A spreadsheet kinetic model and its use to compare ARC and Dewar storage test data for two exothermic decompositions

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Abstract

A spreadsheet for modelling ARC data according to autocatalytic or first-order kinetics has been developed. It has the advantage of producing graphs of model predictions versus experimental data which help greatly in the trial-and-error adjustment of kinetic parameters to obtain a good fit. An additional spreadsheet was also developed to find a single set of kinetic parameters representing the best fit to several experiments at different temperatures. These spreadsheets were used to model ARC data on two compounds which decomposed via an autocatalytic mechanism as indicated from previous Dewar experiments. Model calculations fit the shape of the ARC experimental temperature–time curves quite well. Kinetic parameters calculated by the model from the ARC data compare fairly well with previous Dewar test results on 4-chloroaniline. For 4-nitrophenol, however, ARC and Dewar tests give quite different results. This decomposition follows first-order kinetics in the ARC and autocatalytic kinetics in the previous Dewar experiments, with very different activation energies.

1. INTRODUCTION

A large number of compounds have been tested in the Hoechst AG laboratory for self-heating and subsequent runaway decompositions at various storage temperatures, using an adiabatic Dewar test apparatus [1]. Most of these decompositions proceed by an autocatalytic reaction

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mechanism. Recently, an accelerating rate calorimeter (ARC) was purchased as an additional tool for such investigations.

One purpose of the present investigation was to develop additional calculation methods to model the ARC data obtained from autocatalytic exothermic decompositions. The software furnished with the ARC has only a very simple calculation for decompositions following autocatalytic mechanisms. Moreover, while the ARC software can generate many useful types of plots of the experimental data and values calculated from this data, it has only limited ability to display time–temperature data generated by a kinetic model. The approach selected to remedy this situation was to develop a model using a computer spreadsheet. With a spreadsheet, one can easily present graphical results of model calculations. This is an advantage for fitting the model to experimental data.

Another purpose was to make a preliminary comparison of the previous Dewar test results with results obtained in the ARC. The ARC is a convenient and relatively fast means of investigating exothermic decompositions. However, the influence of the metal ARC sample containers compared to the all-glass environment of the Dewar tests, and possibly other factors, was unknown.

2. EXPERIMENTAL

2.1. *Thermal measurements*

The ARC was purchased from Columbia Scientific Industries, Austin, TX, USA. Spherical sample containers of about 1 inch i.d. made of titanium were used for the experiments with 4-chloroaniline, and similar containers of Hastelloy C were used for the experiments with 4-nitrophenol. The Hastelloy containers were used because they could withstand the higher pressures expected from the decomposition of 4-nitrophenol. The ARC was used in the "isothermal age" mode.

4-Chloroaniline (98%) and 4-nitrophenol were both purchased from Riedel-de Haen.

2.2. *Computer hardware and software*

An IBM PS/2 Model 80 386 with 4 Mbytes of RAM was used. The spreadsheet program used was Lotus 123 version 3.1. A short BASIC program was also written and used to perform the same calculations and compare them with spreadsheet results.

2.3. Calculation methods

2.3.1. Notation

k rate constant
A frequency factor
E_a activation energy
M_b mass of bomb (sample container)
M_s mass of test sample
C_{vb} mean heat capacity of bomb
C_{vs} heat capacity of sample
ϕ thermal inertia
T temperature at time t
T_0 initial temperature
T_f final temperature
T_f^* final temperature corrected for thermal inertia
TMR   time to maximum rate
TMR*   time to maximum rate corrected for thermal inertia
ΔT_{ad} adiabatic temperature rise
ΔT_{ad}^* adiabatic temperature rise corrected for thermal inertia
u conversion
β autocatalytic kinetic parameter

The model spreadsheet, called ARC–MOD2, was designed to model first-order kinetics as well as autocatalytic kinetics from ARC data obtained in the "isothermal age" mode. The theoretical and mathematical basis for describing thermal behavior for first-order kinetics is given in ref. 2, and is represented by the equation

$$dT/dt = k(T_f - T_0) \tag{1}$$

where

$$k = A\, e^{-E_a/RT} \tag{2}$$

The corresponding differential equation for autocatalytic kinetics, (ref. 1, pp. 97–99) is

$$dT/dt = k\Delta T_{ad}(1 - u)(u + \beta) \tag{3}$$

where k is again defined by eqn. (2) and β is a parameter related to the degree of autocatalysis. A low value of β means a strong autocatalytic effect. (The simplified autocatalytic equation used in the software supplied with the ARC is equivalent to assuming a vanishingly small β in eqn. (3) and hence only an extremely strong catalytic effect is considered [3].) The terms A, E_a and β (in the autocatalytic model) are treated as adjustable parameters to fit the model to the experimental ARC data.

Other equations used in the model spreadsheet calculations are

$$\phi = 1 + M_b C_{vb}/M_s C_{vs} \quad \text{(thermal inertia)} \tag{4}$$

$$\Delta T_{ad} = T_e - T_0 \quad \text{(adiabatic temperature rise)} \tag{5}$$

$$\Delta T_{ad}^* = \phi \, \Delta T_{ad} \quad \text{(correction for thermal inertia)} \tag{6}$$

$$T_f^* = \phi T_f \quad \text{(correction for thermal inertia)} \tag{7}$$

$$u = (T - T_0)/\Delta T_{ad} \quad \text{(conversion as } f(\text{temperature}))\tag{8}$$

In the model spreadsheet, dT in eqn (1) or (3) is treated as the independent variable. Starting with the value T_0, the temperature is incremented by dT in each row of the spreadsheet until the value of T_f is reached. The values of k, eqn. (2), u, eqn. (8), and finally dt, eqn. (3), are calculated in each row, and the dt values summed to yield the time t. The rate of temperature rise dT/dt is also calculated. To calculate model results at specified ϕ factors, especially $\phi = 1$, the final temperature and the adiabatic temperature rise used in these calculations are corrected for thermal inertia according to eqns. (6) and (7). The temperature increment dT is not constant, but starts at a very small value and increases with every row of the spreadsheet. The reason for this will be given in the Discussion section, below.

To validate a kinetic model, it is also necessary to describe the behavior of a substance at other temperatures with the same kinetic parameters A, E_a, and β, in addition to fitting a set of ARC data at a single temperature. This "best fit" set of parameters is found as follows. The set of data at one temperature is fitted so the model TMR exactly matches the experimental TMR, and the values of E_a, β, and A are recorded. This is repeated for several values of E_a and β. TMR values are then predicted using the ARC–MOD2 spreadsheet for each of the other sets of experimental data using the previously determined combinations of E_a, A and β. Finally, the set of values of these three parameters which results in the minimum relative TMR error squared, summed over all experiments, is found. A spreadsheet called OPTIMAL has been developed for this purpose. The summed error squared is presented in graphical form as a function of E_a and β for ease in interpretation and optimization.

Both spreadsheets are available from the first author, along with detailed notes and instructions for use.

3. RESULTS

3.1. *Testing the kinetic model spreadsheet*

The results of calculations of the time to maximum rate by the model spreadsheet and those obtained using a BASIC program were compared. In the BASIC program, the increment and number of iterations (up to 100,000)

TABLE 1

Test of kinetic model spreadsheet against numerical integration via a BASIC program

β	Kinetic/thermal parameters			Calculation method		
				BASIC program TMR	ARC–MOD2 spreadsheet TMR	% Error
	ΔT_{ad}	E_a	A			
Autocatalytic model						
1×10^{-1}	600	200	1×10^{14}	3409	3414	+0.1
1×10^{-1}	600	100	1×10^{5}	4871	4873	+0.3
1×10^{-1}	100	200	1×10^{15}	1416	1418	+0.1
1×10^{-1}	100	100	1×10^{6}	1767	1771	+0.3
1×10^{-9}	600	200	1×10^{16}	2771	2774	+0.1
1×10^{-9}	600	100	1×10^{7}	2230	2231	+0.04
1×10^{-9}	100	200	1×10^{16}	3100	3102	+0.06
1×10^{-9}	100	100	1×10^{7}	2540	2539	−0.04
1×10^{-12}	600	200	1×10^{16}	3936	3939	+0.08
1×10^{-12}	600	100	1×10^{7}	3128	3127	−0.03
1×10^{-12}	100	200	1×10^{16}	4264	4269	+0.01
1×10^{-12}	100	100	1×10^{7}	3400	3401	+0.03
First-order model						
	600	200	1×10^{13}	4147	4153	+0.1
	600	100	2×10^{4}	3513	3516	+0.09
	100	200	1×10^{14}	2951	2965	+0.5
	100	100	1×10^{5}	4604	4608	+0.09

were selected so that halving dT made an insignificant change (<0.01%) in TMR. Calculations with relatively high and low values of β, E_a, A and adiabatic temperature rise ΔT_{ad} were compared. Results are given in Table 1. Calculations with different values of A at the same E_a, β and ΔT_{ad} have been omitted. This is because TMR scales directly with $1/A$, and there is no effect on relative error.

3.2. *Exothermic decomposition experiments*

The ARC–MOD2 spreadsheet was used to fit ARC data obtained at several different temperatures for the two compounds 4-chloroaniline and 4-nitrophenol. The ϕ-corrected adiabatic temperature rise used in these calculations was the mean of the ΔT_{ad}^* for the individual ARC runs. A typical set of experimental data (4-chloroaniline at $T_0 = 240$°C) is shown in Fig. 1. Examples of the fit of the model to the experimental data for 4-chloroaniline at $T_0 = 220$°C and for 4-nitrophenol at 230°C are shown in Figs. 2 and 3. Two model-generated curves are shown in each figure. The
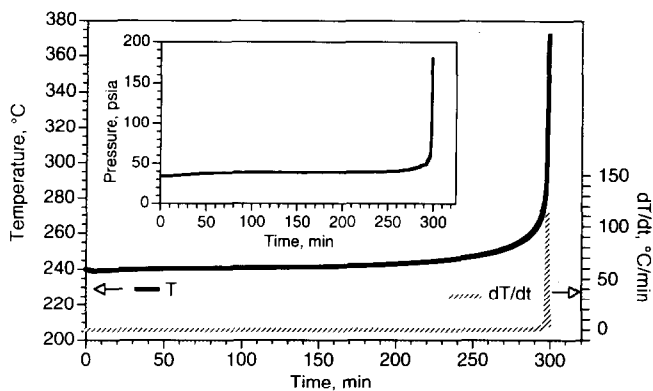
Fig. 1. ARC experimental time–temperature data for chloroaniline at an initial temperature of 240°C. Inset: pressure increase over the same time period.
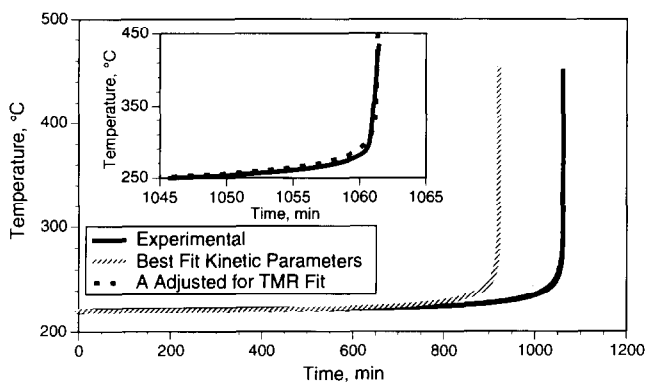

Fig. 2. Fit of autocatalytic model to ARC time–temperature data for 4-chloroaniline at an initial temperature of 220°C. Inset: detail of fit near the region of maximum curvature.
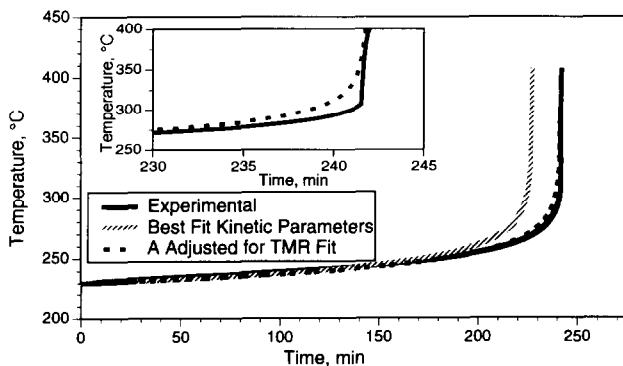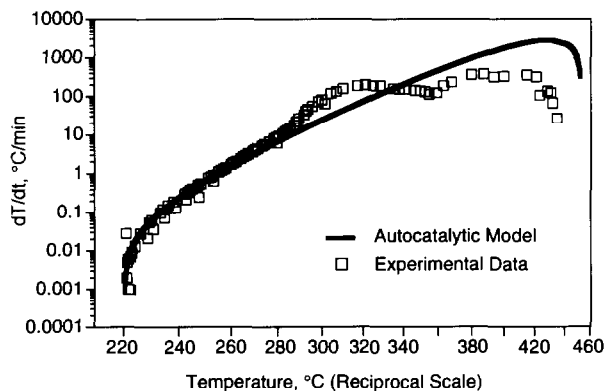

Fig. 3. Fit of autocatalytic model to ARC time–temperature data for 4-nitrophenol at an initial temperature of °C. Inset: detail of fit near the region of maximum curvature.

Fig. 4. Rate of temperature rise as a function of reciprocal temperature for 4-chloroaniline.

E_a, A and β values for the first model curve are the best fit values for the entire set of experiments at different temperatures for this compound. A second model curve, in which A is adjusted for an exact fit to the experimental TMR, is also included to show the fit of the model to the shape of the experimental temperature–time curve. Plots of the rate of temperature rise dT/dt against reciprocal temperature for both model and experimental data are given in Figs. 4 and 5.

Experimental data and the fit of the model were similar for other initial temperatures, with some of the model curves fitting the experimental data slightly better than the examples shown, and some fitting slightly less well.

The results of ARC analyses and model calculations compared to previous Dewar test results are given in Table 2. For 4-nitrophenol, curve-fitting data from both the autocatalytic and first-order models are given. The dependence of induction time on initial temperature is shown for the ARC model and Dewar tests in Fig. 6.
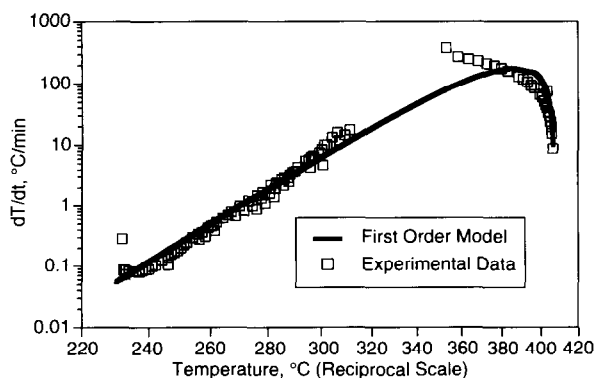

Fig. 5. Rate of temperature rise as a function of reciprocal temperature for 4-nitrophenol.

TABLE 2

Results of spreadsheet model fitting to ARC data for 4-chloroanaline and 4-nitrophenol

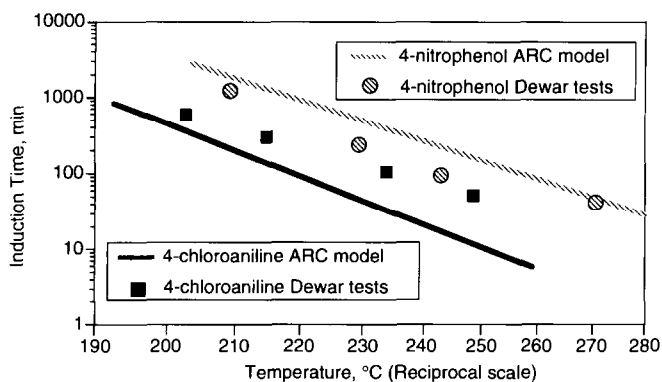| Compound (model)	Best fit kinetic parameter	Initial temp./ °C	ϕ	TMR exper./ min	TMR model/ min	% error	TMR model corr. to $\phi = 1/\text{min}$
4-Chloroanaline	$E_a = 145 \text{ kJ mol}^{-1}$	220	2.77	1060.9	920.8	−13.2	677.3
(autocatalytic)	$A = 9.15 \times 10^{12}$	230	4.49	432.2	524.4	+21.3	339.9
	$\beta = 0.001$	240	4.61	297.7	268.7	−9.9	175.3
		240	4.43	306.0	276.2	−9.7	175.3
		260	4.54	74.7	77.1	+3.1	50.2
4-Nitrophenol	$E_a = 175 \text{ kJ mol}^{-1}$	210	7.74	1215.5	1179.1	−3.0	146.8
(autocatalytic)	$A = 2.448 \times 10^{14}$	220	5.97	349.2	389.1	+11.4	62.4
	$\beta = 2$	230	7.64	241.6	225.4	−6.7	28.3
		240	8.61	124.3	118.4	−4.8	13.0
		250	7.53	45.3	48.9	+7.9	6.2
		250	7.72	54.5	50.3	−7.7	6.2
4-Nitrophenol	$E_a = 175 \text{ kJ mol}^{-1}$	210	7.74	1215.5	1178.5	+3.0	141.6
(first-order)	$A = 5.10 \times 10^{14}$	220	5.97	349.2	384.9	+10.2	61.1
		230	7.64	241.6	225.4	−6.7	27.3
		240	8.61	124.3	119.3	−4.0	12.6
		250	7.53	45.3	49.0	+8.1	6.0
		250	7.72	54.5	50.4	−7.6	6.0

Fig. 6. Comparison of induction time (TMR) as a function of reciprocal temperature as measured by Dewar test and ARC.

4. DISCUSSION

4.1. *Development of the kinetic model spreadsheets*

Previous evaluations of autocatalytic models used BASIC or other computer programs to perform the numerical integration of the differential equations involved [1]. A spreadsheet has one distinct advantage over a BASIC program: graphs comparing the experimental thermal behavior with that predicted by the model can be displayed almost instantaneously. This is particularly useful because the fitting of a kinetic model to experimental data is a trial-and-error process, involving adjustment of 2 or 3 factors (activation energy E_a, frequency factor A and autocatalytic parameter β).

Compared to a BASIC program, there is one serious problem to be overcome in developing a successful spreadsheet model: when the β parameter of the autocatalytic model is small, extremely small values of differential temperature dT are required to approach the true integral value by summing finite increments. With a BASIC program, this is merely a matter of making the increments very small, increasing the number of iterations, and letting the program run for a relatively long time.

In a spreadsheet, however, dT increments and the subsequent calculations each occupy several columns across a row. Each row corresponds to one iteration within a BASIC program. Attempting to increase the number of rows can quickly use up the available computer memory and increase the calculation time enormously. In the present case (Lotus 1, 2, 3 spreadsheet on an IBM computer with 4 Megabytes RAM), about 2000 rows is the practical maximum.

This limitation was overcome by using a changing, rather than fixed, dT increment. The temperature increment is made very small in the beginning of the reaction, but grows slowly with each step by a small factor (1.015) until it is equal to 1. It then remains at 1 for the remainder of the calculation. The appropriate small initial value of dT is calculated automatically so that the final temperature T_f is reached within the 2000 rows available. The reason for limiting dT to 1 is that larger values will produce unacceptable errors in the calculation of k. As seen in Table 1, the worst-case relative error for ARC–MOD2 using this approach is 0.5%. these results are completely satisfactory.

4.2. *Exothermic decomposition experiments*

The data for 4-chloroaniline in Table 2 indicate that the ARC data can be fitted reasonably well by an autocatalytic model. The experiment with $T_0 = 230°C$ fits less well than the others, but there is no reason other than its poorer fit to exclude it.

The activation energy for the ARC model and that for the Dewar test

compare reasonably well, as do the final pressures. However, the ϕ-corrected ΔT_{ad} for the ARC is more than six times greater than the observed value in the Dewar test ($\phi \approx 1$). There is also a discrepancy of up to a factor of about 2 in the induction times at a given temperature. The model for the ARC data generally predicts longer induction times than those observed in the Dewar tests. One possible explanation for the discrepancies between the ΔT_{ad} values determined by the two methods might be as follows. The ΔT_{ad}^* value from the ARC is a calculated value while that determined in the Dewar method is an experimental value. Because of the rather large ϕ value, the experiment in the ARC does not reach the same *actual* temperature as that in the Dewar, and different physical and chemical processes may occur in the two cases. Unfortunately, in this case, the actual temperatures observed in the Dewar and ARC experiments were very similar, ruling out this explanation. Alternatively, it might be that despite similarities in other aspects, a different reaction is actually taking place in the ARC, possibly catalyzed by the metal walls of the ARC sample bomb. For the present, the reason for the large difference in adiabatic temperature rise remains unknown.

It is apparent, expecially from the dT/dt versus $1/T$ plot of Fig. 4, that the decomposition taking place is not a simple, single reaction. Nevertheless, the fit of the model in the beginning portion of the curve and the accurate prediction of the process leading up to a runaway decomposition are most important from a safety standpoint. The departures in the heating rate from the model predictions at higher temperatures take place in a very short time period at the end of the long induction time. At this point, the process has been set in motion and it is probably too late to do anything about it anyway.

Overall, a moderately good case can be made for similar behavior of 4-chloroaniline in the ARC and in the Dewar tests: at least, it clearly seems to follow an autocatalytic mechanism.

Note that the dependence of TMR on ϕ for an autocatalytic reaction is no longer the simple approximation TMR* = TMR/ϕ. This result is approached when β becomes very large, but at low β values, ϕ has a smaller effect on TMR. For example, for 4-chloroaniline with $\beta = 0.001$, the corrected TMR values in Table 2 are roughly three times larger than those predicted from the simple first-order approximate solution. The relationship between β and the correction to TMR for thermal inertia is further illustrated in Fig. 7 for a hypothetical reaction with thermal and kinetic parameters similar to those in the present investigation. The correction factor is also influenced by ΔT_{ad} and E_a but not so strongly as by β. Given the relationship of ϕ to β, two otherwise identical ARC runs with significantly different ϕ factors may be a good way of determining β. This point requires further investigation.

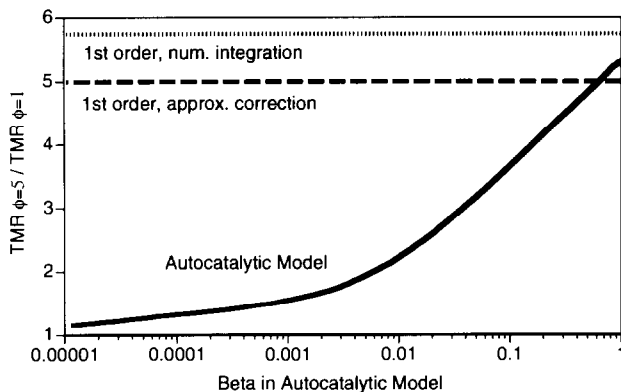The results of ARC experiments on 4-nitrophenol are very different

Fig. 7. Relationship between autocatalytic parameter β and the correction of TMR for thermal inertia for a hypothetical exothermic decomposition with $T_0 = 200°C$, $\Delta T_{ad}^* = 500°C$, $E_a = 160 \text{ kJ mol}^{-1}$, $\phi = 5$.

from those found earlier in the Dewar tests. The autocatalytic model fits the data well only with a large value of β, and in fact, a first-order model fits slightly better. Given the strong interaction of β and the ϕ-correction discussed above, it might be suspected that the two ARC experiments with ϕ values considerably different from the others ($T_0 = 220$ and $240°C$) exert an undue influence on the model fit. However, exclusion of these two experiments makes hardly any difference in the results. A first-order reaction with an E_a value of around 170–180 kJ mol^{-1} is still indicated. The best-fit model activation energy is much higher than the apparent activation energy found earlier in the Dewar tests, and the adiabatic temperature rise and final pressure is also higher (Table 3). The difference in activation energy is also apparent in Fig. 6, and the induction times predicted by the ARC model are considerably shorter, expecially at higher temperatures.

As in the case of 4-chloroaniline, Fig. 5 indicates that the decomposition

TABLE 3

Comparison of ARC and Dewar test exothermic decomposition data

Compound	Experimental method	$E_a{}^a$ kJ mol^{-1}	Mean ΔT_{ad} K	Mean max. press./bar
4-Chloroaniline	ARC	145	645	25
	Dewar	124	100	21
4-Nitrophenol	ARC	175	1354	125
	Dewar	117	>300[b]	31

[a] For the Dewar test, the apparent activation energy from the slope of the plot of ln(TMR) vs. $1/T$.

[b] The final temperature was over the 500°C upper measurement limit.

of 4-nitrophenol is also not a single, simple reaction. The remarks made earlier about the importance of the initial stages of the process relative to the later stages also apply here.

All these differences indicate that different reactions or reaction mechanisms are taking place in the ARC and in the Dewar tests. Previous experiments in glass sample containers definitely indicated an autocatalytic mechanism for the decomposition of 4-nitrophenol [4]. The influence of the Hastelloy ARC sample bomb is therefore suspected in the present case.

5.   CONCLUSIONS

A spreadsheet for modelling ARC data from a single experiment with autocatalytic or first-order kinetics was developed. It has the advantage of producing graphs of model predictions versus experimental data which help greatly in the trial-and-error fitting process. An additional spreadsheet has also been developed to optimize the fit of the kinetic parameters to several experiments on nitrophenol; however, ARC and Dewar tests give quite different results. The decomposition follows first-order kinetics in the ARC and autocatalytic kinetics in previous experiments in glass, with very different activation energies.

ACKNOWLEDGEMENTS

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