AN ADIABATIC SELF-IGNITION TESTING APPARATUS *

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ABSTRACT

With this apparatus, very strict adiabatic self-heating tests can be carried out relatively easily on small samples of a wide variety of chemical substances. The apparent activation energy and frequency factor of a slow heating reaction can also be evaluated, under zero-order adiabatic assumption, from heating profiles recorded accurately in temperature ranges of a few degrees above the starting temperature.

INTRODUCTION

Recently, researches on the self-ignition test or storage test have been actively undertaken throughout the world. Thus, several types of apparatus, based on the adiabatic calorimetric principle, have been developed for thermal hazard evaluation of chemical substances.

Earlier, in 1954, Raskin and Robertson made an adiabatic apparatus using an on–off heating system [1]. However, the accuracy of adiabatic control of this apparatus was not very satisfactory. The temperature difference between the center of the sample and the furnace atmosphere after automatic operation commenced was of the order of ± 1 K, and the stability of the control after the start was of the order of ± 2 K h^{-1}.

Pasman made an adiabatic storage testing device in 1967, using a Dewar vessel of 1.5 l capacity as the cell [2]. His adiabatic control technique was also on–off mode. Although without proven evidence, he reported that he had succeeded in detecting a heat generation rate, $\dot{q}_{gen}$, of 10 μW g^{-1} with TNT.

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In 1976 Lemke reported the so-called adiabatic heat accumulation storage method to obtain kinetic data for quantitative evaluation of the self-heating behaviors of chemical substances of industrial scale [3]. In Lemke's device the sample is packed in a Dewar vessel of 0.5 l capacity. The vessel is set inside a pressure container, through which certain heating medium can be circulated. However, the experimental conditions were not strictly adiabatic in this case. The ambient temperature, T_a, was always maintained 0.2 K higher than the sample temperature, T_s, during a run *.

Townsend and Tou made a device, called the accelerating rate calorimeter, applying PID temperature control technique [4], as was the case in the device used here. This calorimeter is unique in that it provides pressure information in addition to the temperature of the reaction system under the adiabatic condition. However, the device appears to aim at searching the whole process of practical, rather rapid, exothermic reactions, and to be useful for tests of industrial scale. Although data on the adiabatic performance of this calorimeter has not yet been mentioned, the minimum detectable rate of increase in temperature is 0.6 K h^{-1}, according to the maker's brochure [5].

We have tried to develop a new adiabatic self-ignition testing apparatus (an adiabatic self-heating process recorder) to study self-heating phenomena more precisely than hitherto, applying the PID–SCR temperature control technique to the adiabatic control.

STRUCTURE AND PERFORMANCE

A block diagram of the apparatus is shown in Fig. 1, and the overall view in Fig. 2.

Design philosophy

(i) The PID–SCR temperature control technique was applied to the adiabatic control. In addition, other devices were used to attain as complete control as possible. Thus a pre-amplifier was incorporated before the PID controller to amplify the temperature difference, ΔT, between T_s and T_a. Then a zero suppression circuit was made up of this amplifier to compensate the slight stray or pseudo thermal electromotive force of the differential thermocouple. Such stray thermal electromotive forces of differential thermocouples may still appear even if T_s and T_a are physically the same, and even if the two thermocouples, showing much the same thermal electromotive force over certain temperature ranges, are selected to make up a

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* It is easier to keep a definite temperature difference between T_s and T_a than to continuously maintain the thermal equilibrium state between them in the temperature control technique.
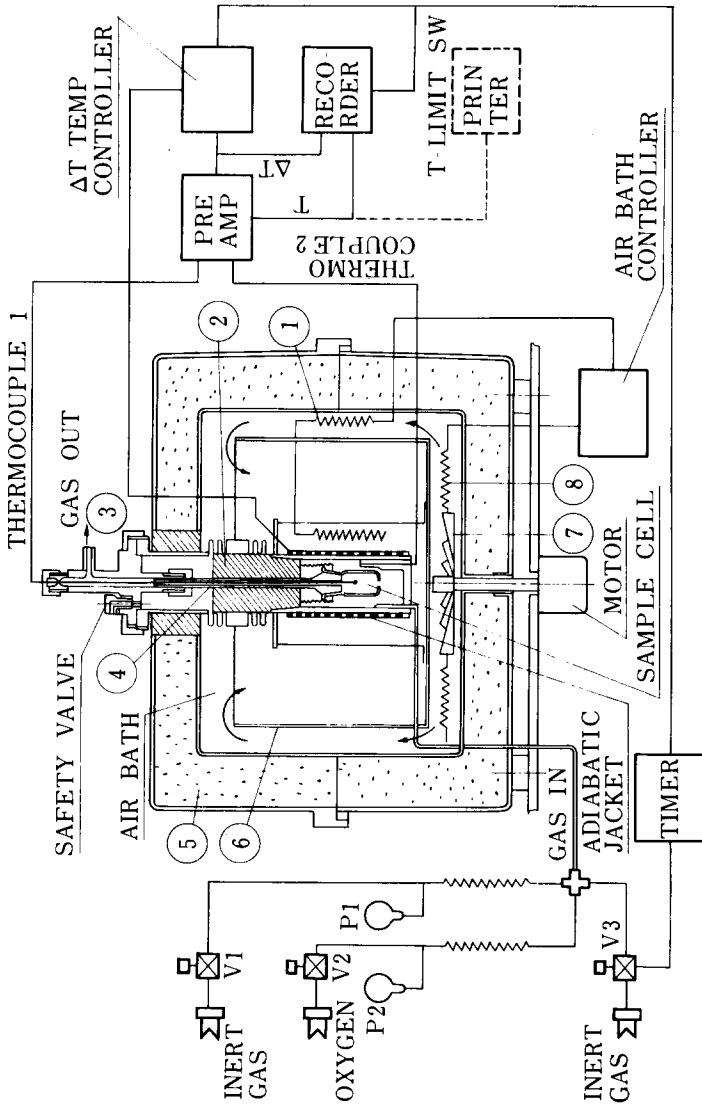
Fig. 1. Block diagram of the adiabatic self-ignition testing apparatus. 1, Thermometer; 2, glass wool; 3, sample cell assembly; 4, silica tube; 5, glass wool; 6, wind guide plate; 7, fan; 8, heater.

Fig. 2. Overall view of the apparatus.

differential thermocouple. Further, a cold junction which utilizes the thermo-electric effect was adopted. Ultimately an adiabatic control was achieved of the order of ± 0.2 μV or ± 0.005 K at the initial stages of slow heating of the sample. The minimum detectable rate of increase in temperature of this apparatus was less than 0.025 K h^{-1}.

(ii) Adiabatic control was not carried out between the sample and the inside wall of the vessel, but between the sample and its atmosphere. This was to enable the true adiabatic condition to be established around the sample.

(iii) An air bath was adopted instead of a liquid bath, because of the much lower heat capacity of the former than that of the latter. This enabled the control to follow T_s even at the stages of rapid heating of the sample.

Sample cell assembly and adiabatic jacket

The sample is packed in a silica cell of ca. 2 ml capacity. The cell is fixed on the end of a silica tube. The tube serves as both a gas vent and a conduit pipe for a thermocouple for measuring T_s. Then the cell assembly is set on the center line in an adiabatic jacket, which is in turn inserted into the air bath. The jacket is a nickel cylinder, closed at the bottom, coated with a ceramic material for insulation. The jacket can follow the rate of increase in T_s up to 20 K min^{-1} with an electric heater. The space between the inside wall of the jacket and the silica tube is filled with glass wool to even out the temperature distribution around the cell. The distribution is found to be

within ± 0.05 K in the space 20 mm above and below the cell, while adiabatic control is in action.

Gas supplying system

An oxidizing or inert gas is preheated to the air bath temperature in a thin copper pipe, 50 cm long, which is set in the air bath. Then the gas flows into the jacket and is heated up to T_a, which is nearly equal to the simultaneously rising T_s by adiabatic control, by passing through a nickel pipe, 1 mm outer diameter, which is welded onto the inside wall of the jacket. Finally, the gas passes into the sample cell through a hole at the bottom of the cell.

Temperature measuring system

One thermocouple covered with a Pyrex glass capillary tube is inserted into the center of the sample to measure T_s. The other thermocouple to measure T_a is inserted from the bottom side into a thin nickel tube, which penetrates the bottom plate of the jacket. The tube is set ca. 1 mm from the inside wall of the jacket such that the thermocouple measures the actual temperature of the atmosphere around the cell, as stated in (ii) of "design philosophy". The points of the two thermocouples are held on the same level surface. Then a differential thermocouple is made from the two. The
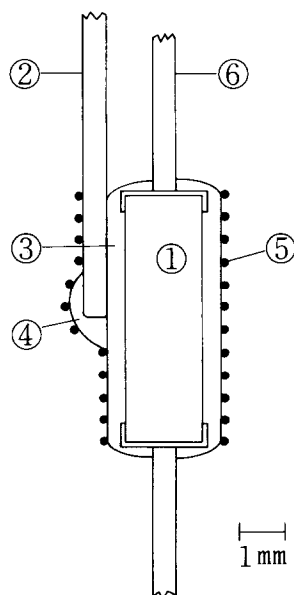

Fig. 3. Setting state of the resistor–thermocouple complex. 1, Heating metal wire; 2, CA stainless-steel-sheath thermocouple; 3, epoxide resin; 4, glue; 5, cotton thread; 6, lead wire.

thermocouples used are Philips CA sheath thermocouples, 0.5 mm outer diameter, and were selected such that their thermal electromotive force was much the same over a temperature range from room temperature to 200°C, to be suitable for adiabatic control.

Performance of adiabatic control

Some heating states of a sample were simulated by evolving minute quantities of electrical heat in a resistor of ca. 10Ω, ca. 2.5 mm diameter and 6 mm long, which was set in the cell without gas flow at 60°C (Fig. 3), using a constant current power source. As a result, it was observed that the rate at which T_s increased gradually decreased, as T_s increased away from the initial value, that is, the starting temperature; or it was observed that the time elapsed before the thermocouple began to detect the heating of the resistor gradually became longer with decreasing the electric heat generation rate, $\dot{Q}_{elec}$ (Fig. 4). The latter phenomenon is probably due to the heat capacity of the resistor–thermocouple complex. However, under these situations, T_s increased almost linearly with time during ca. 100 min from the start of heating detection. Then, $\dot{Q}_{elec}$ was plotted against the temperature increment, ΔT_s, of the resistor 100 min after the thermocouple began to catch the heating (Fig. 5). The plot shows that a good proportionality holds between the two. Since the plot passes through the origin, we can consider that the sample heating in the range 2–3 K above the starting temperature is
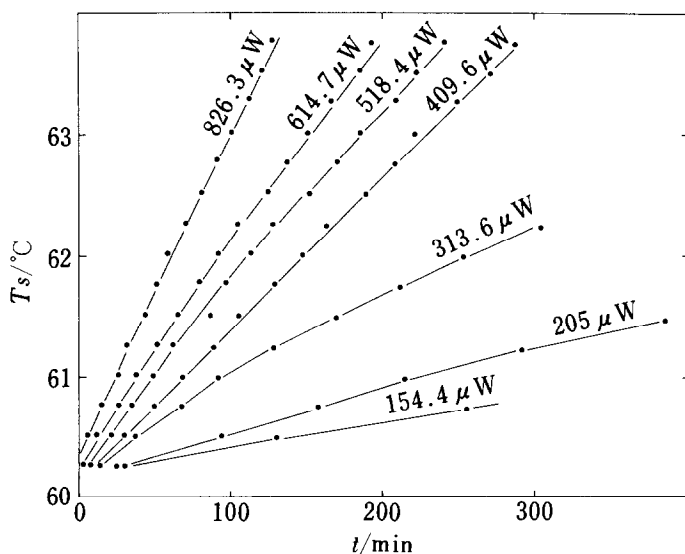

Fig. 4. Variation of resistor temperature, T_s, with time for various power supply rates, $\dot{Q}_{elec}$, starting at 60°C.
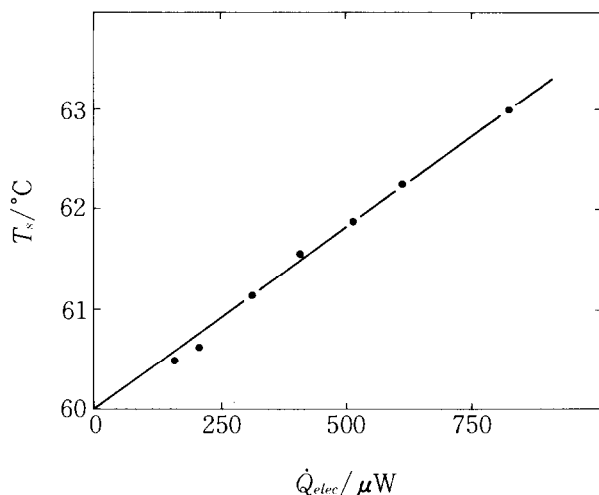
Fig. 5. Relation between $\dot{Q}_{elec}$ and increment of T_s 100 min after the thermocouple began to catch the heating of the resistor. Data correspond to those of Fig. 4.

recorded under an almost completely adiabatic condition in this apparatus. It may serve as an example of this fact that Arrhenius plots, based on eqn. (2) mentioned later, on some definite value of ΔT_s less than 2–3 K, usually result in very good straight lines for most cases.

However, as seen in Fig. 4, it is clear that the adiabatic control gradually becomes broken, the farther T_s increases away from the initial T_s value. Although the situation is such, it has been confirmed that the actual ignition can be brought about in the cell, in such runs where higher $\dot{q}_{gen}$ can be expected, as with samples having higher molar heat of reaction, ΔH, or as at elevated starting temperatures. However, it would be difficult to apply a simple mathematical model to the heating profiles recorded in such cases.

EXPERIMENTAL PROCEDURE

The experimental procedure for oxidatively heating substances is described here. The procedure for self-heating substances was reported elsewhere [6].

Starting procedure

A definite amount of sample is packed in the cell which has a hole at the bottom. Next, the thermocouple for measuring T_s is inserted into the sample. Then the sample cell assembly is set in the adiabatic jacket, and inert gas is usually supplied at a rate of 2 ml min^{-1}. The initial temperature is selected

as desired by setting a temperature dial on the air bath. Then the power is switched on, that is, bath heating is started. The sample temperature is gradually increased, and within several tens of minutes it reaches the starting temperature. Under such circumstances, usually 90 min after the power-on, zero-suppression procedure is carried out. Immediately after that, the supply of oxidizing gas, adiabatic control and recording of the heating process are commenced.

Recording of the heating process

After the start, T_a is automatically controlled by the PID–SCR control system to always satisfy the condition, $\Delta T = |T_s - T_a| = 0$. As a result, the heat evolved is almost accumulated in the sample and T_s increases gradually. The air bath temperature is maintained at the starting temperature during a run.

To facilitate calculation of kinetic parameters, T_s is printed out every minute on a digital recorder as the numerical value of thermal electromotive force of the thermocouple for T_s: its minimum unit is 10 μV. Apart from that, the heating profile of the sample is recorded using one pen of a two-pen strip-chart recorder. The value of ΔT is monitored simultaneously with the other pen of this recorder. The ΔT pen tends to drift gradually toward the plus side, that is, a state in which $T_s > T_a$ held, as the rate of increase of T_s increases. This fact is useful in checking a temperature range in which the condition, $\Delta T = 0$, holds. The ΔT pen is also useful in judging whether or not the thermal equilibrium is attained around the cell immediately before the start. As soon as T_s reaches a temperature preset on the strip-chart recorder, a limit switch works so that the main electric source is automatically cut off. However, in most cases, the measurement is interrupted after an appropriate heating profile is gained.

AN EQUATION FOR THE SELF-HEATING PROFILE UNDER A ZERO-ORDER ADIABATIC ASSUMPTION

When a sample heats spontaneously at a temperature $T_s(K)$, eqn. (1) holds under a zero-order adiabatic assumption, based on the principle of energy conservation.

$$c\rho \frac{dT_s}{dt} = \Delta H A \exp\left(-\frac{E}{RT_s}\right) \tag{1}$$

where c(J g^{-1} K^{-1}), ρ(g cm^{-3}) and ΔH(J mole^{-1}) are the specific heat, density and molar heat of reaction of the sample, respectively. E(J mole^{-1}) and A(mole cm^{-3} min^{-1}) are the apparent activation energy and frequency factor of the rate constant of the exothermic reaction, respectively.

If we assume that the heating rate, dT_s/dt, remains effectively constant, that is, if the reaction is zero-order, within minute temperature ranges near T_s, eqn. (1) can be integrated to yield

$$\ln\left[\Delta t \text{ min}^{-1}\right] = \frac{E}{RT_s} + \ln\left[\frac{\Delta T_s c\rho}{\Delta HA} \text{ min}^{-1}\right]$$ (2)

where Δt(min) is the time taken for the sample temperature to rise by a definite minute temperature increment, ΔT_s(K), above the starting temperature, T_s. Equation (2) can be applied to the heating profile recorded by this apparatus in ranges of a few degrees above the starting temperature. Then the gradient, a, and intercept, b, of an experimental formula, $\ln \Delta t = (a/T_s) + b$, can be expressed as, $a = E/R$ and $b = \ln(\Delta T_s c\rho/\Delta HA)$, respectively. Thus E is evaluated from a, and A from b, if ΔH and $c\rho$ are known.

It is shown that the b value depends on ΔT_s and $c\rho$ values. Actually, it has been confirmed that the $\ln \Delta t$ vs. $1/T_s$ plots on several ΔT_s values, for the same heating profile, become parallel to one another. However, plotting on a ΔT_s value as small as possible is preferable to make eqn. (2) valid.

SOME COMMENTS ON THIS APPARATUS

Using this apparatus, considerably strict adiabatic self-heating tests can be carried out relatively easily with small sample amounts. The apparent activation energy and frequency factor of a slow heating reaction can also be evaluated, under a zero-order adiabatic assumption, from heating profiles recorded in ranges of exactly a few degrees above the starting temperature. Plots shown in Figs. 4 or 5 may give a clue in determination of the calorific value that a substance generates when it heats in the cell. From this viewpoint it can be said that the apparatus has a potential capacity, unlike the usual calorimeter in which complete combustion is carried out, to measure minute quantities of heat evolved in any incomplete or partial reaction. Such a subject has scarcely been studied so far. However, modification of the apparatus design should be made as desired, to suit special experimental requirements and to get improved adiabatic performance.

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