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Effect of temperature gradient in sample cells of adiabatic calorimeters on data interpretation

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ABSTRACT

The thermal behavior of sample cells (bombs) of the ARC and VSP adiabatic calorimeters has been investigated by applying mathematical simulation. Influence of temperature gradient in a calorimetric bomb on the inaccuracy of kinetic parameters evaluated from adiabatic data has been analyzed. Then possible errors in kinetics-based predictions caused by the inaccuracy of kinetic parameters were identified by the example of two important hazard indicators – adiabatic time to maximum rate, TMR, and the self-accelerating decomposition temperature, SADT. A new control method for maintaining sample adiabaticity is proposed that provides obtaining the most correct experimental data suitable for creation of reliable kinetics.

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1. Introduction

Adiabatic calorimetry is well known as one of the main methods for investigation of reaction hazards. It can be very useful for initial screening of reactive chemicals and mixtures and for getting more detailed data necessary for evaluation of potential reaction hazards. An important advantage of the method is that the results obtained can be scaled-up relatively easily to simulate unwanted behavior of a large reactor or the whole process. Furthermore adiabatic calorimetry gives valuable information that can be successfully used for evaluation of reaction kinetics. Estimation of some basic kinetics is required for implementing such typical procedures as correction of experimental results due to thermal inertia [1], assessment of adiabatic TMR [2,3], evaluation of SADT (e.g. [4,5]). More detailed kinetics can be successfully used for simulation-based assessment of reaction hazards.

One of the primary ideas the adiabatic data interpretation is based on is that the temperature and concentration gradients within the sample are negligible (that is, the system close to uniform). This allows simple determination of the reaction heat, easy evaluation of basic kinetics, etc. The main origin of possible deviation from uniformity is heat loss from the sample to the cell (bomb) material – the thermal inertia. This violates adiabaticity of the sample and causes appearance of temperature gradients in a sample. The gradient may result in errors even when performing such simple data analysis as estimation of reaction heat. More serious errors can be made when evaluating kinetics from experimental data. Though thermal processes in an adiabatic calorimeter were considered to a certain extent in several articles [6–8] this subject needs further more detailed analysis with the specific focus on the influence of the temperature gradient on the correctness of data interpretation in general and on reliability of kinetics in particular. Nowadays the latter aspect is increasingly important because adiabatic data are more and more often used as a source for creation of complex kinetic models (e.g. [9–12]).

This paper represents the results of such in-depth analysis. First, the correlation between the non-uniformity and conditions of heat exchange between calorimetric bomb and external oven/heater that maintains adiabaticity for the bomb will be discussed. The assessment of possible errors of kinetic parameters evaluated under the assumption that temperature is uniform will follow. Effect of these errors on accuracy of hazard assessment will be demonstrated by the example of estimating the adiabatic TMR and SADT.

Direct experimental investigation of this problem is very difficult if not impossible. Therefore the alternative mathematical simulation approach has been used. All calculations presented in the article are based on the abstract kinetic models of an N-order and autocatalytic reactions to reveal the peculiarities of thermal behavior and avoid superfluous complications. Furthermore idealized instruments are considered, that is, possible heat losses along the construction elements of a calorimeter are not taken into account and the ideal retardation-free control system that maintains adiabaticity is assumed.

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Nomenclature

t	time (s)
T	temperature (K)
ΔT	adiabatic temperature rise, $\Delta T = T - T_0$ (K)
$Q(t)$	current heat generation due to a reaction (kJ/kg)
Q^∞	heat of reaction (kJ/kg)
W	reaction rate (s^{-1})
α	conversion
$f(\alpha)$	kinetic function
k	rate constant (s^{-1})
k_0	pre-exponential factor (s^{-1})
E	Activation energy (J/mol)
z	autocatalytic constant
n	reaction order
φ	thermal inertia (phi-factor)
R	universal gas constant (J/mol/K)
m	mass (kg)
c	specific heat (J/kg/K)
λ	thermal conductivity coefficient (W/m/K)
q	heat flux (W/m^2)
U	heat transfer coefficient ($W/m^2/K$)
δ	bomb wall thickness (m)

Indices

c	center of a calorimetric bomb
w	outer surface of the bomb wall
f	oven, heater
o	initial value
eff	effective value
s	reacting substance (sample)
b	calorimetric bomb
is	thermal insulator
max	maximum value
min	minimum value

Abbreviations

ARC	the accelerating rate calorimeter
VSP	the vent sizing package
TMR	adiabatic time to maximum rate
SADT	self-accelerating decomposition temperature

2. Methods of maintaining adiabaticity utilized in ARC and VSP

Deviation of the sample from adiabaticity depends not only on thermal inertia which is defined by the mass heat capacity of the bomb but on the features of the method used for maintaining adiabaticity of the bomb. This is because in general there is heat exchange between the bomb and the oven/heater of the calorimeter (hereafter referred as calorimeter). It means that not only the bomb material absorbs heat from the sample but it can also lose some heat outward or receive it from the calorimeter.

All the further discussion will concern two main types of adiabatic calorimeters–the Accelerating Rate Calorimeter, ARC [13] and the Vent Sizing Package, VSP [14] (and similar instrument Phi-Tec), therefore the features of maintaining adiabaticity utilized in these instruments will be considered first.

2.1. ARC

The spherical bomb is placed in the cavity of the rugged nickel plated copper calorimeter. The control thermocouple is clipped on the outer surface of the bomb. The same thermocouple is used for measurements, that is, for sampling of the temperature response.

The control system maintains the equality of the calorimeter temperature T_f and the bomb wall temperature T_w: $T_f = T_w$. If this condition is ensured precisely (the ideal control system) there is no heat exchange between the bomb and the calorimeter, which is equivalent to assigning the adiabatic insulation on the bomb wall (zero heat flux):

$$q_w = 0, \tag{1}$$

In this case the bomb thermal behavior is entirely defined by the bomb thermal inertia measured by the phi-factor:

$$\varphi = 1 + \frac{(c_b m_b)}{(c_s m_s)}. \tag{2}$$

The ARC bomb 2.5 cm diameter and about 9 cm^3 volume must withstand pressure of up to 100 bar, therefore the bomb wall is typically quite thick and the φ-factor may exceed 2. This may result in temperature gradient that impedes data interpretation. If the sample is a low-viscous liquid the gradient can be reduced or completely eliminated by applying the forced agitation but in the case of a solid or viscous sample the problem persists.

2.2. VSP

The cylindrical bomb is surrounded by the heater. The space between the heater and the bomb is filled with insulating material. The control/measurement thermocouple is set in the bomb center. The control system maintains equality of the heater temperature, T_f, and the center temperature, T_c: $T_f = T_c$. As the bomb wall temperature will differ from the center temperature, heat exchange between the bomb and the heater takes place. This can be expressed by the following boundary condition on the outer surface of the bomb:

$$T_f = T_c; \qquad -\lambda \left.\frac{\partial T}{\partial n}\right|_w = U_{eff}(T_f - T_w), \tag{3}$$

where n means outer normal to the wall.

The VSP bomb is much bigger than that of ARC. Its volume is about 110 cm^3, the wall is very thin (~0.1–0.15 mm), and hence the thermal inertia is usually much lower: typically $\varphi < 1.1$. One important fact is that due to the features of the method used for maintaining adiabaticity φ – factor for the VSP cannot be calculated by formula (2) because the walls receive some heat from the heater. The amount of this heat depends on the intensity of heat exchange (i.e. defined by the U_{eff} value). As a result the effective value of φ – factor will be smaller than that calculated from (2) and should be somehow determined.

2.3. Alternative method

In addition to the two above-mentioned methods that are currently in use a new method is proposed in this work for maintaining adiabaticity. The essence of this method is that the control system maintains equality between T_w and T_c:

$$T_w = T_c. \tag{4}$$

It follows from Eq. (3) that the alternative method is equivalent to the previous one provided that heat exchange between the bomb and the calorimeter is very intensive, i.e. $U_{eff} \to \infty$. It will be demonstrated that this method ensures the most correct data and, at the same time, can be implemented with minimal modifications of the existing instruments.

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Table 1
Kinetic parameters of the reactions.

Reaction	k_0, s^{-1}	$\ln(k_0)$,	E, kJ/mol	n	$n1$	$n2$	z	Q^∞, kJ/kg
1st order	2.415×10^7	17	80	1	–	–	–	400
Autocatalytic	5.693×10^8	20.16	80	–	1	1	0.01	400

Table 2
Thermal–physical properties of samples and bomb material.

Property	Sample	Bomb material
Density, kg/m^3	1000	7000
Specific heat; J/kg/K	2000	600
Thermal conductivity coefficient; W/m/K	0.2	20
Thermal expansion coefficient (for liquid only), K^{-1}	0.001	–
Dynamic viscosity (for liquid only), Pa·s.	1×10^{-3}	–

3. Simulation of the bomb thermal behavior

To reveal the temperature gradient within the ARC and VSP bombs and its effect on correctness of resulting data thermal behavior of a bomb containing solid and liquid reacting exothermically were analyzed by numeric solution of the non-stationary conjugate problem of heat transfer in the sample and the bomb wall. The ARC experiments have been modeled both for solid and for liquid samples whereas the VSP experiments have been modeled for solid sample only.

The model comprising a non-stationary thermal conductivity equation with non-linear energy source due to an exothermic reaction, dQ/dt, and kinetic equation was used for simulation of heat transfer in a solid sample. The non-stationary thermal conductivity equation described heat transfer in the walls.

The experiment with a liquid was simulated assuming that no agitation is applied. In this case the system of non-stationary Navier–Stokes equations for incompressible liquid with energy source had been solved. The Boussinesq approximation was used to take into account density variation. The non-stationary thermal conductivity equation described heat transfer in the walls. The non-slip and impermeability conditions were defined on the inner surface of the walls.

In both these cases the continuity of temperatures and heat flows was assumed on the sample–wall interface.

The ThermEx and ConvEx packages from the CISP TSS software were used for numeric simulation. The detailed consideration of the models and numeric methods has been published [15].

Two different reactions were examined – of 1st order and autocatalytic type. They are defined by the formal model [11]:

$$\frac{\partial \alpha}{\partial t} = W(\alpha, T); \tag{5a}$$

$$W = f(\alpha) k_0 \exp\left(\frac{-E}{RT}\right); \qquad \frac{\partial Q}{\partial t} = Q^\infty \frac{\partial \alpha}{\partial t} \tag{5b}$$

where $f(\alpha) = (1-\alpha)^n$ for the N-order reaction and $f(\alpha) = (1-\alpha)^{n1}(z+\alpha^{n2})$ for the autocatalytic reaction. Initial conditions are: $t = 0$, $\alpha = 0$ and $T = T_0$. When simulating the reaction in a liquid sample the convective term has been added to right hand of the kinetic Eq. (5a).

The kinetic parameters of the exemplary reactions (5a,b) and properties of samples and bomb material used for simulation are presented in Tables 1 and 2, respectively.

3.1. Temperature gradient within the ARC bomb

The fully filled metal bomb with radius 1.5 cm and wall thickness $\delta = 1$ mm has been considered. From the sample and bomb material properties the thermal inertia is $\varphi = 1.483$.

When simulating the process data on time dependency of T_w, T_c and their derivatives were collected for further analysis. Fig. 1a shows variation of temperatures in time for the solid sample for both the reactions examined, the self-heat rates are presented in Fig. 1b in Arrhenius axes. For comparison, the results for the system without temperature gradient (uniform system) were added.

Fig. 2 depicts variation of the maximum temperature drop in the ARC bomb as a function of maximum conversion. One can clearly see the appearance of the significant temperature gradient at conversions exceeding 0.3–0.5. The most dramatic gradient is observed for the autocatalytic reaction.

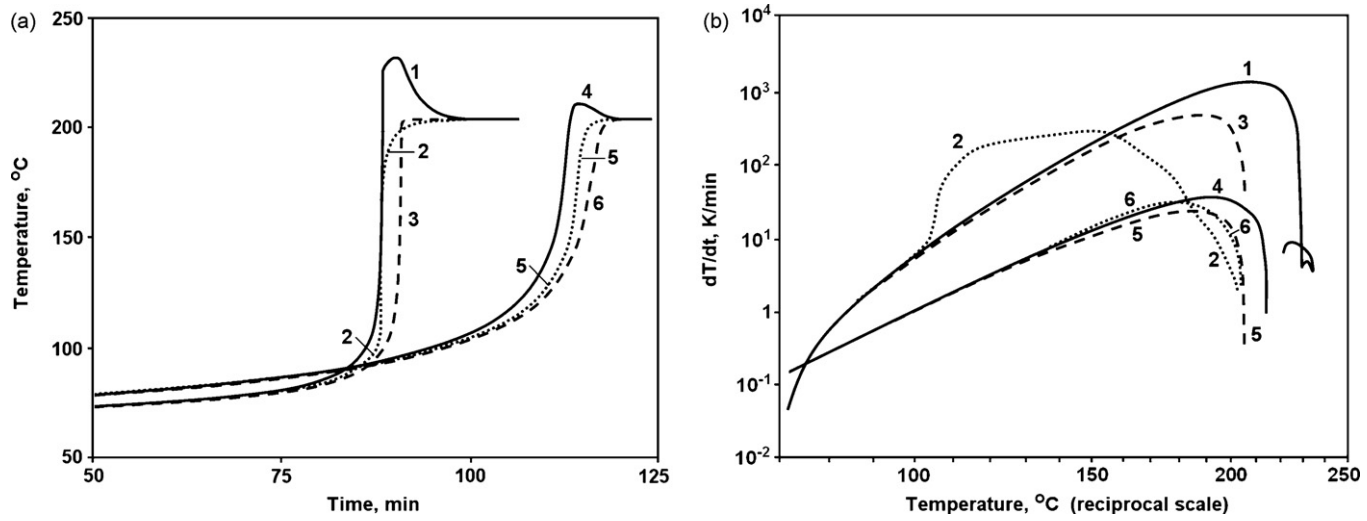

Fig. 1. Simulation of T_w and T_c variation for the ARC bomb with the solid sample. (a) Temperature profiles; (b) self-heating rates; 1 – 3 – autocatalytic reaction; 4 – 6 – first-order reaction; 1, 4 – center; 2, 5 – bomb wall; 3, 6 – uniform system.

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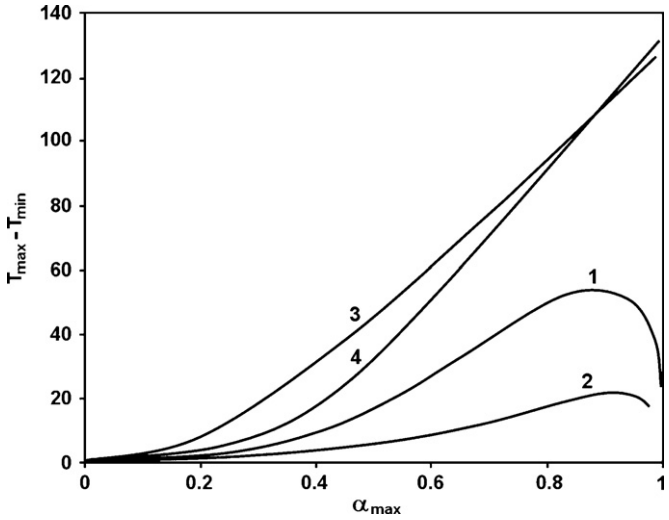

Fig. 2. Dependency of the temperature gradient on maximum conversion in the ARC bomb. T_{max}, T_{min} – maximum and minimum values of temperature; first-order reaction: 1 – solid sample, 2 – liquid sample; autocatalytic reaction: 3 – solid sample, 4 – liquid sample.

Temperature maximum in the solid sample is located in the center. Natural convection in the liquid results in appearance of temperature stratification along the bomb height so that the temperature maximum emerges in the upper part of the bomb. Convection lowers the temperature gradient to some extent but it remains very significant.

It may seem that self-acceleration of a reaction has strong impact on the thermal behavior of the bomb – the autocatalytic reaction demonstrates a much higher temperature gradient, the shape of self-heat rate curve (2, Fig. 1b) is unusual. Nevertheless more detailed analysis shows that chemical nature of a reaction is not as important as the level of self-heat rate. Observable peculiarities of thermal behavior are determined by the relation between the rate of heat generation and the rate of heat transfer in the sample. If the reaction is fast enough thermal conductivity cannot provide efficient heat transfer from the bomb center to the wall, which results in appearance of very specific temperature profile across the bomb and distortion of the time dependency of the wall temperature. Typical temperature distributions in the bomb cross-section are shown in Fig. 3. The profiles correspond to maximum gradients.

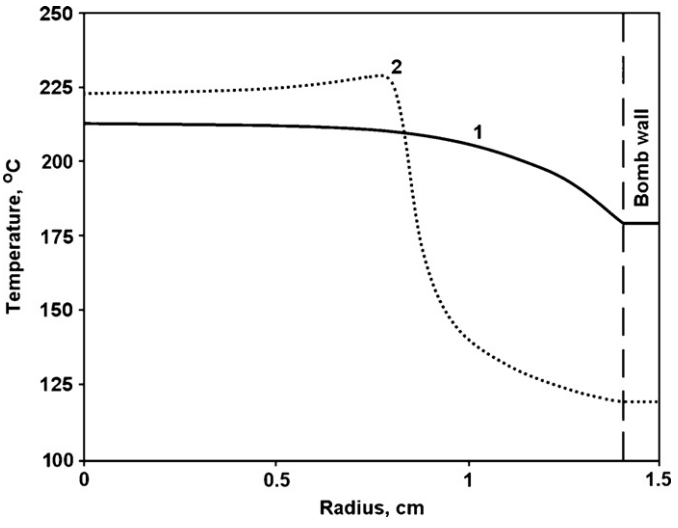

Fig. 3. Temperature distribution in the bomb with solid sample. 1 – first-order reaction; 2 – autocatalytic reaction.

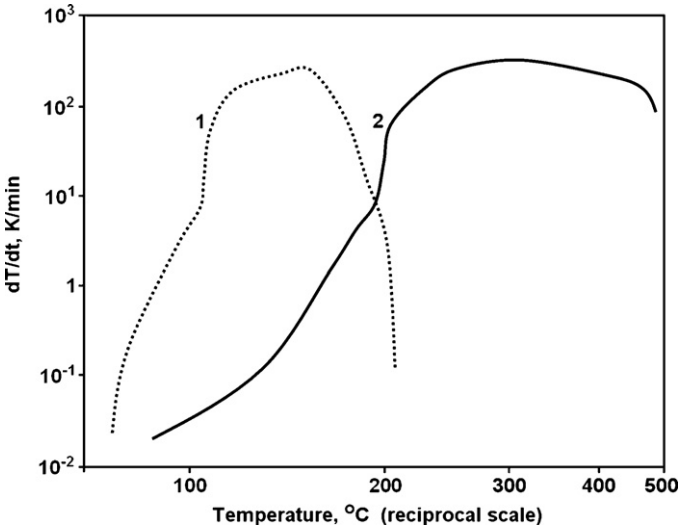

Fig. 4. The self-heat rates derived from T_w. 1 – self-heat rate for the autocatalytic reaction; 2 – self-heat rate observed in the real ARC experiment.

The profile for the first-order reaction (curve 1) is smooth though reveals significant temperature gradient. On the contrary, the profile for the faster reaction (the autocatalytic one in this case) demonstrates that the thermal behavior is close to propagation of the reaction front (curve 2). At first, when the reaction front is far from the wall, T_w rises slowly, then as the front approaches the wall, T_w varies faster and faster which results in appearance of the hump on the self-heat rate graph derived from T_w (curve 2 in Fig. 1b).

One can suspect that the somewhat strange shape of the self-heat rate curve is an artifact due to some defects of simulation. Nevertheless similar results are not rare cases in the practice of adiabatic experiment and some ARC users might recall them (one real example is presented in Fig. 4 together with the simulated data for the autocatalytic reaction). This specific shape of the self-heat rate curve can be interpreted as the evidence of essential temperature gradient and as an indication that traditional methods of data treatment may lead to wrong results.

3.2. Temperature gradient within the VSP bomb

The VSP bomb is the vertical cylinder made of metal with height equals to 5 cm, outer radius 2.66 cm and wall thickness $\delta = 0.25$ mm. The bomb is fully filled with a solid sample. The formal value of phi-factor calculated from (2) is $\varphi = 1.062$.

In accordance with the method used for maintaining adiabaticity in VSP the boundary condition (3) on all the bomb sides was used when simulating reaction course.

No data for the value of U_{eff} was found therefore it was estimated by formula:

$$U_{eff} = \frac{\lambda_{is}}{\Delta}, \tag{6}$$

where Δ is the thickness of the insulator layer.

For a typical porous insulator $\lambda_{is} \approx (0.03–0.08)$ W/m/K; assuming $\Delta \approx 5$ mm one will get $U_{eff} \approx (6–16)$ W/m^2/K. Therefore the mean value $U_{eff} = 10$ W/m^2/K was used for simulation. The effect of U_{eff} on the thermal behavior has been also examined.

Fig. 5 depicts dependency of the maximal temperature drop in the bomb on maximal conversion at $U_{eff} = 10$ W/m^2/K. Furthermore Fig. 5 presents the results of simulation for the alternative method (4) which is equivalent to $U_{eff} \to \infty$.

One can see that due to low thermal inertia of the VSP bomb difference between the temperature gradient for slow (first-order)

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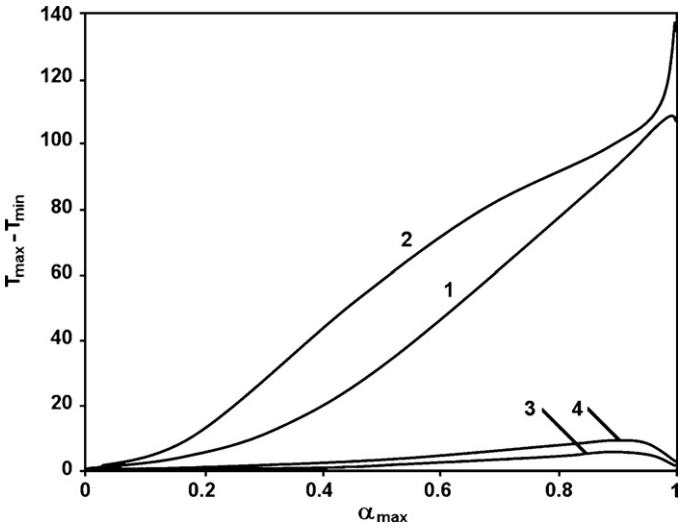

Fig. 5. Dependency of the temperature gradient on maximum conversion in the VSP bomb, T_{max}, T_{min} – maximum and minimum values of temperature. *VSP control method* (U_{eff} = 10 W/m^2/K): 1 – first-order reaction; 2 – autocatalytic reaction; *Alternative method* ($T_w = T_c$): 3 – first-order reaction; 4 – autocatalytic reaction.

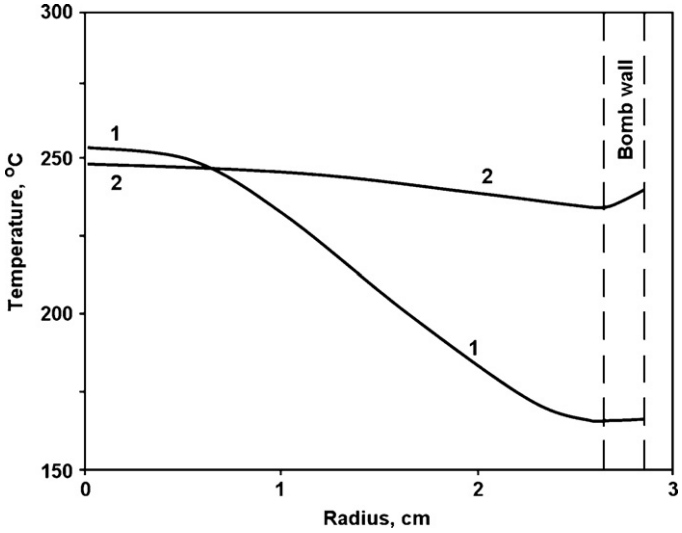

Fig. 7. Temperature distribution in the VSP bomb at maximum temperature gradient, first-order reaction; 1 – U_{eff} = 10 W/m^2/K; 2 – U_{eff} = 500 W/m^2/K.

and fast (autocatalytic) reaction is essentially smaller than in the case of ARC experiment. The important observation is that the alternative control method allows significant reduction of the gradient thus providing much more uniform temperature distribution.

As it was noted earlier the real (effective) φ-factor for the VSP is smaller than that calculated by formula (2) because the walls receive some amount of heat from the heater. Dependency of the effective φ-factor on the intensity of heat exchange is presented in Fig. 6. This was obtained by simulation of the VSP bomb thermal behavior for the first-order reaction.

The value of the φ_{eff} has been estimated from the relation that bounds maximum adiabatic temperature rise and reaction heat:

$$\Delta T_{max} = Q^{\infty}/c_s/\varphi_{eff}. \quad (7)$$

It can be seen that for very weak heat exchange ($U_{eff} \to 0$, the ARC control method) φ_{eff} approaches the formal value calculated from (2). On the contrary, when heat exchange is very intensive ($U_{eff} > 300$ W/m^2/K) φ_{eff} tends to 1 which is equivalent to applying the alternative control method.

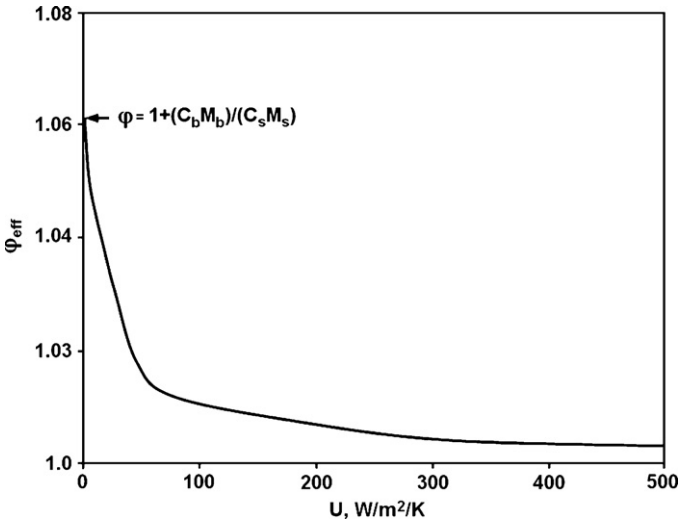

Fig. 6. Dependency of φ_{eff} on the heat transfer coefficient U_{eff} for VSP.

In order to examine efficiency of the alternative method the thermal behavior of the VSP bomb was simulated with the wall thickness δ = 2 mm (i.e. about 10 times greater than for real bomb). The estimated φ_{eff} was 1.008 whereas the formal value calculated from (2) is 1.527. This confirms that the alternative method provides almost complete adiabaticity for the sample.

Fig. 7 demonstrates the effect of φ_{eff} on the temperature distribution in the VSP bomb with thick wall.

4. Influence of the temperature gradient in the calorimetric bomb on the results of kinetics evaluation

The applicability of adiabatic calorimetry to investigation of reaction kinetics is strongly defined by the possibility to minimize the temperature gradient in the bomb. A problem is that all the kinetics evaluation methods are based on the model of a well-stirred reactor:

$$\begin{aligned} c_s\varphi\frac{dT}{dt} &= Q^{\infty}W(\alpha, T); \\ \frac{d\alpha}{dt} &= W(\alpha, T) \end{aligned} \quad (8)$$

In other words, it is always assumed that temperature and concentrations distributions in a sample are close to uniform otherwise the kinetic analysis proves to be practically impossible because of the need in extremely difficult and time-consuming calculations.

As was demonstrated if φ_{eff} exceeds 1, heat absorption by the bomb wall results in significant temperature gradients so that model (8) becomes inapplicable. Thus the condition $\varphi_{eff} \to 1$ is the obligatory requirement for an adiabatic experiment to produce correct kinetic data.

What would be the errors of estimates of the kinetic model parameters due to temperature gradient in a sample if kinetics is evaluated on the basis of the simplified process model (8)? To answer this question the kinetics evaluation was performed by using data on temperature variation and self-heat rate collected when thermal behavior of the ARC and VSP bombs were simulated. The non-linear optimization was applied for parameters estimation. The results obtained using the ForK software [11] are presented in Tables 3 and 4. There are several important conclusions.

1. For both the reactions examined VSP data provide evaluation of more accurate kinetics.

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Table 3
Estimates of kinetic parameters for the first-order reaction.

Calorimeter's type, features of data				Estimates of kinetic parameters			
Instr.	Sample	Response[a]	Control method	$\ln(k_0)$	E, kJ/mol	n	Q, kJ/kg
ARC	Solid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	18.6	84.8	1.1	401.9
ARC	Solid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	19.1	86.0	1.0	399.1
ARC	Liquid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	17.79	82.37	1.07	401.3
ARC	Liquid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	17.02	80.11	0.96	400
VSP	Solid	T_c, dT_c/t	$T_f = T_c$; $\varphi = 1.062$	16.9	79.7	1.0	395.9
VSP	Solid	T_c, dT_c/t	$T_w = T_c$; $\varphi = 1.062$	16.9	79.9	1.0	424.4
VSP	Solid	T_c, dT_c/t	$T_w = T_c$, $\varphi_{eff} = 1$	16.9	79.9	1.0	399.6
VSP	Solid	T_c, dT_c/t	$T_w = T_c$, $\delta = 2$ mm; $\varphi = 1.527$	17.0	79.9	1.0	609.9
VSP	Solid	T_c, dT_c/t	$T_w = T_c$, $\delta = 2$ mm, $\varphi_{eff} = 1$	17.0	79.9	1.0	399.6

[a] Here response means data used for kinetics evaluation.

Table 4
Estimates of kinetic parameters for the autocatalytic reaction.

Calorimeter's type, features of data				Estimates of kinetic parameters			
Instr.	Sample	Response	Control method	$\ln(k_0)$	E, kJ/mol	$n1$, $n2$, z	Q, kJ/kg
ARC	Solid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	28.93	97.56	$n1 = 4.43$, $n2 = 1.98$, $z = 0.0013$	409
ARC	Solid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	18.81	74.55	$n1 = 0.56$, $n2 = 1.29$, $z = 0.0095$	400
ARC	Liquid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	24.89	92.43	$n1 = 2.04$, $n2 = 1.22$, $z = 0.01$	401
ARC	Liquid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	20.36	80.548	$n1 = 0.87$, $n2 = 1.03$, $z = 0.011$	401
ARC,	Solid	T_c, dT_c/t	$T_w = T_c$, $\varphi_{eff} = 1$	19.98	79.28	$n1 = 0.96$, $n2 = 1.03$, $z = 0.0095$	400
VSP,	Solid	T_c, dT_c/t	$T_f = T_c$; $\varphi = 1.062$	19.8	79.0	$n1 = 0.9$, $n2 = 1.0$, $z = 0.010$	402.3
VSP	Solid	T_c, dT_c/t	$T_f = T_c$; $\delta = 2$ mm; $\varphi = 1.527$	20.0	79.6	n1 = 0.888, n2 = 1.0, z = 0.010	529.5
VSP	Solid	T_c, dT_c/t	$T_w = T_c$, $\varphi_{eff} = 1$	20.2	80.0	$n1 = 1.0$, $n2 = 1.0$, $z = 0.010$	400.5
VSP	Solid	T_c, dT_c/t	$T_w = T_c$, $\delta = 2$ mm, $\varphi_{eff} = 1$	20.1	79.8	$n1 = 1.0$, $n2 = 1.0$, $z = 0.010$	400.3

2. Kinetic parameters evaluated from ARC data noticeably differ from the original parameters. In the extreme case of fast autocatalytic reaction usage of the wall temperature as a kinetic response does not allow evaluation of the kinetics that would be capable of reasonable fit of data. Use of the center temperature improves the situation to some extent but estimates of kinetic parameters are still far from the exact values.
3. The alternative control method (4) provides reliable kinetic data that allow evaluation of almost exact values of kinetic parameters in both ARC and VSP cases. Here it should be taken into account that the bomb walls are heated mostly by the calorimeter/heater, therefore the effective value of phi-factor must be used. Although exact value of φ_{eff} is unknown, one can safely take $\varphi_{eff} = 1$.

5. Effect of errors in kinetic parameters on prediction of reaction hazard

The important question is how the errors of reaction kinetics (non-adequacy of the model stricture or errors of the parameters) affect the accuracy of predictions based on the model. To answer this question the influence of the errors of kinetic parameters discussed in previous section on the results of calculation of two widely used hazard indicators – the adiabatic time to maximum rate, TMR, and the self-accelerating decomposition temperature, SADT, was estimated.

The TMR has been calculated for a well-stirred reactor by using the ReRank software [3].

SADT was calculated for a metal barrel (height 0.5 m, radius 0.14 m and wall thickness 7 mm) with reactive chemical in accordance with the conditions of the H1 test [16,17]. Boundary conditions of the third kind with $U = 10\ \mathrm{W/m^2/K}$ have been set on all the surfaces of the barrel. In the case of a solid the same mathematical model was used as for simulation of the VSP bomb. SADT for the liquid has been calculated on the basis of the model of well-stirred tank. The ThermEx and ConvEx programs were applied for SADT calculation of solid and liquid respectively. Results of calculations are presented in Tables 5 and 6.

These results demonstrate that for both the reaction types kinetics evaluated from VSP data gives more accurate estimates of TMR that are in acceptable vicinity of the exact values.

Estimates of TMR based on ARC kinetics for the first-order reaction are appreciably (30–35%) overstated which results in unacceptable underestimate of reaction hazard. In the case of an autocatalytic reaction estimates of TMR based on ARC kinetics are even less acceptable because they are much bigger than the exact values. Application of the alternative control method principally

Table 5
Calculated SADT and TMR(20 °C) for the first-order reaction.

Calculated by exact kinetic model: SADT for solid = 29 °C; SADT for liquid = 46 °C; TMR(20 °C) = 104.3 h					
Instr.	Sample	Response	Control method	SADT, °C	TMR(20 °C), h
ARC,	Solid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	32	141.3
ARC	Solid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	32	138.2
ARC	Liquid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	47	120.7
ARC	Liquid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	46	106.4
VSP	Solid	T_c, dT_c/t	$T_f = T_c$; $\varphi = 1.062$	29	103.5
VSP	Solid	T_c, dT_c/t	$T_w = T_c$; $\varphi = 1.062$	28	104.0
VSP	Solid	T_c, dT_c/t	$T_w = T_c$, $\varphi_{eff} = 1$	29	110.9

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Table 6
Calculated SADT and TMR(20 °C) for the autocatalytic reaction.

Calculated by exact kinetic model: SADT for solid = 21 °C; SADT for liquid = 26 °C; TMR(20 °C) = 129.6 h					
Instr.	Sample	Response	Control method	SADT, °C	TMR(20 °C), h
ARC,	Solid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	29.4	350
ARC	Solid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	18.5	90
ARC	Liquid	T_w, dT_w/t	$q_w = 0$; $\varphi = 1.483$	34	260
ARC	Liquid	T_c, dT_c/t	$q_w = 0$; $\varphi = 1.483$	26	134
VSP	Solid	T_c, dT_c/t	$T_f = T_c$; $\varphi = 1.062$	21	123.4
VSP	Solid	T_c, dT_c/t	$T_w = T_c$; $\varphi = 1.062$	21	120.5
VSP	Solid	T_c, dT_c/t	$T_w = T_c$, $\varphi_{eff} = 1$	21	124.4
ARC	Solid	T_w, dT_w/t	$T_w = T_c$, $\varphi_{eff} = 1$	21	124.4

improves the situation – in this case estimates of TMR are only slightly (5%) smaller than the exact values.

SADT is less sensitive to the errors of the kinetics. For the first-order reaction estimates of SADT are close to the exact values; the difference does not exceed 3 °C. For the autocatalytic reaction maximum deviation on the unsafe side is 8 °C and corresponds to the kinetics evaluated from ARC data when standard control method has been used. As in the previous case application of the alternative control method significantly improves the situation.

6. Conclusions

Analysis of temperature gradients within sample cells (bombs) of ARC and VSP adiabatic calorimeters by applying method of mathematical simulation reveal several important peculiarities that have strong impact on correctness of experimental data.

1. Even if the walls of the calorimetric bomb are very thin (low thermal inertia) serious temperature gradients may appear (up to 100 °C and more) when running experiments with solid samples or with liquids without forced agitation.
2. New control method proposed in this article allows significant reduction of temperature gradient that does not exceed several degrees. The essence of the method is that the control system maintains equality between the temperature in the bomb center and the temperature of the bomb wall. Almost uniform temperature distribution can be achieved not only for standard thin-wall bombs but also for the bombs with thick walls. As in this case the main amount of energy for heating the bomb walls is supplied by the calorimeter/heater the value $\phi_{eff} \approx 1$ can be safely taken for data treatment.
3. Sensitivity of the kinetics to model inaccuracy (applying model of a well-stirred bomb instead of the model with distributed parameters) caused by temperature gradient in the sample depends primarily on the reaction rate and is less sensitive to the reaction type. For slower reactions both ARC and VSP data allow estimates of the kinetic parameters to be obtained that are reasonably close to the exact values. For fast reactions use of ARC data results in significant errors in the estimates of kinetic parameters whereas more accurate parameters can be estimated on the basis of VSP data. Use of the alternative control method ensures the best basis for kinetics evaluation regardless of the type of adiabatic calorimeter and rate of a reaction.
4. Inaccuracy of the kinetic model affects correctness of the estimates of hazard indicators. Time indicators (e.g. the adiabatic TMR) are most sensitive and can result in serious understatement of reaction hazard. Temperature indicators (e.g. the SADT) are less sensitive to the errors of kinetic parameters.

It is important to realize that the idealized instruments have been considered so far. More detailed analysis of the effects of heat losses along the construction elements and calorimeter's inertia and possible retardation of the control system is required as well as more detailed consideration of the impact of reaction features (self-acceleration, reaction complexity, etc.). Nevertheless the results of this work not only reveal possible consequences of appearance of temperature gradient in an adiabatic bomb but also indicate the direction of essential improvement of the instruments.

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