Critical Temperatures for the Thermal Explosion of Chemicals

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Preface

Knowledge regarding the two characteristic temperatures, the $T_c$ and the SADT,* which are used to express the thermal instability of a chemical of the TD type and that of a chemical of the AC type,** having each an arbitrary shape and an arbitrary size, placed each in the atmosphere under isothermal conditions,*** respectively, is indispensable in temperature control to prevent such a chemical from exploding thermally.

In this connection, when charged in the open-cup cell, or confined in the closed cell, in accordance with the self-heating property of the chemical, and subjected to the adiabatic self-heating test started from a $T_s$, if 2 cm$^3$ of a chemical continues to self-heat over the $T_s$ at a rate depending on the value of $T_s$ in accordance with the Arrhenius equation, after its having been warmed up to the $T_s$, the self-heating behavior of the chemical is said to be of the TD type. In this sense, the oxidatively-heating behavior of 2 cm$^3$ of a gas-permeable oxidatively-heating substance, such as sawdust, coal dust or oil-soaked lagging, charged in the draft cell, into which an arbitrary oxidizing gas is supplied, and subjected to the adiabatic oxidatively-heating test started from a $T_s$, is also of the TD type. It is, therefore, possible to calculate the critical temperature for the spontaneous ignition or $T_c$ for a gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, in the same manner as applied to the calculation of the $T_c$ for a chemical of the TD type.

In order to determine the $T_c$ for a chemical of the TD type, including every gas-permeable oxidatively-heating substance, and the SADT for a chemical of the AC type, including every powdery chemical of the quasi-AC type, having each an arbitrary shape and an arbitrary size, placed each in the atmosphere under isothermal conditions, it has been required so far to follow, by experimental measurements, the whole self-heating process of the chemical up to the actual thermal explosion, or up to the actual spontaneous ignition. The actual explosion, or ignition, experiment, however, requires much effort, time, space and material and, therefore, is dangerous and expensive. Very few values of $T_c$ or SADT are thus available at present.

On the other hand, there have certainly been some cases so far, in each of which the value of $T_c$ for a chemical of the TD type was attempted to calculate

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* For the individual definitions of the $T_c$ and the SADT, refer to Notation.
** A classification of self-heating chemicals is introduced in Chapter 3.
*** The adjective, isothermal, or, non-adiabatic, is used to express such a state that the temperature of the atmosphere which surrounds a self-heating chemical is maintained at a definite value throughout the self-heating process of the chemical, with the result that the heat generated by the exothermic decomposition reaction of the chemical is allowed to transfer from the chemical to the atmosphere. The same is true of the oxidatively-heating process of a gas-permeable oxidatively-heating substance.
by substituting the physical quantities, such as $\lambda$, $c$, $\rho$, $U$ and $S$, and the chemical quantities, such as $E$, $A_0$ and $\Delta H$, all of which require to be measured separately by specific experimental methods, respectively, of the chemical into either of the two equations constituting the thermal explosion theory, i.e., the Semenov equation and the Frank-Kamenetskii or F-K equation.

Such calculations have, however, been haunted by the uncertainty of measured values, especially, of the chemical quantities, $E$, $A_0$ and $\Delta H$, which specify as a whole the rate of heat generation per unit volume per unit time in the early stages of the self-heating process of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, because these chemical quantities are very difficult to measure precisely by means of conventional experimental techniques. The values of $E$ and $A_0$ of a chemical may be determined by thermal analysis, or by measuring the rate of the exothermic decomposition reaction, of a small quantity of the chemical at temperatures far higher than room temperature, respectively. Such circumstances are, however, not necessarily the same as those which lead to the actual thermal explosion, or to the actual spontaneous ignition, of the chemical. That is, the experimental conditions of the forced external heating for the chemical followed by a rapid rate of increase in temperature of the chemical are clearly different from the actual conditions of the spontaneous heating of the chemical itself followed by a slow rate of increase in temperature of the chemical. Besides, although the value of $\Delta H$ of an ordinary substance in general is measured based on the complete combustion reaction, there is always a possibility that the value of $\Delta H$ which a chemical of the TD type, including every gas-permeable oxidatively-heating substance, generates in the early stages of the self-heating process, or of the oxidatively-heating process, is that of an incomplete exothermic decomposition reaction, or of an incomplete oxidative decomposition reaction, accompanied with the formation of some transient and unstable intermediate.

Now, are introduced herein entirely new and simple procedures to calculate the $T_c$ for a chemical of the TD type, including every gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, and, the SADT for a chemical of the AC type, including every powdery chemical of the quasi-AC type, having an arbitrary shape and an arbitrary size, confined in an arbitrary closed container of the corresponding shape and size, and placed in the atmosphere under isothermal conditions.

The procedure to calculate the $T_c$ for a chemical of the TD type, including every gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, is, in particular, based on the basic concept of the thermal explosion theory that whether the thermal explosion or the spontaneous ignition of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed in the atmosphere under
isothermal conditions, occurs or not is decided, based on the balance between the rate of heat generation in the chemical and the rate of heat transfer from the chemical to the atmosphere at the critical state for the thermal explosion which exists at the end of the early stages of the self-heating process. According to this procedure, we require neither to follow by experimental measurements the whole self-heating process of the chemical of the TD type up to the actual thermal explosion, or up to the actual spontaneous ignition, to determine the $T_c$, nor to measure the values of the chemical quantities, $E$, $A_0$ and $\Delta H$, respectively, to calculate the $T_c$.

For the purpose of calculating the $T_c$ for a chemical of the TD type, including every gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, we have only to perform, on the one hand, several adiabatic self-heating tests, or several adiabatic oxidatively-heating tests, which are started from each $T_s$ with mutual intervals of $1\sim2$ K, in order to calculate the heat generation data of the chemical, for $2 \text{ cm}^3$ each of several samples of the chemical charged, or confined, each in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical, for the time required for the temperature of each sample of the chemical to increase by $1.25$ K from the corresponding $T_s$ in the adiabatic self-heating test, or from the corresponding standard temperature in the adiabatic oxidatively-heating test, respectively, and, we have only to measure, on the other hand, the heat transfer data of the chemical, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, in temperature differences of $1.25$ K between the inside of the chemical and the atmosphere, under conditions of no air circulation.

In Chapter 1, after both the Semenov and the F-K equation were derived, it is confirmed that both equations express the balance between the rate of heat generation in a chemical of the TD type, including every gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, and, the rate of heat transfer from the chemical to the atmosphere at the critical state for the thermal explosion which exists at the end of the early stages of the self-heating process, respectively. It is then concluded that the Semenov equation is appropriate for the calculation of the $T_c$ for a liquid chemical of the TD type and the F-K equation is appropriate for the calculation of that for a solid chemical of the TD type, including every gas-permeable oxidatively-heating substance.

In Chapter 2, is derived the adiabatic temperature increase equation, which holds between the rate of heat generation per unit volume per unit time in the early stages of the self-heating process of a small-scale chemical of the TD type, including every small-scale gas-permeable oxidatively-heating substance, having the spatially uniform distribution of internal temperature, subjected to either of the two kinds of adiabatic tests, and, the rate of increase in temperature of the chemical, assuming the effect of the concentration of the chemical on the
rate of the exothermic decomposition reaction in the early stages of the self-heating process to be of the zeroth order.

In Chapter 3, a classification of self-heating chemicals, except gas-permeable oxidatively-heating substances, is introduced. Treatments of gas-permeable oxidatively-heating substances are made in Chapters 7 and 8. Self-heating chemicals are divided into two large groups, i.e., the thermal decomposition or TD type and the autocatalytic reaction or AC type. The TD type is subdivided into liquid chemicals, for each of which the Semenov equation is applied to calculate the $T_c$, and, solid (powdery, in reality) chemicals, for each of which the F-K equation is applied to calculate the $T_c$. On the other hand, the AC type is subdivided into high explosives of the true AC type and powdery chemicals of the quasi-AC type.

When confined in the closed cell and subjected to the adiabatic self-heating test started from a $T_s$, or to the isothermal storage test performed at a $T_t$, 2 cm$^3$ of a chemical of the AC type, including every powdery chemical of the quasi-AC type, does not continue to self-heat over the $T_s$ or the $T_t$; rather, it starts to self-heat after the lapse of the induction period of the autocatalytic reaction, or of the quasi-autocatalytic reaction, of the chemical in both tests. That is, the self-heating behavior of a chemical of the AC type is not of the TD type, so that it is impossible to apply either of the two equations of the thermal explosion theory to the calculation of the $T_c$ for the chemical. Instead, it is possible to calculate the SADT for a chemical of the AC type, including every powdery chemical of the quasi-AC type, having an arbitrary shape and an arbitrary size, confined in an arbitrary closed container of the corresponding shape and size, and placed in the atmosphere under isothermal conditions, by applying an empirical formula holding for the induction period of the autocatalytic reaction, or of the quasi-autocatalytic reaction, of 2 cm$^3$ of the chemical subjected to the isothermal storage test.

The $T_c$ for a chemical of the TD type, including every gas-permeable oxidatively-heating substance, depends on its shape and size. On the other hand, the SADT for a chemical of the AC type, including every powdery chemical of the quasi-AC type, does not depend, in principle, on its size or quantity. The difference between the concept of the $T_c$ and that of the SADT is discussed at the end of this chapter.

In Chapter 4, an adiabatic self-heating process recorder is explained in detail. This recorder is used to perform the adiabatic self-heating test, or the adiabatic oxidatively-heating test, which is started from a $T_s$, in order to calculate ultimately the heat generation data of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, for 2 cm$^3$ of the chemical charged, or confined, in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical, for the time required for the temperature of the chemical to increase by 1.25 K from the $T_i$ in
the adiabatic self-heating test, or from the corresponding standard temperature in the adiabatic oxidatively-heating test.

Is then explained in detail the procedure to calculate the values of the two coefficients, \( a \) and \( b \), of an empirical formula. This formula is obtained directly from the adiabatic temperature increase equation derived in Chapter 2 and holds for the self-heating process, or for the oxidatively-heating process, in the early stages, of 2 cm\(^3\) of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, charged, or confined, in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical, and subjected to either of the two kinds of adiabatic tests. The values of the two coefficients, \( a \) and \( b \), thus calculated, of the empirical formula are then used as the heat generation data of the chemical, together with the heat transfer data, to calculate the \( T_c \) for the chemical, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, by applying the reduced form of the Semenov equation or that of the F-K equation.

Although any other existent adiabatic self-heating process recorders are also useful for the calculation of the heat generation data of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, the recorder used in a series of adiabatic self-heating tests, or in a series of adiabatic oxidatively-heating tests, described herein is introduced in this chapter. It is, however, hoped that any new and simple apparatus functioning better than the recorder used herein has clearly some defects.

In Chapter 5, is first explained the reason why the Semenov equation is applicable to the calculation of the \( T_c \) for an arbitrary volume of a liquid charged in an arbitrary container and placed in the atmosphere under isothermal conditions without stirring the liquid or without circulating air around the container.

In this connection, the self-heating behavior of every self-heating liquid chemical, with the exception of liquid high explosives, such as nitroglycerin, of the true AC type, is of the TD type. A self-heating liquid chemical of the TD type or self-heating liquid chemicals of the TD type are, therefore, described herein simply as a liquid or liquids.

The procedure to calculate, by applying the reduced form of the Semenov equation, the \( T_c \) for an arbitrary volume of a liquid charged in an arbitrary container and placed in the atmosphere under isothermal conditions is then introduced by taking the procedure to calculate the value of the BAM test for 400 cm\(^3\) of 99 % tert-butyl peroxybenzoate (TBPB), assuming that it is charged in a 500 cm\(^3\) Dewar flask used in the BAM (Bundesanstalt für Materialforschung und -prüfung, Berlin) heat-accumulation storage test and is placed in the atmosphere under isothermal conditions, as an example. Results
obtained for ten organic liquid peroxides, including TBPB, are successively presented.

In Chapter 6, the procedure to calculate, by applying the reduced form of the F-K equation, the $T_c$ for a powdery chemical of the TD type, having some one of several specific shapes as well as an arbitrary size, confined in an arbitrary closed container of the corresponding shape and size and placed in the atmosphere under isothermal conditions, is introduced by taking the procedure to calculate the $T_c$ for 98% $\alpha$, $\beta$-azobis(isobutyronitrile) (AIBN), assuming that it is confined in a fiber drum, 39.5 cm in inside diameter, 59.2 cm in inside length, and is placed in the atmosphere under isothermal conditions, as an example. Results obtained for ten powdery chemicals of the TD type, including AIBN, are successively presented.

In Chapter 7, is explained in detail the procedure to perform several adiabatic oxidatively-heating tests, which are started from each $T_s$ with mutual intervals of $1 \sim 2$ K, in order to calculate the heat generation data of a gas-permeable oxidatively-heating substance, for 2 cm$^3$ each of several samples of the substance charged each in the draft cell, into which an arbitrary oxidizing gas is supplied, for the time, $\Delta t$, required for the temperature of each sample of the substance to increase by 1.25 K from the corresponding standard temperature, respectively.

In this connection, as stated already, the oxidatively-heating behavior of a gas-permeable oxidatively-heating substance, such as sawdust, coal dust or oil-soaked lagging, is also of the TD type. A gas-permeable oxidatively-heating substance of the TD type or gas-permeable oxidatively-heating substances of the TD type are, therefore, described herein simply as a gas-permeable oxidatively-heating substance or gas-permeable oxidatively-heating substances.

Besides, whenever the adiabatic oxidatively-heating test is performed for an oxidatively-heating liquid, such as unsaturated fatty acid, the liquid is tested, in principle, in the form of oil-soaked adsorbent cotton at relatively low temperatures, or in the form of oil-soaked glass wool at relatively high temperatures. And, the $T_c$ for a heap of the oil-soaked adsorbent cotton, or the $T_c$ for that of the oil-soaked glass wool, having some one of the several specific shapes as well as an arbitrary size, placed in the atmosphere under isothermal conditions, is also calculated in the same manner as applied to the calculation of the $T_c$ for a heap of a gas-permeable oxidatively-heating substance.

For the above reasons, both gas-permeable oxidatively-heating substances and oxidatively-heating liquids are dealt with as gas-permeable oxidatively-heating substances all together herein.

In Chapter 8, the sawdust of every wood species is dealt with as a representative of gas-permeable oxidatively-heating substances. The individual oxidatively-heating properties of the sawdusts of fifteen wood species, which are measured, on the one hand, by TG-DTA performed in air, and, on the other hand, by the adiabatic oxidatively-heating test performed in air, respectively, are first described.
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In Chapter 9, is introduced the procedure to calculate the SADT for a high explosive of the true AC type, having an arbitrary shape and an arbitrary size, confined in an arbitrary closed container of the corresponding shape and size, and placed in the atmosphere under isothermal conditions, by applying the empirical formula holding for the induction period of the autocatalytic reaction of 2 cm$^3$ of the high explosive confined in the closed cell and subjected to the isothermal storage test, by taking the procedure to calculate the SADT for collodion cotton (12.19 % N) as an example. Results obtained for eight high explosives of the true AC type, including collodion cotton, are successively presented.

Although any other existent isothermal storage testing devices are also useful for the calculation of the SADT for a chemical of the AC type, including every powdery chemical of the quasi-AC type, the device used to perform a series of isothermal storage tests described herein is introduced in this chapter.

Finally in Chapter 10, is introduced the procedure to calculate, in the same manner as applied to the calculation of the SADT for a high explosive of the true AC type, the SADT for a powdery chemical of the quasi-AC type, having an arbitrary shape and an arbitrary size, confined in an arbitrary closed container of the corresponding shape and size, and placed in the atmosphere under isothermal conditions, by applying the empirical formula holding for the induction period of the quasi-autocatalytic reaction of 2 cm$^3$ of the chemical confined in the closed cell and subjected to the isothermal storage test, by taking the procedure to calculate the SADT for 97 % lauroyl peroxide as an example. Results obtained for five powdery chemicals of the quasi-AC type, including lauroyl peroxide, are successively presented.

In conclusion, the following three points are added.

First, every chemical becomes liable to self-heat after a long-term storage; in the meantime, very fresh products of chemicals in general are also more liable to self-heat than the normal ones, irrespective of whether they are of the TD type or of the AC type. It is, therefore, possible that the true value of $T_c$, or that of SADT, is fairly lower than that calculated herein. Measures for this are to assign a due safety margin to each value of $T_c$ or SADT calculated herein. It is for the above reasons that a temperature 30 K lower than the value of the BAM test, or that of SADT, calculated for each of organic liquid peroxides, powdery chemicals of the TD type, high explosives of the true AC type and powdery
chemicals of the quasi-AC type, is proposed herein as the upper limit temperature for the safe handling of the chemical.*

Secondly, there is also a possibility that the value of $T_e$, or that of SADT, for a chemical including some impurity, which may promote or catalyze the exothermic decomposition reaction, or the autocatalytic reaction, of the chemical, is considerably lower than that for the pure chemical. For instance, some cases are known, in each of which a chemical reacts with the material of the cell in which the chemical is charged, or confined, in thermal analysis or in some thermal instability test. It is, however, of course possible to calculate the value of $T_e$, or that of SADT, for an arbitrary self-heating mixture by applying some one of several kinds of procedures presented herein.

Thirdly, it is hoped that some apparatus, by means of which the value of $T_e$, or that of SADT, for an arbitrary self-heating chemical, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, is calculated automatically based on some one of several kinds of procedures presented herein, is developed in the future.

* Theoretically speaking, it is not very appropriate to specify the upper limit temperature for the safe handling for a chemical of the TD type, including every gas-permeable oxidatively-heating substance, because the $T_e$ for a chemical of the TD type is not a temperature value specific to the chemical; rather, it depends on its shape and size. Nevertheless, it is also certain that the size of a chemical of the TD type corresponding to a value of $T_e$ 30 K lower than that calculated herein for the chemical is a tremendous one. At all events, however, it is certain that the best way for us is to avoid accumulating any self-heating chemical in bulk at all times. A subject relevant to this point is argued in Subsection 6.7.2.
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10.1 Introduction

10.2 Procedure to perform several isothermal storage tests at each $T_t$, with mutual intervals of $1 \sim 2$ K, in order to calculate the values of the two coefficients, $a$ and $b$, of Equation (59), \[ \ln \Delta t = a/T_t + b \], holding for the induction period of the quasi-autocatalytic reaction of 2 [cm$^3$] of a powdery chemical of the quasi-AC type confined in the closed cell and subjected to the isothermal storage test, for 2 cm$^3$ each of several samples of the chemical confined each in the closed cell, for the time, $\Delta t$, from the insertion of each cell into the isothermal storage testing device till the start of the quasi-autocatalytic reaction occurring simultaneously with the finish of melting of the chemical at the corresponding $T_t$, respectively

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Notation

\( A_0 \)  
Frequency factor in the rate constant of the exothermic decomposition reaction, of the zeroth order, of a chemical of the TD type, including every gas-permeable oxidatively-heating substance; or, frequency factor in the rate constant of the decomposition reaction, of the zeroth order, of a high explosive of the true AC type to generate the autocatalyst \([\text{mol}/(\text{cm}^3\cdot\text{min})]\).

**AC type**  
Autocatalytic reaction type.

\( A_n \)  
Frequency factor in the rate constant of the exothermic decomposition reaction, of the n-th order, of a chemical of the TD type, including every gas-permeable oxidatively-heating substance; or, frequency factor in the rate constant of the decomposition reaction, of the n-th order, of a high explosive of the true AC type to generate the autocatalyst \([(\text{mol})^{1-n}/(\text{cm}^3)^{1-n}\cdot(\text{min})]\).

\( a \)  
Numerical coefficient defined by Equation (44) or Equation (59).

\( b \)  
Numerical coefficient defined by Equation (44) or Equation (59).

\( b \)  
Point of time when 2 [cm\(^3\)] of a chemical of the AC type, including every powdery chemical of the quasi-AC type, confined in the closed cell and subjected to the isothermal storage test performed at a \( T_t \) starts the autocatalytic reaction or the quasi-autocatalytic reaction.

\( C \)  
Molar heat capacity [cal/(mol\cdot K)].

[\( C \)]  
Molar concentration of a chemical [mol/cm\(^3\)].

\( c \)  
Specific heat capacity [cal/(g\cdot K)].

\( c\rho \)  
Heat capacity per unit volume [cal/(cm\(^3\)\cdot K)].

\( d \)  
Day.

\( \text{div} \)  
Divergence operator.

\( E \)  
Activation energy in the rate constant of the exothermic decomposition reaction of a chemical of the TD type, including every gas-permeable oxidatively-heating substance; or, activation energy in the rate constant of the decomposition reaction of a high explosive of the true AC type to generate the autocatalyst [cal/mol].

\( e \)  
Base of natural logarithm.
EOT  Exothermic onset temperature.

grad  Gradient operator.

h  Hour.

h  Film coefficient of heat transfer [cal/(cm²·min·K)].

J₀  Zeroth order Bessel function.

J₁  First order Bessel function.

K  Equilibrium constant.

k₀  Rate constant of the exothermic decomposition reaction, of the zeroth order, of a chemical of the TD type, including every gas-permeable oxidatively-heating substance; or, rate constant of the decomposition reaction, of the zeroth order, of a high explosive of the true AC type to generate the autocatalyst [mol/(cm³·min)].

kᵣ  Rate constant of the exothermic decomposition reaction, of the n-th order, of a chemical of the TD type, including every gas-permeable oxidatively-heating substance; or, rate constant of the decomposition reaction, of the n-th order, of a high explosive of the true AC type to generate the autocatalyst [(mol)¹ⁿ/(cm³)¹ⁿ·(min)].

L  Liter.

l  Wall thickness of a liquid container [cm].

ln  Natural logarithm.

m  meter.

m  Mass [g].

n  natural number.

Q  Electric heat generated per unit time in a resister-thermocouple composite set in a draft cell in order to simulate the self-heating process of a chemical of the TD type, including every gas-permeable oxidatively-heating substance [cal/min].

q₁  Quantity of heat generated per unit time in the whole volume of a fluid filled in the container and placed in the atmosphere maintained at a Tₐ [cal/min]

q₂  Quantity of heat transferred per unit time from a fluid filled in the container and placed in the atmosphere maintained at a Tₐ, through the whole fluid surface, across the container walls, to the atmosphere [cal/min].

R  Gas constant [cal/(mol·K)].
Radius [cm].

Whole fluid surface [cm²].

Temperature at which the self-accelerating decomposition reaction, or the autocatalytic reaction, or the quasi-autocatalytic reaction, that may lead to the ultimate thermal explosion of a chemical of the AC type, including every powdery chemical of the quasi-AC type, having an arbitrary shape and an arbitrary size, confined in an arbitrary closed container of the corresponding shape and size, and placed in the atmosphere under isothermal conditions, starts just 7 d after the placement of the container in the atmosphere maintained at the temperature [K].

To put it concretely, the SADT of a chemical of the AC type, including every powdery chemical of the quasi-AC type, is a value of \( T_t \) corresponding to a value of \( \Delta t \) of 10,080 min, \( i.e. \), 7 d, in Equation (59), \( \ln \Delta t = a/T_t + b \), holding for the induction period of the autocatalytic reaction, or of the quasi-autocatalytic reaction, of 2 cm³ of the chemical confined in the closed cell and subjected to the isothermal storage test.

As a matter of fact, however, the SADT may be regarded as the critical (or the lowest) temperature below which the thermal explosion of a chemical of the AC type, including every powdery chemical of the quasi-AC type, cannot occur.

Semenov number [dimensionless] (Se = \( 1/e = 0.367879 \cdots \)).

Second.

Point of time when the adiabatic control for 2 cm³ of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, charged, or confined, in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical, and subjected to either of the two kinds of adiabatic tests started each from a \( T_s \), and, the record of the self-heating process of the chemical, are started, respectively.

Temperature of a chemical, or, that of a substance [K].

Temperature of the atmosphere, \( i.e. \), air at atmospheric pressure, in which a chemical of the TD type, including every
gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, is placed under isothermal conditions [K].

(When a container, in which a liquid is charged, is placed in a set-up in order to measure the main heat transfer data of the liquid, the $T_a$ is expressed as the $T_{set-up}$.)

$T_{atm}$ Temperature of the atmosphere around 2 cm$^3$ of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, charged, or confined, in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical, and subjected to either of the two kinds of adiabatic tests started each from a $T_s$ [K].

(After the start of the adiabatic control, the $T_{atm}$ is raised automatically by the adiabatic control in order that the condition, $\Delta T_{diff} = T - T_{atm} = 0$, may always hold.)

$T_c$ Critical (or the lowest) temperature below which the thermal explosion of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed in the atmosphere under isothermal conditions, cannot occur [K].

TD type Thermal decomposition type.

$T_s$ Starting temperature in the adiabatic self-heating test, or in the adiabatic oxidatively-heating test, performed for 2 cm$^3$ of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, charged, or confined, in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical [K].

$T_{set-up}$ Temperature of the atmosphere in a set-up, in which the main heat transfer data of a liquid charged in the container is measured [K].

$T_i$ Testing temperature in the isothermal storage test performed for 2 cm$^3$ of a chemical of the AC type, including every powdery chemical of the quasi-AC type, confined in the closed cell [K].

$t$ Time [min].

$U$ Mean overall coefficient of heat transfer from a fluid filled in the container and placed in the atmosphere under isothermal conditions.
conditions, through the whole fluid surface, across the container walls, to the atmosphere [cal/(cm²·min·K)].

\( V \) Volume [cm³].

\( x \) Spatial coordinates [cm].

**Greek Symbols**

\( \alpha \) Thermal diffusivity [cm²/min].

\( \alpha_e \) Effective thermal diffusivity of a powdery chemical of the TD type, including every gas-permeable oxidatively-heating substance [cm²/min].

\( \beta_n \) Positive roots of \( J_0(\beta_\text{cylinder} r_{cylinder}) = 0 \).

\( \Delta \) Laplacian operator.

\( \Delta \xi \) Dimensionless Laplacian operator.

\( \Delta H \) Molar heat of reaction [cal/mol].

\( \Delta T \) Difference between the temperature of a chemical and the \( T_s \) in the adiabatic self-heating test, or in the adiabatic oxidatively-heating test [K].

(The adiabatic self-heating test, or the adiabatic oxidatively-heating test, which is started from a \( T_s \), performed for 2 cm³ of a chemical of the TD type, including every gas-permeable oxidatively-heating substance, charged, or confined, in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical, is interrupted as soon as the temperature of the chemical increases by the definite value of \( \Delta T \) of 1.25 K from the \( T_s \).)

\( \Delta T_{\text{diff}} \) Temperature difference, in the adiabatic self-heating test, or in the adiabatic oxidatively-heating test, between the \( T_{\text{ref}} \) and the \( T_{\text{atm}} \), or between the temperature of a chemical and the \( T_{\text{atm}} \) K.

\( \Delta T_{\text{rad}} \) Radial temperature difference effected in the non-steady state between the periphery and the axial center of the specimen of a powdery chemical of the TD type, including every gas-permeable oxidatively-heating substance, charged in a cylindrical cell heated at a very slow rate, \( \phi \), [K].

\( \Delta t \) Time required for the temperature of 2 cm³ of a chemical of the TD type, including every gas-permeable
oxidatively-heating substance, charged, or confined, in some one of the open-cup, the draft or the closed cell, in accordance with the self-heating property of the chemical, and subjected to either of the two kinds of adiabatic tests started each from a $T_s$, to increase by the definite temperature difference, $\Delta T$, of 1.25 K from the $T_s$ [min].

- $\delta$: Frank-Kamenetskii’s $\delta$ [dimensionless].
- $\delta_c$: Frank-Kamenetskii number [dimensionless].
- $\theta$: Dimensionless temperature.
- $\kappa$: Heat transfer factor used by N. N. Semenov.
- $\lambda$: Thermal conductivity [cal/(cm·min·K)].
- $\xi$: Dimensionless coordinates.
- $\pi$: Ratio of the circumference to the diameter.
- $\rho$: Specific gravity, or density [g/cm$^3$].
- $\tau$: Dimensionless time.
- $\tau_{ad}$: Frank-Kamenetskii’s adiabatic induction period.
- $\phi$: Rate of increase in temperature, or, heating rate [K/min].

**Subscripts**

- $a$: of the atmosphere around a chemical of the TD type, including every gas-permeable oxidatively-heating substance, having an arbitrary shape and an arbitrary size, placed under isothermal conditions.
- $atm$: of the atmosphere around 2 cm$^3$ of a chemical charged, or confined, in some one of the four types of cells, i.e., the open-cup, the draft, the touch-flow or the closed cell, in accordance with the self-heating property of the chemical, and subjected to either of the two kinds of adiabatic tests.
- $autocatalyst$: of an autocatalyst.
- $c$: critical.
- $cylinder$: of an infinite cylinder.
- $diff$: difference.
- $e$: effective.
- $elec$: electric.
- $f$: fluid.
- $h$: high.
inner
l
liq
lim
n
rad
r-cylinder
ref
r-inner
s
set-up
solid
t
threshold
0

inner.
low.
liquid.
limiting.
of the n-th order.
radial.
at the periphery of an infinite cylinder.
of the reference material.
at an arbitrary inner radius.
starting.
of a set-up.
solid
testing.
at the threshold.
of the zeroth order; or, at the axial center of an infinite cylinder.