Full Papers

Screening Adiabatic Calorimetry: Simulating $\varphi = 1$ in Glass Test Cells by Increasing the Concentration

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Abstract:
When a runaway reaction occurs in a large vessel in a chemical plant, the thermal inertia of the system will be very low (phi-(φ) close to unity). To mimic this behavior in an adiabatic reaction calorimeter, it is advisable to perform the measurements in a test cell with a φ factor close to unity as well. From a practical point of view, this is not always easy to realize. In this paper, we describe a possible way of simulating the behavior at $\varphi = 1$ in test cells with higher thermal inertia. This approach consists of leaving out an amount of solvent which matches exactly the thermal mass of the measuring cell. By doing so, the total adiabatic temperature rise will be reproduced correctly. Changing the concentration, however, will alter the reaction kinetics as well. This will lead to an overestimation of the maximum selfheat rate and an underestimation of the time to maximum rate. Hence, the error which is introduced is on the safe side of reality and, therefore, acceptable for screening purposes. The influence of different experimental parameters on the reliability of the result is discussed. The validity of this approach is demonstrated with a couple of examples.

1. Introduction

When a cooling failure occurs in a large scale chemical reaction vessel in which an exothermic reaction takes place (either a synthetic reaction or a decomposition reaction), the temperature in the system will start to rise. Such a vessel will behave more or less as a perfectly insulated system, in which there is no heat exchange between the vessel and the surroundings (the system is behaving adiabatically). At first, the temperature in the reaction mass will start to rise relatively slowly, but as the reaction continues, the temperature will increase and hence the reaction will proceed at a progressively faster pace.[1] The reaction rate will continue to increase with temperature, up to the point where the rate starts to drop again because of the depletion of the reagents. A typical temperature profile of a runaway reaction under adiabatic conditions is given in Figure 1. As indicated in the figure, there are three main features of such a temperature profile which are of interest: the adiabatic temperature rise
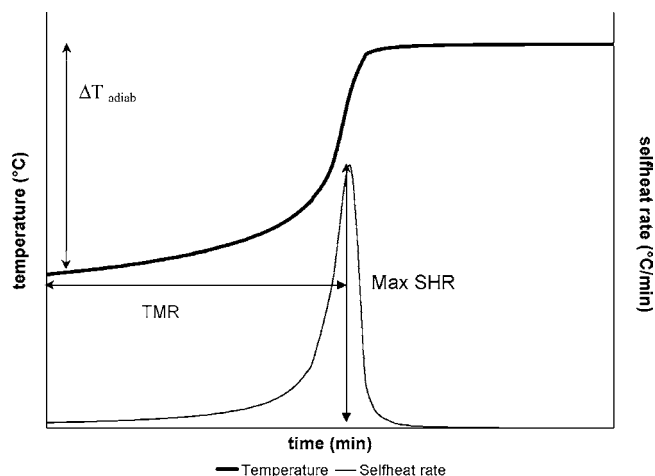

Figure 1. **Temperature profile of an adiabatic runaway reaction (thick line, left axis) and the corresponding selfheat rate (thin line, right axis). The key parameters obtained from adiabatic experiments are indicated.**

(ΔT_{adiab}), the time to maximum rate (TMR), and the maximum selfheat rate (max SHR). The adiabatic temperature rise is simply the total temperature rise which will be caused by an exothermic reaction when run under perfect adiabatic conditions. The selfheat rate is defined as the first derivative of the temperature vs time; it indicates at which rate (in °C/min) the temperature is increasing. The selfheat rate is at any time directly correlated to the energy content of the reaction mass. The maximum SHR is very often reported in runaway studies, since it is indicative of the relative speed with which the reaction proceeds, and it is an important factor for vent sizing calculations as well. Finally, the time to maximum rate (TMR) is an important figure as well. It indicates the time between the very first detection of the start of the temperature rise and the point where the SHR is at its maximum. The TMR gives guidance on the maximum time one would have to respond to a sudden cooling failure. If the TMR of a runaway reaction at a certain temperature is more than 8 or 24 h, it is generally considered to be safe for processes with a turnover time on the order of magnitude of 24 h (for continuous processes or distillations, a more conservative approach is often preferred). If the measured TMR under certain reaction conditions would be on the order of minutes, this would obviously leave no time to take appropriate measures to stabilize the situation.

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(1) Grewer, T. *Thermal hazards of chemical reactions*; Elsevier: Masterdam, 1994.

The behavior of an adiabatic system is hard to predict for an organic chemist, since it differs considerably from the thermal behavior of reaction masses as encountered in small scale experiments in the lab. This difference in behavior is due to the relatively large heat losses encountered in small scale experiments, as compared to the close to perfect thermal insulation of a reactor at production scale.[2] Therefore, adiabatic reaction calorimeters are commonly used in safety testing labs for the study of such runaway behavior. The most commonly known adiabatic instruments are the Accelerating Rate Calorimeter (ARC),[3,4] the Phi-Tec,[5] the VSP,[6] the Dewar vessel,[7] and the APTAC.[4] In these instruments, small scale experiments, typically in the range of 3 to 500 mL, can be performed in adiabatic conditions. This makes it possible to simulate several worst case scenarios in the lab and to extrapolate these data directly to plant scale conditions. Since these instruments are specifically designed for this kind of runaway studies, they can cope with the broad temperature and pressure ranges needed (typically up to 350 °C and 100 bar, respectively).

2. The φ-Factor

Apart from the fact that a vessel at production scale behaves as a perfectly insulated system (fully adiabatic), there is another factor which makes it difficult to simulate large scale runaway behavior in small scale experiments: the φ-factor. The φ-factor is defined by the following formula:[8]

$$\varphi = (m_c * c_{pc} + m_s * c_{ps})/m_s * c_{ps}$$

with m_c being the mass of the container (vessel at large scale or sample cell at small scale), m_s being the mass of the sample (reaction mass), and c_{pc} and c_{ps} being the heat capacity of this container and sample, respectively. This factor is a measure of which fraction of the thermal mass of the entire system is due to the thermal mass of the reaction mixture and which part is due to the container. In large scale equipment, the φ-factor of a vessel during a runaway will be close to unity: i.e., the thermal mass of the vessel itself (mainly the jacket) will be low compared to the thermal mass of the reaction mixture (i.e., $\varphi = 1$). In small scale laboratory equipment, the φ-factor is usually significantly higher than 1. The influence of the φ-factor on the runaway behavior of a system is very pronounced, as can be seen in Figures 2 and 3. In Figure 2, the same adiabatic runaway profile is given for a sample being tested in two different test cells, one with a (hypothetical) φ-factor of 1 and the other one with a φ-factor of 2 (runs simulated in AKTS[9]). As can be seen, the experimental curves differ drastically. In every aspect, the curve obtained with $\varphi = 1$ is by far more severe than the one obtained with $\varphi = 2$. The actual figures for the
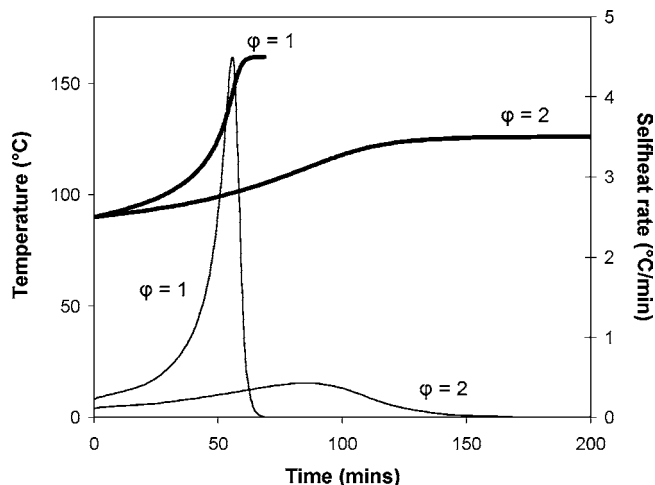
Figure 2. The same runaway profile measured hypothetically at $\varphi = 1$ and at $\varphi = 2$. The thick curves represent the temperature profile (left axis), whereas the thin curves represent the selfheat rate (right axis). Note especially the large difference in the maximum selfheat rate (AKTS simulation).
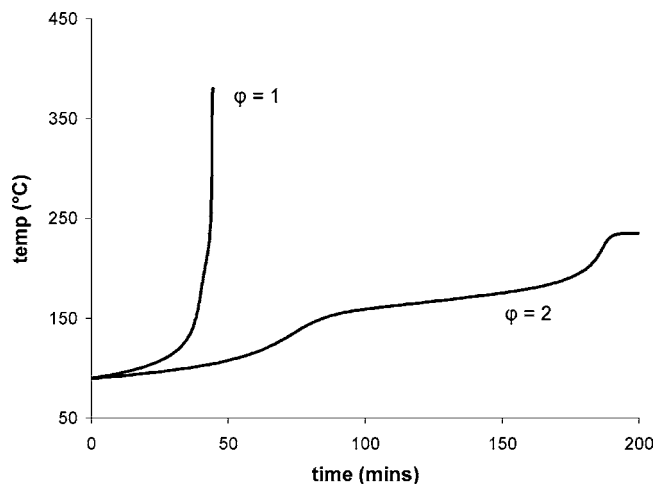
Figure 3. The same runaway profile measured hypothetically at $\varphi = 1$ and at $\varphi = 2$. The reaction consists of two consecutive reactions. In the run at $\varphi = 2$, both reaction steps can be observed, whereas they overlap in the run at $\varphi = 1$ (AKTS simulation).

Table 1. Key figures of the runaway profiles from Figures 2 and 3[a]

	ΔT_{adiab} (°C)	TMR (min)	max SHR (°C/min)
Figure 2, $\varphi = 1$	72	56	4.5
Figure 2, $\varphi = 2$	36	86	0.43
Figure 3, $\varphi = 1$	290	44	630
Figure 3, $\varphi = 2$	144	85	1.7
		191	5

[a] Note especially the dramatic effect of the φ-factor on the maximum SHR.

adiabatic temperature rise, TMR, and maximum selfheat rate are given in Table 1. Figure 3 also gives the runaway behavior of one reaction in a test cell with a (hypothetical) φ-factor of 1 as compared to the same run in a test cell with a φ-factor of 2. In this case, however, the difference between the two runs is even more pronounced. The reaction consists of two consecutive reactions, and running this reaction at

(2) Barton, J.; Rogers, R. *Chemical reaction hazards*; Institution of Chemical Engineers: Rugby, UK, 1993.
(3) www.thtuk.com.
(4) http://www.tiaxllc.com/technologies/tech_tiaxproducts.
(5) www.helgroup.com.
(6) www.fauske.com.
(7) www.chilworth.co.uk.
(8) Townsend, D. I.; Tou, J. C. *Thermochim. Acta* **1980**, *37*, 1.
(9) Advanced Kinetics and Technology Solutions: www.akts.com (AKTS thermokinetics software).
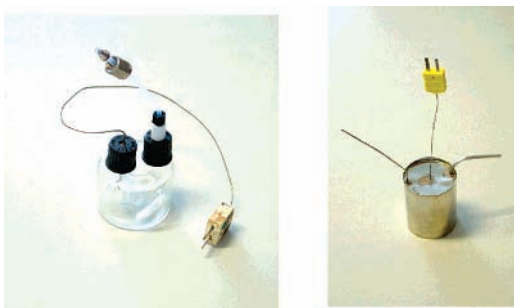
Figure 4. Two types of test cells used in the phi-tec adiabatic calorimeter: glass test cell (left) and metal test cell (right).

$\varphi = 1$ will result in a temperature profile where the first exotherm continues into the second one, leading to a very rapid temperature rise. In the run with $\varphi = 2$, the temperature rise from the first exotherm will be far less pronounced, and this will lead to a significant time interval between the two exotherms. Hence the severity of this run will be significantly lower than that of the run with $\varphi = 1$. Here as well, the key figures of the runaway reaction are depicted in Table 1. The figures in this table show that the influence of the φ-factor on the runaway behavior is very pronounced. The problem lies not so much in the difference in the adiabatic temperature rise, since it scales linearly with φ and can therefore be extrapolated to other φ-factors easily. The influence on the TMR and the maximum SHR is less straightforward, as can be seen from the figures. Neither of those can be extrapolated easily from one φ-factor to the other if the detailed kinetics of the reaction are not known. Note especially the very pronounced influence of the φ-factor on the maximum selfheat rate: a doubling in the φ-factor leads in our first example to a 10-fold decrease in selfheat rate! This clearly demonstrates the importance of the φ-factor and, hence, of the possibility to perform tests in the lab which mimic the large scale conditions as closely as possible.

3. Experimental Section

a. Phi-tec. The adiabatic experiments were performed in the Phi-Tec II adiabatic reaction calorimeter. Glass test cells were used as depicted in Figure 4. For the low φ measurements, thin walled glass was used; for the high φ measurements a can made from thicker glass and with an extra thick bottom plate was used.

1. Methanolysis of Acetic Anhydride. For the low $\varphi(=1.4)$ run, 14.61 g of acetic anhydride and 16.21 g of THF were introduced into the low φ can. The system was allowed to stabilize at 35 °C, after which 9.18 g of methanol were injected. The reaction then proceeded adiabatically. After a slight endotherm (mixing), the exothermic reaction started immediately. For the high $\varphi(=1.77)$ run with a concentration correction, 18.26 g of acetic anhydride, 11.48 g of methanol, and 10.27 g of THF were used in the high φ can.

2. Reaction of NaNO$_2$ with NH$_4$Cl. For the low $\varphi(=1.18)$ run, 3.78 g of NaNO$_2$ and 7.56 g of NH$_4$Cl were mixed with 48.66 g of water in the low φ can. This mixture was then brought to 45 °C, where the reaction started and was allowed to go to completion adiabatically. For the high $\varphi(=1.31)$ run, 4.23 g of NaNO$_2$ and 8.47 g of NH$_4$Cl were mixed with 47.3 g of water in the high φ can. This mixture was then brought to 45 °C, where the reaction started and was allowed to go to completion adiabatically.

b. Simulations. For the AKTS simulations,[9] all predictions were based on a model for the decomposition of cyanamide in water (either taking into account the entire decomposition or only the first part of this two-stage reaction).

All dynochem simulations[10] were based on a hypothetical first-order reaction A + B → C, with intermediate values for both reaction rate and activation energy. The reaction heat and starting temperatures were chosen in such a manner as to get runaway profiles as they are often obtained in adiabatic experiments (onset temperatures 40 to 80 °C, adiabatic temperature rises of ±100 °C).

4. Differerent Test Cells for Adiabatic Testing

The experimental work on which this study is based has been performed in the Phi-Tec II adiabatic reaction calorimeter (manufactured by HEL − UK). There are two different types of test cells which can be used in this instrument: metal test cells and glass test cells. A picture of both types of test cells is given in Figure 4.

a. Metal Test Cells. This type of test cells is the most popular of the two amongst most phi-tec users. The main reason for this is their inherently low φ-factor. They are made of very thin walled stainless steel and, therefore, are very light. This explains their low φ-factor, typically somewhere around 1.1. Working with this type of cans has some disadvantages as well, however. They can only be used once, which makes them relatively expensive. Introducing strongly heterogeneous samples in this type of test cells is far from trivial either, since the standard versions only have a $^1/_8$ inch feeding tube (although some versions with screw caps exist as well). The fact that they are made from steel makes visual inspection of sample heterogeneity, sample appearance before and after the run, etc. rather difficult. Finally, some reactions cannot be run in metal test cells because of the possible catalytic activity of the stainless steel. For all these reasons, metal test cells are not the first choice for phi-tec testing in our lab.

2. Glass Test Cells. Obviously, some of the disadvantages from the metal test cells are overcome when using glass test cells: visual inspection is easy, introducing the sample is also a lot easier since the glass cans possess two openings of 8 mm in diameter, and catalytic effects of the test cell itself are not an issue. The cans are relatively easy to clean and hence reusable, which makes them cheaper for routine testing. The thermocouple can usually be used for several consecutive experiments as well. This type of cells has the disadvantage that they are often hard to keep gastight at temperatures above 200 to 225 °C, due to the limited temperature range of the Teflon coated silicone septa used for the connection of the can to the tubing leading to the pressure transducer. Another, and probably the most important, disadvantage of this type of test cells is their relatively

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(10) Software from Performance Fluid Dynamics: www.scale-up.com.

Table 2. Example of the calculation of the φ-correction[a]

	mass test cell (g)	A (g)	B (g)	solvent (g)	concn A/B (g/g)	φ
ideal case ($\varphi = 1$)	0	10	10	50	10/70	1
uncorrected run	70	10	10	50	10/70	1.4
corrected run	70	14	14	42	14/70	1.4

[a] For the calculation, the definition of the φ-factor as given in the text is used, assuming a glass test cell with $c_p = 0.8$ J/g K and a c_p for A, B, and solvent = 2 J/g K.

high φ-factor (usually in the range 1.25−1.5). To overcome this disadvantage, the following strategy for adiabatic testing in glass test cells was developed.

5. φ-Correction by Concentration Change

The classical way of correcting for the φ-factor is by fitting the kinetic data with an *n*-th order reaction and then calculating the corrected temperature curve. There are some practical disadvantages to this approach however. Determining the reaction kinetics is not always straightforward, and often these kinetics can be complicated, with large deviations from *n*-th order behavior. Therefore a more practical experimental approach would be useful.

The possibility of compensating for the φ-factor by changing the concentration of the reaction mixture was first raised in a Technical Information Sheet from Thermal Hazards Technologies.[11] In this document, the authors state that simply substituting the heat capacity of the test cell by reducing the amount of solvent used will give results identical to performing the test at $\varphi = 1$. In principle, this seems a very attractive and elegant solution for a commonly encountered problem. The idea behind it is relatively simple: for reactions in solution, the heat of reaction in an adiabatic experiment will increase the temperature of the reacting species, the solvent, and the sample cell. If a part of the solvent whose thermal mass matches exactly that of the sample cell is left out, the overall thermal mass of the system will be comparable to that of a system with a φ-factor of 1. In practice, this means that the concentration of the reacting species (expressed in gram of reactant per gram of solution) should be multiplied exactly by the φ-factor. An example of how the "corrected" concentration is calculated is given in Table 2. However, the authors did not emphasize one very important aspect of the story, namely the change in reaction kinetics when changing the concentration of reacting species. From the above, it can be easily understood that the adiabatic temperature rise from a $\varphi = 1$ experiment can be reconstructed correctly in this manner, since the higher concentration of reagents will provide the extra heat needed to warm the sample cell. But since the concentration is altered, the reaction kinetics of the system will change as well. Common chemical reactions proceed faster at higher concentrations, and of course this will be the case here as well. A faster reaction rate at any temperature will lead to a shorter TMR
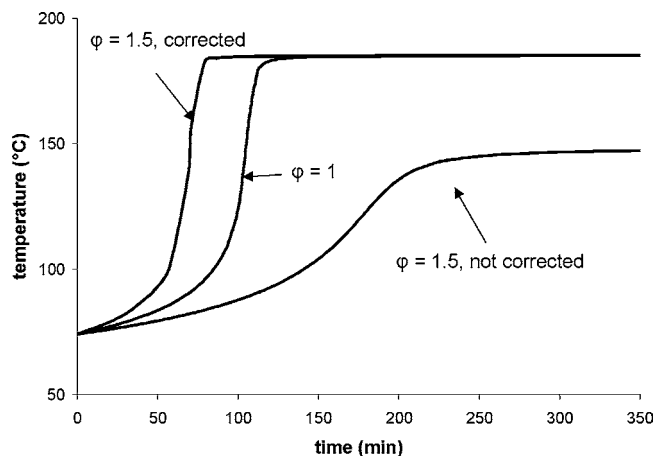
(11) Technical Information Sheet 24: *Tests at ö=1 with the accelerating rate calorimeter*, Thermal Hazard Technology, 1999; see download section at www.thtuk.com.

Figure 5. Simulated runaway profiles at different φ-factors, with and without correction by concentration increase (Dynochem calculations).

Table 3. Key figures of the runaway profiles from Figure 5, influence of the φ-correction by increasing the concentration (Dynochem calculations)

	ΔT_{adiab} (°C)	TMR (min)	max SHR (°C/min)
$\varphi = 1$	111	107	6.3
$\varphi = 1.5$, uncorrected	74	177	0.73
$\varphi = 1.5$, corrected	111	71	10.1

and hence a higher maximum SHR. This is illustrated in Figure 5, where the temperature profile of the same adiabatic reaction in three different reaction conditions is shown. The curve with the label "$\varphi = 1$" gives the temperature profile for the reaction to be studied under perfect adiabatic conditions and run under the "ideal" conditions, i.e., at $\varphi = 1$. The curve labeled "$\varphi = 1.5$ not corrected" gives the temperature profile for the same reaction mass, but this time measured in a test cell with a φ-factor of 1.5 (comparable to standard glass test cells in the phi-tec). The curve labeled "$\varphi = 1.5$, corrected" shows the temperature profile for this reaction in the same test cell but this time with an increase in concentration of the reacting species as described above. It can be seen that the concentration change leads to a correct adiabatic temperature rise. The "concentration corrected" profile reaches maximum faster than the curve of $\varphi = 1$, however, giving rise to both a shorter TMR and a higher maximum SHR (Table 3). At first sight, one could argue that, by using this φ correction, we have simply exchanged one type of measuring error for another. This is of course true, but there are two very important differences between these two types of errors. First of all, we have shifted the error to the "safe side of reality". The experimental curve shows a runaway profile which is worse than the "real" curve (shorter TMR and higher SHR). From a safety perspective, this is an acceptable error, whereas a systematic error to the other side (like when performing the run at $\varphi = 1.5$ without correction) is not acceptable. And second, the error in maximum SHR between the "real" curve and the corrected curve is a lot smaller than the error between the "real" curve and the uncorrected curve. Especially when the maximum
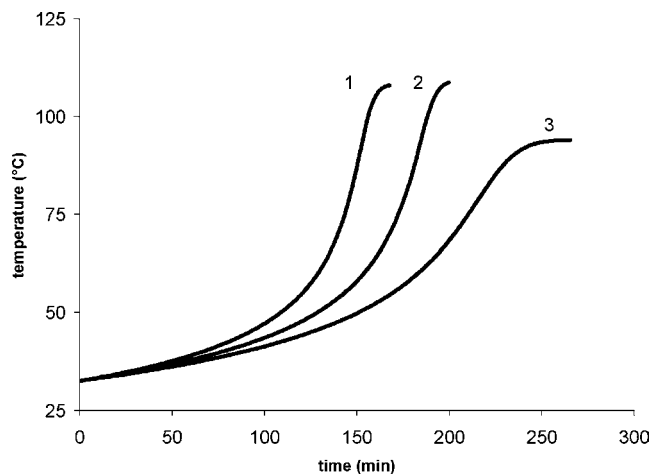
Figure 6. Experimental runaway curves of the methanolysis of acetic anhydride in THF. Curve 1: run at $\varphi = 1.77$, φ-corrected (to $\varphi = 1.4$) by increase in concentration. Curve 2: run at $\varphi = 1.4$. Curve 3: run at $\varphi = 1.77$, not φ-corrected.

Figure 7. Experimental runaway curves of the reaction between sodium nitrite and ammonium hydrochloride in water. Curve 1: run at $\varphi = 1.31$, φ-corrected (to $\varphi = 1.18$) by increase in concentration. Curve 2: run at $\varphi = 1.18$. Curve 3: run at $\varphi = 1.31$, not φ-corrected.

SHR is of importance, the corrected curve will give a better idea of the true value than the uncorrected one.

6. Experimental Examples

The validity of the reasoning behind this approach was proven theoretically but still needed to be validated experimentally. To do so, two model reactions were run in three different conditions: once in a low φ test cell, once in a high φ test cell without correction, and once in a high φ test cell with correction by an increase in concentration. Since we wanted to keep the experimental conditions in all runs as much as possible identical, we choose to perform all experiments in glass test cells. For the low φ runs, a test cell made from relatively thin glass was used, resulting in a φ-factor of approximately 1.4. For the high φ runs, a glass test cell made of thick glass with an extra thick bottom plate was used, resulting in a φ-factor of approximately 1.8. Since the φ correction needed to be made to a φ-factor of 1.4 and not to a φ-factor of 1, the concentration was increased by a factor of $\varphi_{high}/\varphi_{low}$ instead of a factor of exactly φ_{high}. In order for our approach to be valid, the low φ runs and the high φ runs with correction should match each other as closely as possible. Two different test reactions were run under these conditions: the methanolysis of acetic anhydride in THF and the reaction between sodium nitrite and ammonium chloride in water. The experimental curves are shown in Figures 6 and 7, respectively, and the key figures are given in Table 4. The conclusions which were drawn theoretically are confirmed experimentally: by using the φ-correction, the correct adiabatic temperature rise is obtained, the maximum selfheat rate is overestimated, and the TMR is underestimated. Therefore, the experiments prove that the correction gives results which are "on the safe side of reality". When looking at the temperature curves alone, the difference between the three curves might seem rather small, but the main difference between the uncorrected curve and the corrected one lies in the maximum selfheat rate. Here again, it can be seen that the maximum SHR is overestimated
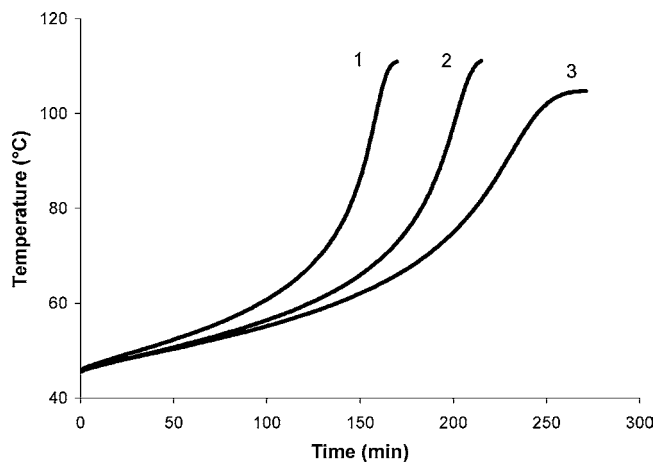
Table 4. Key figures of the runaway profiles from Figures 6 and 7, experimental data confirming the validity of the approach as explained in the text

reaction	figure	φ	corrected	ΔT_{adiab} (°C)	TMR (min)	max SHR (°C/min)
ac. anhydr.	6	1.4	no	75	183	1.9
ac. anhydr.	6	1.77	yes[a]	75	154	2.3
ac. anhydr.	6	1.77	no	61	215	0.7
NaNO$_2$	7	1.18	no	65	201	1.4
NaNO$_2$	7	1.31	yes[b]	65	158	1.8
NaNO$_2$	7	1.31	no	58	232	0.7

[a] Corrected to $\varphi = 1.4$. [b] Corrected to $\varphi = 1.18$.

but that the error made is smaller than the one between the low φ run and the uncorrected run.

7. Possible Problems

Whereas we have proven that this approach is valid in some ideal selected cases, it is worthwhile to take a closer look at some factors which might have an influence on its general applicability.

1. Practical Limitations to Concentration. Sometimes it is simply impossible to change the concentration of the reaction mixture. If the solvent is a reagent at the same time, for instance, the concentration of that particular reagent cannot be increased by leaving out some solvent. Sometimes reaction mixtures are so concentrated that making the φ-correction would lead to a reaction mixture without any solvent at all. There are also adiabatic experiments which need to be performed on reaction mixtures obtained from another lab or from a plant batch where this concentration change cannot be made. For those experiments, the approach described here cannot be used.

2. Wrong Estimation of φ-Factor. Whereas the formula for the calculation of the φ-factor seems straightforward, an accurate determination of the φ-factor is not always trivial. First of all, the heat capacity of the reaction mass is not always known accurately. For solutions, the specific heat capacity of the reaction mass is likely to be close to that of
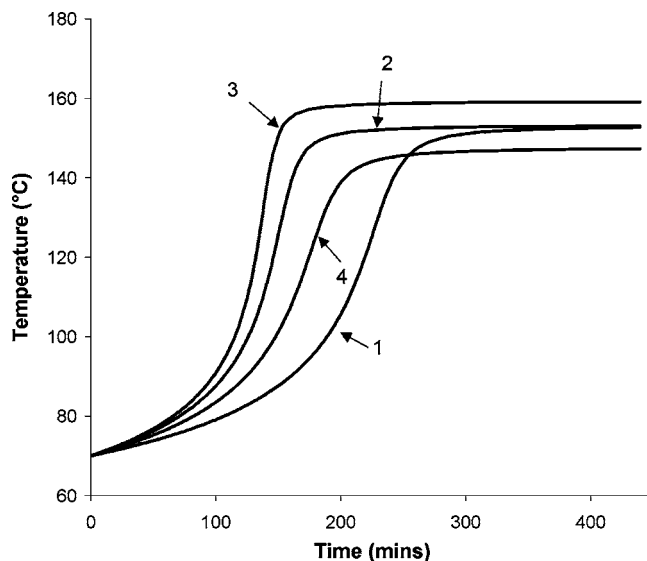
Figure 8. Influence of the accuracy of the estimation of the φ-factor and the consequent concentration correction on the runaway profiles. Curve 1: $\varphi = 1$. Curve 2: actual $\varphi = 1.5$, φ-factor used for concentration correction = 1.5. Curve 3: actual $\varphi = 1.5$, φ-factor used for concentration correction = 1.6. Curve 4: actual $\varphi = 1.5$, φ-factor used for concentration correction = 1.4. See text for further explanation (Dynochem calculations).

the solvent, but in very concentrated processes the deviation can be fairly large. If really necessary, the specific heat capacity can of course be determined in a separate experiment (e.g., in DSC or a reaction calorimeter). A second possible problem in the determination of the φ-factor lies, maybe surprisingly, in the difficulty of determining the mass of the sample container. Usually, the entire sample cell is weighed, and this value is used in the formula. Experience teaches however that this will often lead to an overestimation of the φ-factor. It can therefore be advisable to use the mass of the wetted area of the can, rather than that of the entire can. In Figure 8, the influence of the error of the calculation of the φ-factor on the adiabatic temperature profile is shown. In this figure, four different curves are shown. The first one gives the actual temperature profile for a run with $\varphi = 1$ (ideal case to be matched), and the second one gives the profile for a run in a test cell with a φ-factor of 1.5 and with a correct concentration correction as described above. The two other curves show the influence of a wrong calculation of the φ-factor. In curve number three, the effect of an overestimation of the φ-factor is demonstrated. For this run, a simulation was made of the process run in a test cell with a φ-factor of 1.5, but where the concentration correction was made as if the φ-factor were 1.6. Hence, there

will have been an "overcorrection" (concentration increased by a factor of 1.6 instead of 1.5), leading to a higher adiabatic temperature rise. For curve number four, an underestimation of the φ-factor was simulated (concentration correction for $\varphi = 1.4$, whereas the real φ-factor was 1.5). For both scenarios, it is believed that an error of 0.1 on the actual φ-factor is about the upper limit of a credible miscalculation. In practice, we believe that the φ-factor can be estimated with a precision of at least 0.1. The key figures of these four profiles are given in Table 5. It can be seen here again that the differences in adiabatic temperature rise and TMR are not very large but that the error on the maximum SHR cannot be ignored. Obviously, an overestimation of the φ-factor will lead to too large a correction and, hence, a further overestimation of the maximum SHR. This error will be on the safe side and is therefore acceptable. When underestimating the φ-factor, the correction will be too low, and the maximum SHR of this run will be lower than of that with a correct φ-correction. In fact, this SHR is even slightly lower than that of the $\varphi=1$ run; hence it is marginally on the unsafe side. This analysis shows the importance of a correct determination of the φ-factor. For practical use, we believe that a determination of the φ-factor within 0.1 should be possible, and hence the errors made are believed to be acceptable. Here again, we should stress that this approach is very useful for screening purposes but will not give a perfect representation of a runaway at $\varphi=1$.

3. Sample Homogeneity. Another point of interest is the solubility of the different compounds in the reaction mixture. By increasing the concentration, it is possible that the reaction mixture becomes heterogeneous, whereas it might have been homogeneous in the original recipe. This will pose no problems for producing the correct adiabatic temperature rise, since eventually all reagents are believed to go at least partly into solution and react. If the runaway reaction occurs very rapidly, however, it might be that the mass transfer from solid to liquid (dissolving of the reagent) becomes the limiting factor, resulting in a slower reaction rate. We do not believe that this effect will be very large when correcting for relatively low φ-factors (up to 1.5), but when testing strongly heterogeneous samples, one should always be aware of this fact. Note also that in principle the solubility of a compound increases at higher temperatures, and therefore a reaction mixture which is heterogeneous at the start of the run might very well turn homogeneous during the course of the runaway.

4. Overestimation of Gas Evolution Rate. In cases where a pressure increase during a runaway reaction is caused by the release of a permanent gas (and not only due to vapor

Table 5. Key figures of the runaway profiles from Figure 8, showing the influence a possible error in the determination of the φ-factor has on the φ-corrected adiabatic runaway profiles

description	curve	φ (real)	φ (assumed)	ΔT_{adiab} (°C)	TMR (min)	max SHR (°C/min)
plant scenario	1	1	1	83	224	0.96
φ estimation correct	2	1.5	1.5	83	152	1.44
φ overestimated	3	1.5	1.6	89	135	1.96
φ underestimated	4	1.5	1.4	77	179	0.94

pressure), increasing the concentration of the reagents will lead to an increase of the observed pressure as well. Here again, the severity of the runaway will be overestimated, and the error made is therefore acceptable for screening purposes. For vent sizing calculations, this method is obviously not applicable.

5. Change in Physical Properties of Reaction Mass. By changing the concentration of the reacting species, the physical properties of the reaction mass will change as well. An increase in concentration of the reacting species will change the polarity of the reaction mass, and as a consequence it is possible that the reaction mechanism could change as well. When the correction factor is relatively low (<1.5), we believe that the risk of this actually happening is small, but this possibility should be kept in mind when evaluating the results. Another property that changes when the concentration is increased is the boiling point. If a φ-corrected run is conducted in open conditions, this should be addressed as well. Generally spoken, the experimental boiling point in the φ-corrected conditions will be higher than in the uncorrected case, and hence the experimentally observed heat rate at the boiling point will be an overestimation. Therefore, the error will be on the safe side.

8. Conclusions

We described a method to mimic the runaway behavior at $\varphi = 1$ in screening adiabatic experiments when using test cells with a relatively high φ-factor. To obtain this, the concentration of the reacting species is multiplied by the exact value of the φ-factor. This approach will lead to an accurate determination of the adiabatic temperature rise, whereas the maximum selfheat rate will be overestimated and the time to maximum rate will be underestimated. This means that the obtained runaway profile will be more of a worst-case scenario than the actual runaway at $\varphi = 1$. The error is therefore on the safe side and acceptable from a safety perspective. This method allows a much better evaluation of the maximum SHR of a runaway than when only using uncorrected data from high φ experiments. Some of the factors influencing the reliability of this method were discussed, the most important one being a correct estimation of the φ-factor of the test cell used. Generally speaking, this method seems to be very valuable for routine adiabatic experiments at φ-factors up to 1.5. It should be stressed however that this approach remains an approximation, and appropriate care should be taken in evaluating the results. When in doubt, proper low φ adiabatic testing remains necessary.