < hS < 10.7689$ ,  $1.5355 \text{ kJ/min K} < hS < 7.4166$  and  $1.9622 < hS < 7.7333 \text{ kJ/min K}$  as in Figs. 6–8, respectively. The energy balance and reaction temperatures satisfy the condition of Eq. (20) but violate the conditions of Eq. (21) in this area. Thus, the reaction temperature is unstable in this area.

If the temperatures  $T$  of the reaction system at steady state are less than the temperature of the point  $T_{C,I}$ , i.e.  $T < T_{C,I}$ , its reaction temperatures satisfy the conditions of Eq. (21) again. Accordingly, this system is stable in this area.

Figs. 9–11 show the temperature variations of the points  $T_{C,I}$ ,  $T_{C,E}$ ,  $T_{S,I}$  and  $T_{S,E}$  along the increasing temperature  $T_a$  with volumetric ratios 15:1, 7:1 and 13:3 of hydrogen peroxide to hydrochloric acid, respectively. The magnitudes of these temperatures are in the order of  $T_{S,I} > T_{C,E} > T_{C,I} > T_{S,E}$ . Both the temperatures of the points  $T_{S,I}$  and  $T_{C,E}$  decrease and both the temperatures of the points  $T_{C,I}$  and  $T_{S,E}$  increase gradually with temperature  $T_a$  increase. As soon as the ambient temperature  $T_a$  increases to the temperature of the transition point  $T_{a,tr}$ , all of these four curves of temperature coinciding in one point,  $T_{C,tr}$ . We can determine the temperature at this transition point from

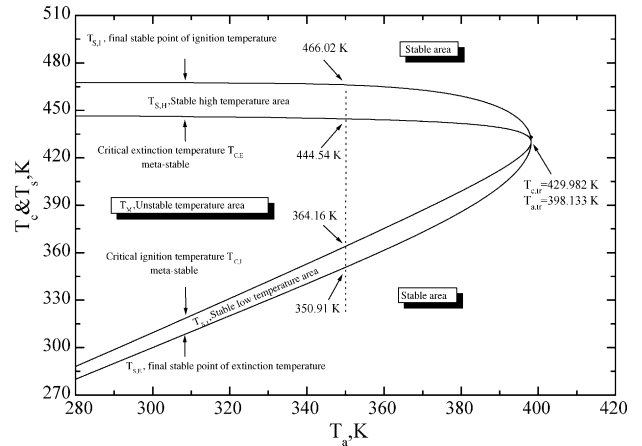


Fig. 9. Critical ignition, extinction, high and low stable temperature curves and transition temperature at various ambient temperatures for the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=15:1$ .

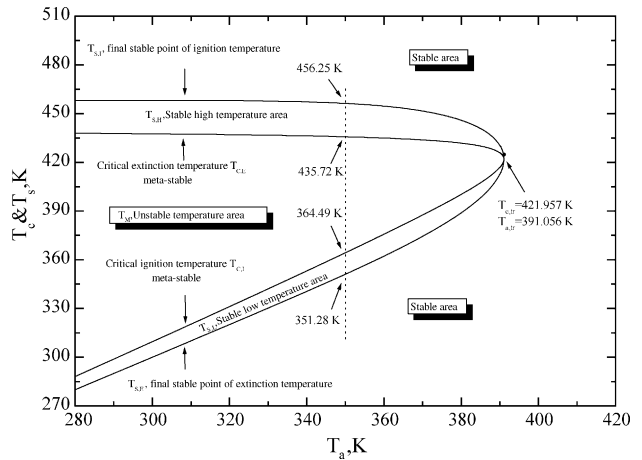


Fig. 10. Critical ignition, extinction, high and low stable temperature curves and transition temperature at various ambient temperatures for the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=7:1$ .

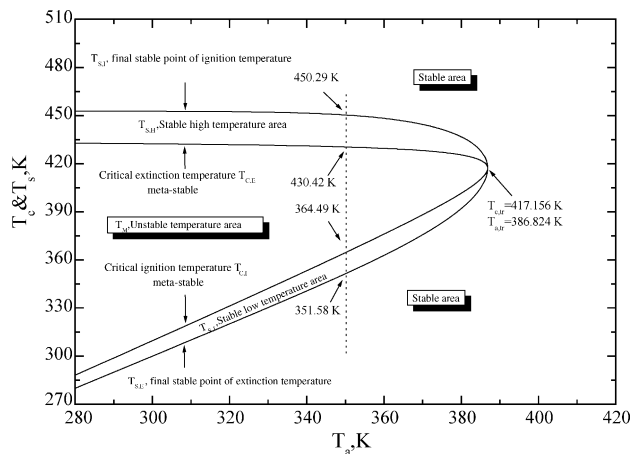


Fig. 11. Critical ignition, extinction, high and low stable temperature curves and transition temperature at various ambient temperatures for the catalytic decomposition reaction of hydrogen peroxide at volumetric ratio  $V_{H_2O_2}:V_{HCl}=13:3$ .

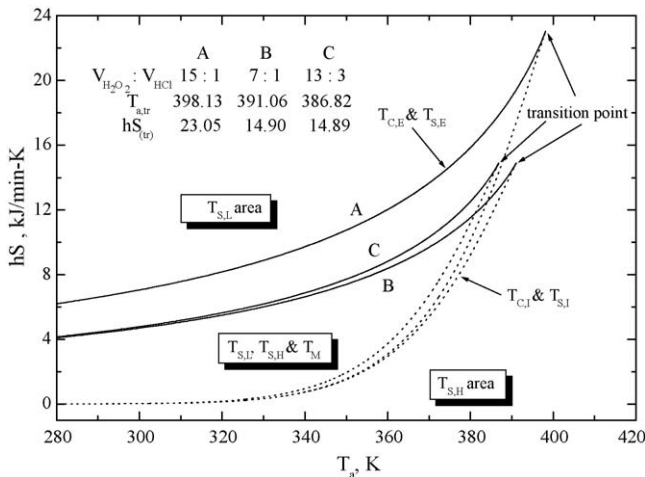


Fig. 12. Dependence of  $hS$  on  $T_a$  at critical runaway temperature of the catalytic decomposition reaction of hydrogen peroxide at various volumetric ratios.

the following equations:

$$T_{a,tr} = \frac{ET_{max}}{E + 4RT_{max}} \quad (22)$$

and

$$T_{C,tr} = \frac{ET_{max}}{E + 2RT_{max}} \quad (23)$$

The values of  $T_{a,tr}$  are equal to 398.133, 391.056 and 386.824 K in Figs. 9–11, respectively. The values of  $T_{C,tr}$  corresponding to the values of  $T_{a,tr}$  are equal to 429.982, 421.957 and 417.156 K, respectively. The reaction temperatures are unstable when they are enclosed by the curves  $T_{C,E}$  and  $T_{C,I}$ . Beyond this area, the temperatures are stable at the steady state of  $Q_g = Q_r$ .

The required values of  $hS$  at critical runaway conditions and stable temperatures can be evaluated by using either Eq. (15) or (16) after the value of  $T_C$  is determined from Eq. (18). The calculated results of  $T_a$  versus  $hS$  at the critical runaway conditions and stable temperatures for the catalytic decomposition reaction of hydrogen peroxide at volumetric ratios 15:1, 7:1 and 13:3 of hydrogen peroxide to hydrochloric acid are shown in Fig. 12. The solid curves of  $hS$  contain the critical extinction temperature  $T_{C,E}$  and final stable extinction temperature  $T_{S,E}$ . While the dash curves of  $hS$  contain the critical ignition temperature  $T_{C,I}$  and final stable ignition temperature  $T_{S,I}$ . The area between these two curves of  $hS$  presents a bullhorn shape, which contains one unstable temperature  $T_M$  and two stable temperatures  $T_{S,L}$  and  $T_{S,H}$ . When the temperatures of  $T_{C,E}$ ,  $T_{S,E}$ ,  $T_{C,I}$  and  $T_{S,I}$  are equal, these two curves of  $hS$  coincide to one transition point that is expressed as  $hS_{(tr)}$ . These values of  $hS_{(tr)}$  are equal to 23.05, 14.90 and 14.89 kJ/min K with volumetric ratios 15:1, 7:1 and 13:3 of hydrogen peroxide to hydrochloric acid, respectively. We can also evaluate the values of  $hS_{(tr)}$  from Eq. (24), which is the combination of Eqs. (16), (22) and (23) simultaneously as follows:

$$hS_{(tr)} = \frac{qVAC_0}{T_{max} - T_0} \exp \left[ - \left( 2 + \frac{E}{RT_{max}} \right) \right] \left( 1 + \frac{4RT_{max}}{E} \right) \quad (24)$$

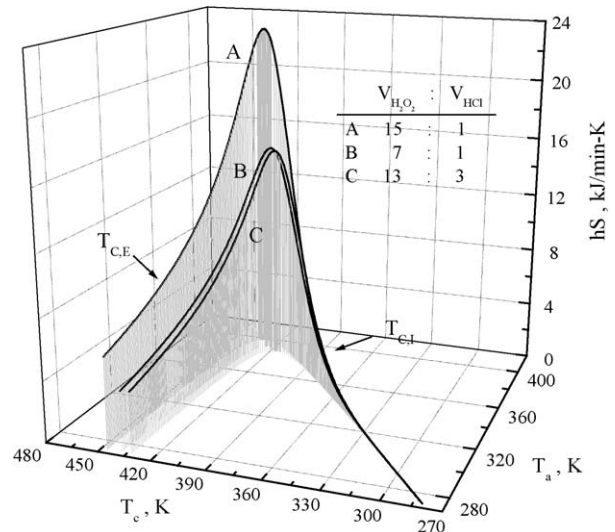


Fig. 13. Relationships  $T_a$ - $T_C$ - $hS$  of the catalytic decomposition reaction of hydrogen peroxide at various volumetric ratios.

The values of  $hS$  above the bullhorn shape region, which contains all of the temperatures that are lower than the temperature  $T_{S,E}$ . The values of  $hS$  below the bullhorn shape region, which contains all of the temperatures that are higher than the temperature  $T_{S,I}$ . Therefore, the values of  $hS$  are stable outside of the bullhorn shape area.

From the above calculations, we correlate the relationships among the variations of  $hS$ ,  $T_a$ ,  $T_C$  and  $T_S$  in the catalytic decomposition reaction of hydrogen peroxide. Fig. 13 reveals the values of  $hS$ , which are affected by the variations of  $T_a$  and  $T_C$  at various volumetric ratios of hydrogen peroxide to hydrochloric acid, respectively. The maximal value of  $hS$  is the transition point that is denoted as  $hS_{(tr)}$ . This transition point is a watershed of temperature. When  $T_C > T_{C,tr}$ , then the value of  $T_C$  is equal to the value of  $T_{C,E}$ . If  $T_C < T_{C,tr}$ , then the value of  $T_C$  is equal to the value of  $T_{C,I}$ . When the value of  $T_a$  is decreased and either the value

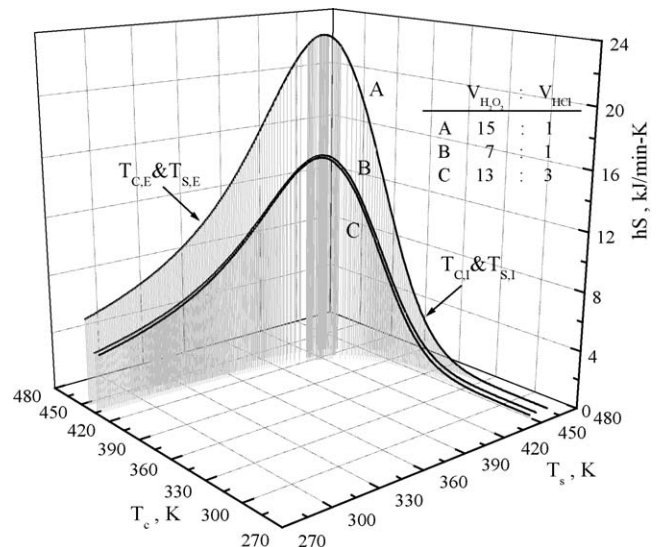


Fig. 14. Relationships  $T_S$ - $T_C$ - $hS$  of the catalytic decomposition reaction of hydrogen peroxide at various volumetric ratios.



of  $T_{C,I}$  is decreased or the value of  $T_{C,E}$  is increased from the temperature of the transition point, the value of  $hS$  is decreased. The behavior of  $hS$  versus  $T_S$  and  $T_C$  at various volumetric ratios of hydrogen peroxide to hydrochloric acid is shown in Fig. 14. When  $T_S > T_{C,tr}$  then the value of  $T_S$  is equal to the value of  $T_{S,I}$ . If  $T_S < T_{C,tr}$ , then the value of  $T_S$  is equal to the value of  $T_{S,E}$ . Similarly, the reaction system requires a maximum value of  $hS$  at the transition point. When either the values of  $T_{S,E}$  and  $T_{C,I}$  are decreased or the values of  $T_{C,E}$  and  $T_{S,I}$  are increased from the temperature of the transition point, the value of  $hS$  is decreased.

#### 4. Conclusion

From the above calculations and analysis, we obtained the following conclusions in this investigation:

1. The catalytic decomposition reaction of high concentration hydrogen peroxide by hydrochloric acid is a non-tempered hybrid system.
2. The criteria of stability and runaway temperature with volumetric ratios 15:1, 7:1 and 13:3 of hydrogen peroxide to hydrochloric acid in the catalytic decomposition reaction of hydrogen peroxide can be evaluated from their kinetic parameters and ambient temperatures. The critical ignition and extinction temperatures can be calculated using Eq. (18). Their required values of  $hS$  are obtained from either Eq. (15) or (16).
3. A reaction system is stable if its reaction conditions satisfy Eq. (21). Conversely, one might say that a reaction system is unstable under the condition of  $\frac{dQ_r}{dT} < \frac{dQ_g}{dT}$ .
4. The unstable temperature area is enclosed by the curves  $T_{C,I}$  and  $T_{C,E}$  in the figures of the correlation of  $T_S$  and  $T_C$  versus  $T_a$ . A reaction system is stable outside this unstable area.
5. The magnitude of temperatures is in the order of  $T_{S,I} > T_{C,E} > T_{C,tr} > T_{C,I} > T_{S,E}$  at steady state. A reaction system requires a maximum value of  $hS$  when its stable temperature is at the transition point.

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