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DATA ACQUISITION AND PROCESSING FOR THE ACCELERATING RATE CALORIMETER

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ABSTRACT

Extensive programs have been written for data acquisition and processing for the Columbia Scientific Industries Accelerating Rate Calorimeter (CSI ARC). Initiation and data processing are menu driven and designed for minimum operator interaction. Upon completion of an experimental run a cover page is printed and the five most-often-used graphs are plotted. The system also allows for the plotting of additional graphs as described in the CSI operators' manual. Finally, the system is also capable of producing a report cover sheet containing a summary of experimental conditions and simple interpretation of the data for up to twelve individual runs.

INTRODUCTION

The Dow Analytical Laboratories have had eight Columbia Scientific Industries Accelerating Rate Calorimeters (CSI ARC) in nearly constant use for about six years. It has been apparent to us for some time that the lack of permanent microprocessor storage was a drawback of the system. A new experiment on the ARC could not be initiated until the previous data file was deleted. This necessitated the plotting of all possible graphs available from the system [1]. This plotting sequence could take from 15 min to 1 h [2] depending on the number of plots required. If any graphs were inadvertantly skipped, the only way to obtain them, or replot any graph, was by hand. A number of the standard plots were oversized (11 × 17″) requiring reduction for report writing and extra storage space for original data files.

Our goal for this project was to permanently store the ARC data on magnetic media and automatically produce the most useful graphs with the ability to generate any of the other plots easily. The basic requirement was that the system be easy to learn and use, so that a laboratory technician could initiate a data collection (and subsequent data processing) in minimum time for a run on an ARC.

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DISCUSSION

We had a DEC LSI 11/23 in the laboratory equipped with serial port interface, two hard disk drives, and two floppy diskette drives, running under RT-11 version 4.0. As the system could not be dedicated solely to the ARCs, we decided only to collect the data passively using an RS-232C interface from each unit. The CSI microprocessors would still be used to control each individual ARC unit.

The system was set up to collect the character information available through the RS-232C interface. This information was the same as that on the system printer tape. Initialization of an experimental run would create a data file on the computer that would collect this character information and open up a data collection channel (indicated by illumination of a light). Termination of data acquisition would simply be accomplished by pressing a button. The computer would then take charge by converting the data, storing the converted files, automatically printing a cover page followed by the plotting of the five ARC graphs most often used in consultation: (self-heat rate vs. temperature, temperature vs. time, pressure vs. time, pressure vs. temperature, and pressure rate vs. temperature), and printing a data list. Data acquisition takes place in foreground memory (written in DEC assembler, MACRO-11), while data processing takes place in background memory (written in FORTRAN IV).

The graphics terminal always displays the master control menu when the system is idle:

Date:	6-June-83	Time:	15:06:34
INSTRUMENT	STATE	ELAPSED RUN TIME	TOTAL RUN TIME
DSC-A	idle	–	–
DSC-B	idle	–	–
DSC-C	idle	–	–
ARC-1	active		
ARC-2	active		
ARC-3	idle		
ARD-1	idle		

Enter 1 to initialize a sample run
2 to plot a sample run during data collection
3 to abort a sample run
4 to print an AL report cover sheet
5 to plot a sample result
6 to perform a library search
7 to initialize a special run
8 to halt the foreground and exit to RT-11 monitor
9 to exit to the RT-11 monitor

In order to initialize an ARC run, the operator chooses option 1 of the master control menu on the graphics terminal. After choosing this option, the operator is then asked which instrument the initialization is for. The computer then determines if the requested instrument is idle. If in use, the operator is given a choice to choose another instrument or exit the program. If the instrument is free, the operator is asked if old sample information is to be recalled for the description, or if new information is to be entered. If the former is chosen, the program proceeds directly to display the descriptive information already in storage, if it can be found. If the computer is unable to recall the information, the operator is given the choice of entering new information or exiting the program. If the operator chooses to enter all new information, a series of brief questions is asked in order to obtain this descriptive material.

The operator is asked to enter the sample number, up to three customer names, addresses, and phone numbers, charge number, and sample description (any entry may be left blank). The operator chooses the sample atmosphere and operator name from option menus. The operator is then asked if there are any special handling instructions for the sample. If there are none, the program proceeds to list the newly entered information. If there are any special handling instructions, the operator is asked if any of these require special safety equipment. In addition, there are eight lines available for any other instructions. The program then proceeds to list the newly entered information in two pages.

Page 1 contains the descriptive information in table form (vide infra). The operator now has an opportunity to correct any mistakes made in entering the information. When satisfied, the operator enters a carriage return. This will then lead to the display of the second page of the information, the special instructions. If none were entered, the word NONE is displayed. The operator, again, has the opportunity to change the information on this page. When satisfied, the operator need only enter a carriage return to have the computer complete the initiation routine by opening up a computer channel to the RS-232C interface to the ARC unit.

The following is an example of the two-page parameter display on the computer terminal:

Initialization of an ARC run Page 1

1 Sample description:

20% Di Tert Butyl Peroxide in Toluene

2 Customer name	Hofelich
3 Customer address	438
4 Second person receiving report	
5 Address of second person	
6 Third person receiving report	
7 Address of third person	
8 Customer phone number	5960

9 Customer charge	0000
10 RCM number	83-398
11 AL number	
12 Analyst name	H. Raykovitz
13 Head space atmosphere	air
14 Stirring rate	0 rev/min
15 Store on cassette tape	NO

Enter the parameter number to modify, or RETURN to proceed

Initialization of an ARC run Page 2

Special instructions for this sample:

NONE

Enter 1 to change the instructions or RETURN to continue

When the initiation routine is complete the green light on the interface box to the ARC unit will be turned on and the master menu will return to the screen with the initialized ARC now containing the message "active".

There are two ways to stop an ARC data acquisition. One way is by pressing the green run button on the interface box. This both turns off the light, and signals to the computer that the run has finished (as evidenced by the status "idle" for the ARC unit on the master menu). The data processing program proceeds automatically (vide infra). The second way to end an ARC data acquisition is from the terminal using master menu option number 3 to abort a sample run. When this option is chosen, the computer then displays the instrument list so that the operator may choose which instrument is to be stopped. The computer then gives the operator the following options:

Enter 1 to delete the data file
2 to save the data file?

If the operator chooses option 1, the instrument status is returned to idle and the file created when the instrument was initialized is destroyed. There is no way to recover a data file if this option is chosen. If option 2 is chosen, the computer proceeds in the same manner as if the button on the interface box had been pressed.

When the interface button is pressed or if the operator chooses option 2 after aborting a run, the computer automatically begins to process the ARC data if the computer background memory area is idle. If the background is not idle, the computer will queue the data file for later processing.

When background memory space is available, the computer begins to process the ARC file. First the file is renamed, and a new file with the old name is created. The old data file (now with a temporary name) is then processed. The data file consists of character data (8 bit ASCII information).

The computer begins to "read" the file, looking for key words. One such word is ENTER. When this work is found, the computer then proceeds to collect the rest of the descriptive information that is available: sample mass, bomb mass, bomb type, and data type (necessary for reading and converting data). This information is converted to real numbers (or integers) and stored in the descriptive information area of the new file (known as the header blocks, since these blocks are the first in the file).

Another important key word is EDIT. EDIT parameters 1 (start temperature), 2 (end temperature), 3 (rate threshold), 4 (heat step), 11 (wait time), and 12 (isothermal wait time) are all converted to real numbers and stored in the header blocks.

The computer is capable of reading an ARC LIST file in the same manner since the only difference between a real-time and a LISTing is the arrangement of the information.

When the computer reads HEAT, WAIT, SEARCH, or EXOTHERM, it then expects to find data. If the line meets the data criterion (a dot "." in the fifth space of the line), the computer will convert that line to real numbers according to the data type: 0, time, temperature, and rate; 1, the same as data type 0 with pressure; 3, the same as data type 1 with delta temperature. In the data file, the data lines are labeled according to their type: 0, continuing EXOTHERM data or any unlabeled data line; 1, beginning of an EXOTHERM; 2, SEARCH data; 3, WAIT data; and 4, HEAT data. Although only EXOTHERM and SEARCH data are currently used in plotting, all of the data are available for future use.

The computer ignores all other information printed by the ARC. When the processing is complete, the file is first shortened and then made permanent on the hard disk (the last fifty files are kept on the hard disk). The file is automatically copied to a floppy diskette for permanent storage. If the floppy diskette is missing, the operator is informed via a message on the terminal. The last thing done in the data processing program is to create an entry for the new file in the sample run indexing file. The file name, sample number, backup floppy diskette number, file type (ARC), and a brief description are entered. The computer then sends control to the printing/plotting programs.

The system utilizes a Hewlett-Packard 7245B plotter/printer for output. The first page of the output is a run report page (Fig. 1). This page contains the operating parameters of the run, the descriptive information entered when the run was started, a calculation of the thermal ratio, phi, a list of the special instructions (if there were any), a paragraph describing the experimental procedure, and a statement of general precautions.

This report page is followed by five plots. They are: self-heat rate vs. temperature (Fig. 2), temperature vs. time (Fig. 3), pressure vs. time (Fig. 4), pressure vs. temperature (Fig. 5), and pressure rate vs. temperature (Fig. 6). All plots contain EXOTHERM data. In addition, the two pressure plots (4 and 5) also contain SEARCH data. The SEARCH data are plotted as single points rather than as a continuous line, so as to distinguish them from EXOTHERM data. The plots are followed by the data list. The first page of such a list is contained in Fig. 13.

Accelerating Rate Calorimetry

Analytical Laboratories, Michigan Division, Dow Chemical Company

RCM 83-398 ARC run on 31-MAY-83 at 10:08:46

20% Di Tert Butyl Peroxide in Toluene

Submitted by: T. Hofelich From: 438 Building
Phone number: 6-5960 Charge number:
Run by: H RAYKOVITZ ARC # 2

The ARC Experimental Conditions

Bomb type	No. 1, .032" wall, 1" Titanium	
Bomb weight, Mb	8.820	g
Sample weight, Ms	4.310	g
Total volume of the system, Vb (approx)	9.0	mL
Sample volume, Vs (approx)	5.0	mL
Head space volume, Vg (approx)	4.0	mL
Head space atmosphere	air.	
Heat capacity of the bomb, Cb	0.130	cal/deg C g
Heat capacity of the sample, Cs (assumed)	0.500	cal/deg C g
Starting temperature	80	deg C
End temperature	250	deg C
Heat step	5.00	deg C
Wait time	15	min
Isothermal wait time	0	min
Calorimetric rate threshold	0.020	deg C/min
Stirring rate	0	rpm
Store on cassette tape	NO	

Thermal ratio, ø = 1 + (Mb Cb)/(Ms Cs) 1.53

WARNING: The calculation of ø is based on an assumed or estimated average sample heat capacity over the experimental temperature range.

Special instructions for this sample:

NONE

EXPERIMENTAL

The specified amount of the sample is introduced into the sample bomb which is in turn fitted to the calorimeter lid. The calorimeter is then rapidly heated to the initial temperature after which either an isothermal age mode or a WAIT-SEARCH-HEAT sequence is entered to look for exothermic reaction self-heating. When less than the self-heat rate threshold is observed during the SEARCH mode or at the end of the isothermal age time, a heat step is applied to the calorimeter contents. A WAIT-SEARCH-HEAT process is repeated until the self-heat rate of the bomb exceeds the threshold rate at which time the reaction is allowed to proceed on its own under nearly adiabatic conditions. Detailed procedures for the ARC can be found in the CSI operating manual.

GENERAL PRECAUTIONS

Accelerating rate calorimetry offers a useful method for evaluating exothermic runaway processes. However, caution should be used when relating the ARC data to an actual plant process since ø for an ARC experiment is usually very different from ø for a large-scale reaction. In addition, special consideration is needed when kinetic complications are present in the ARC data. For example, the effects of autocatalysis or inhibitors can vastly change the runaway reaction in chemical storage situations.

Consultation with Reactive Chemicals is recommended in the applications of ARC data to plant processes. Extrapolation of the data outside the experimental range is generally unwise.

Fig. 1. ARC experimental run report page containing experimental conditions and general precautions.

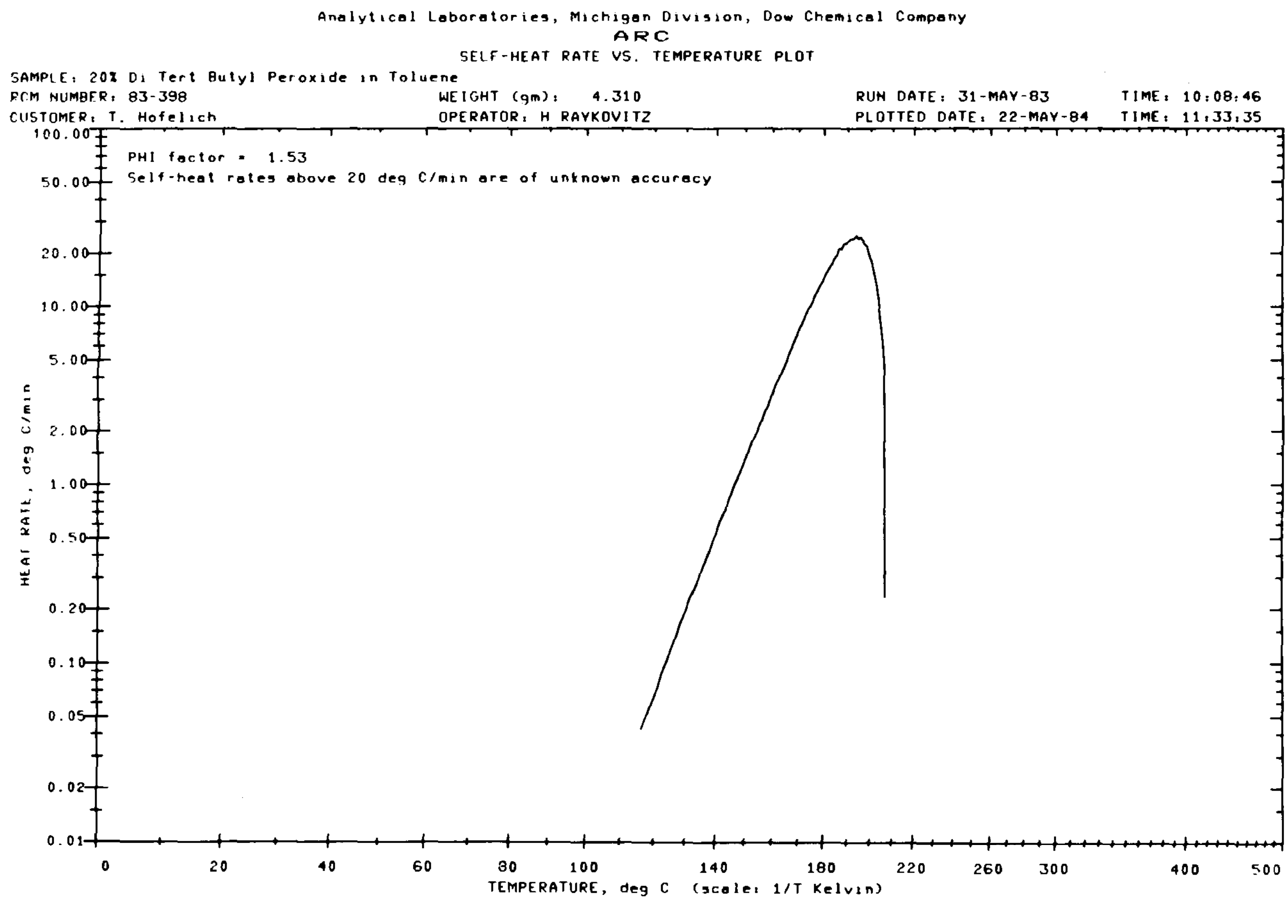

Fig. 2. Graph of self-heat rate vs. temperature in °C plotted as log of rate vs. $1/T$ in K.

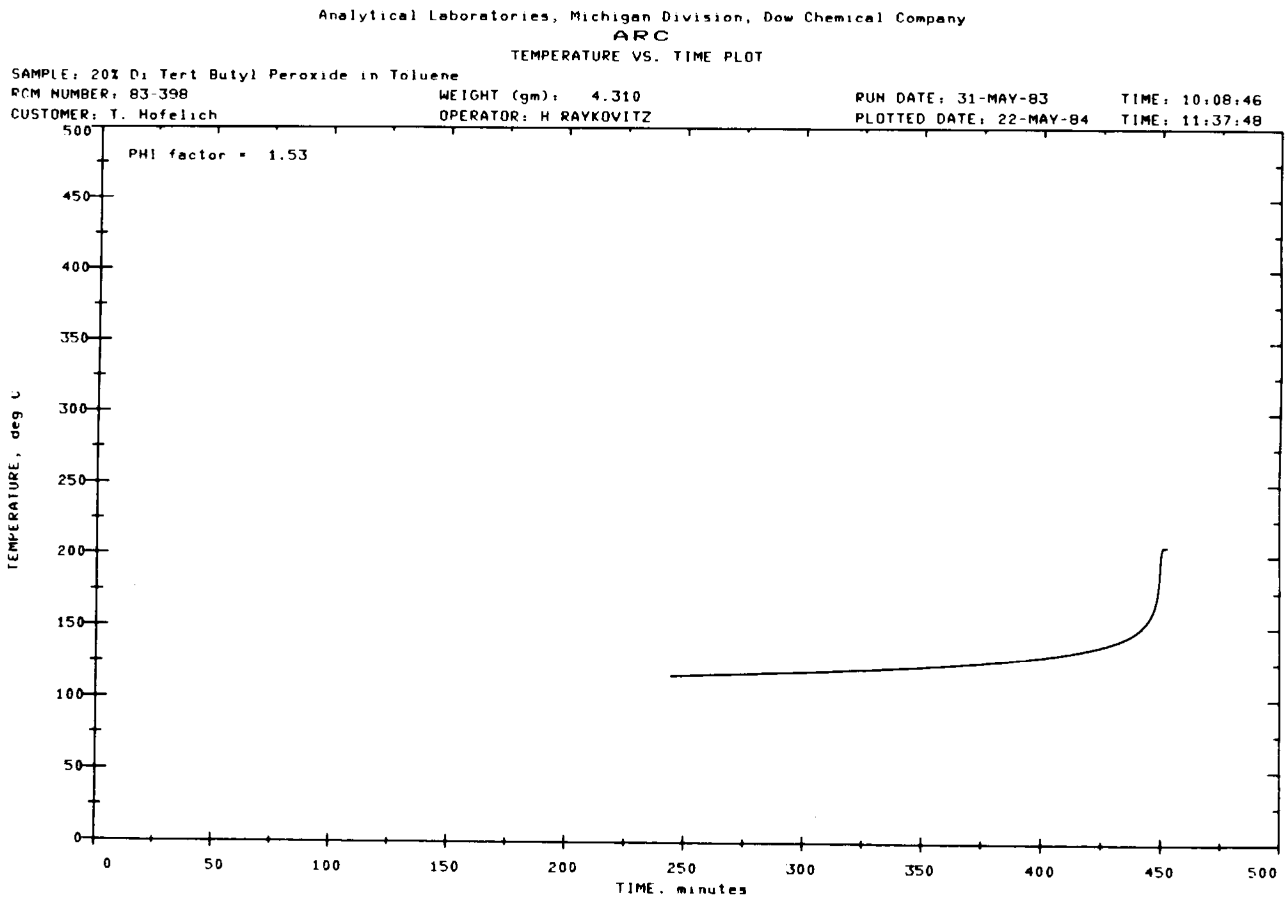

Fig. 3. Plot of temperature in °C vs. time in min.

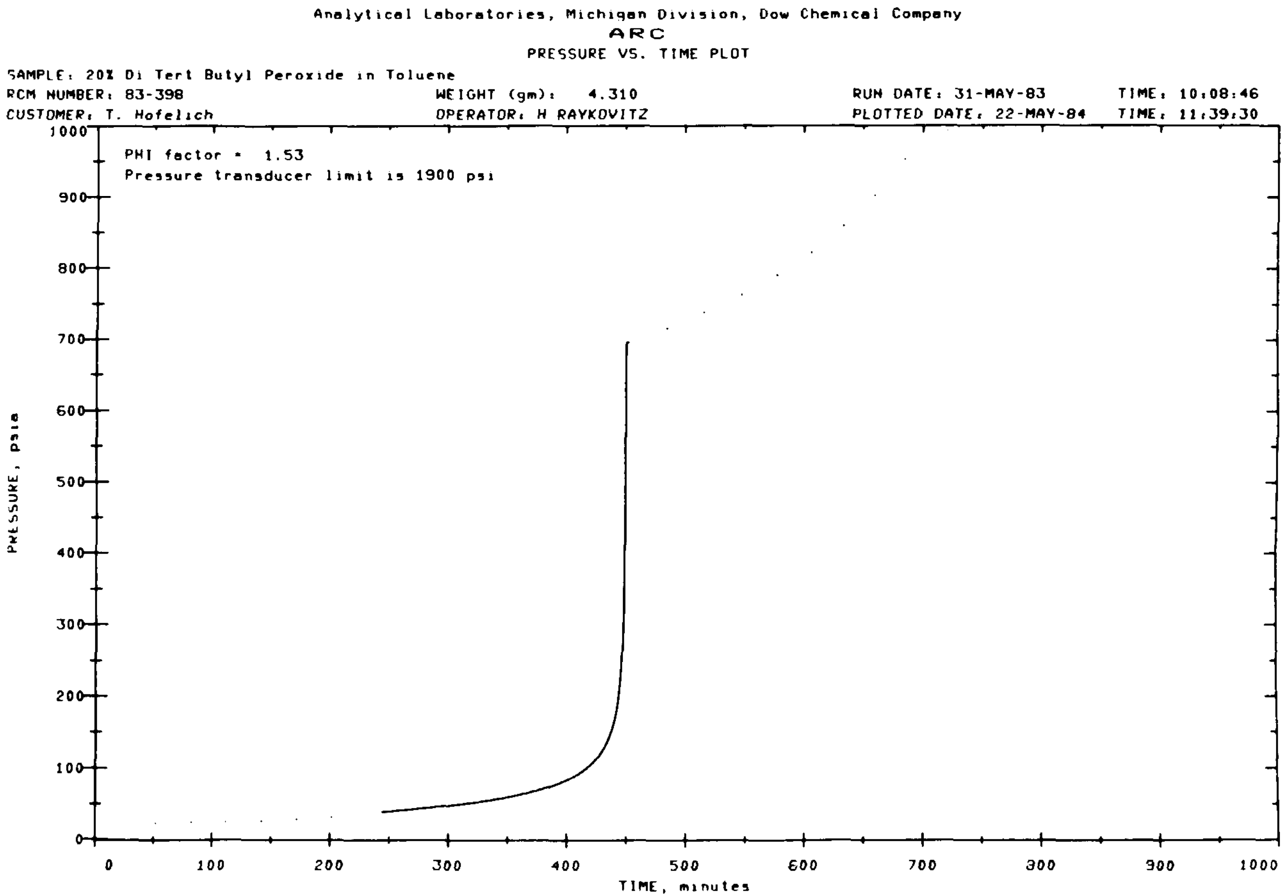

Fig. 4. Plot of pressure in psia vs. time in min.

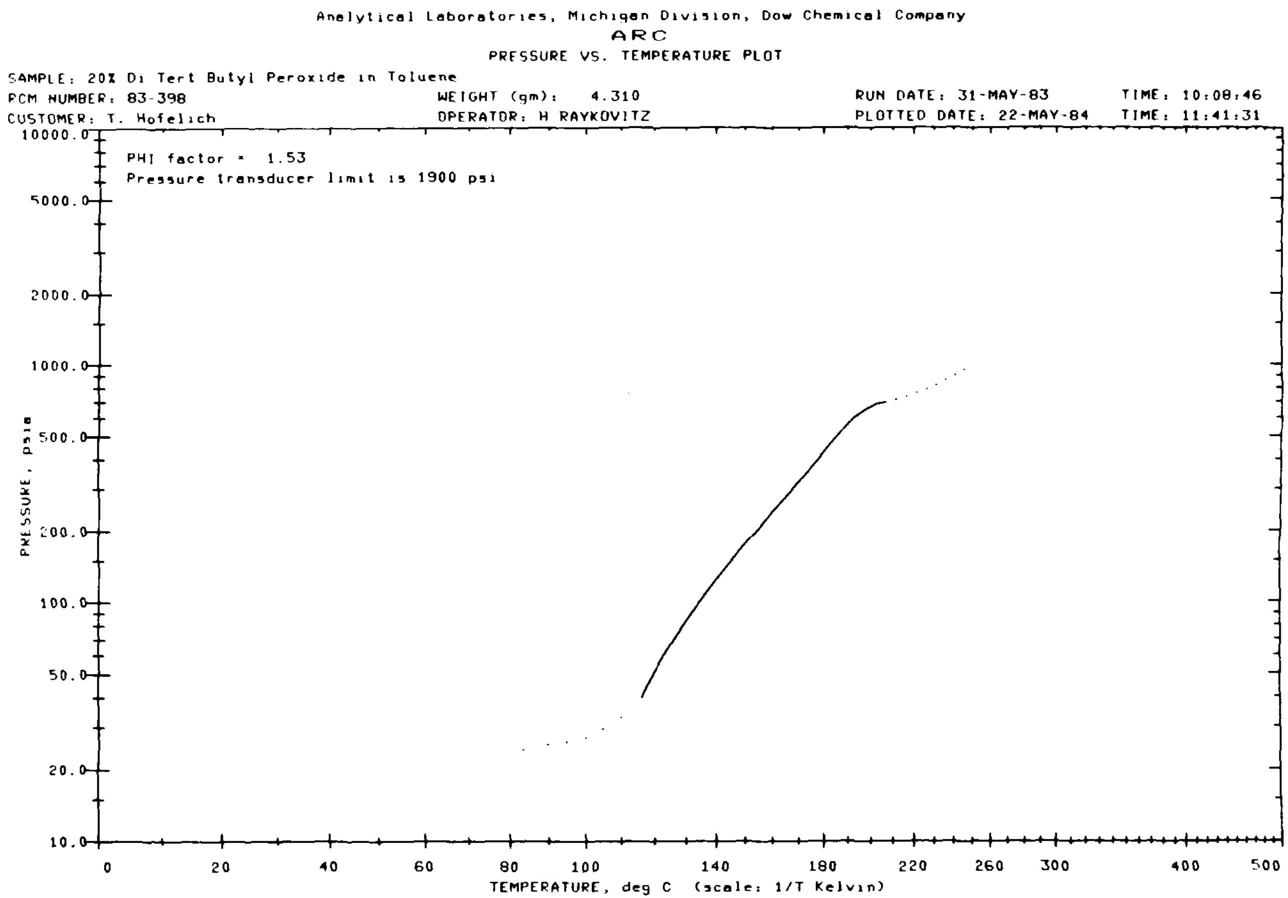

Fig. 5. Graph of pressure in psia vs. temperature in °C plotted as log of pressure vs. $1/T$ in K.

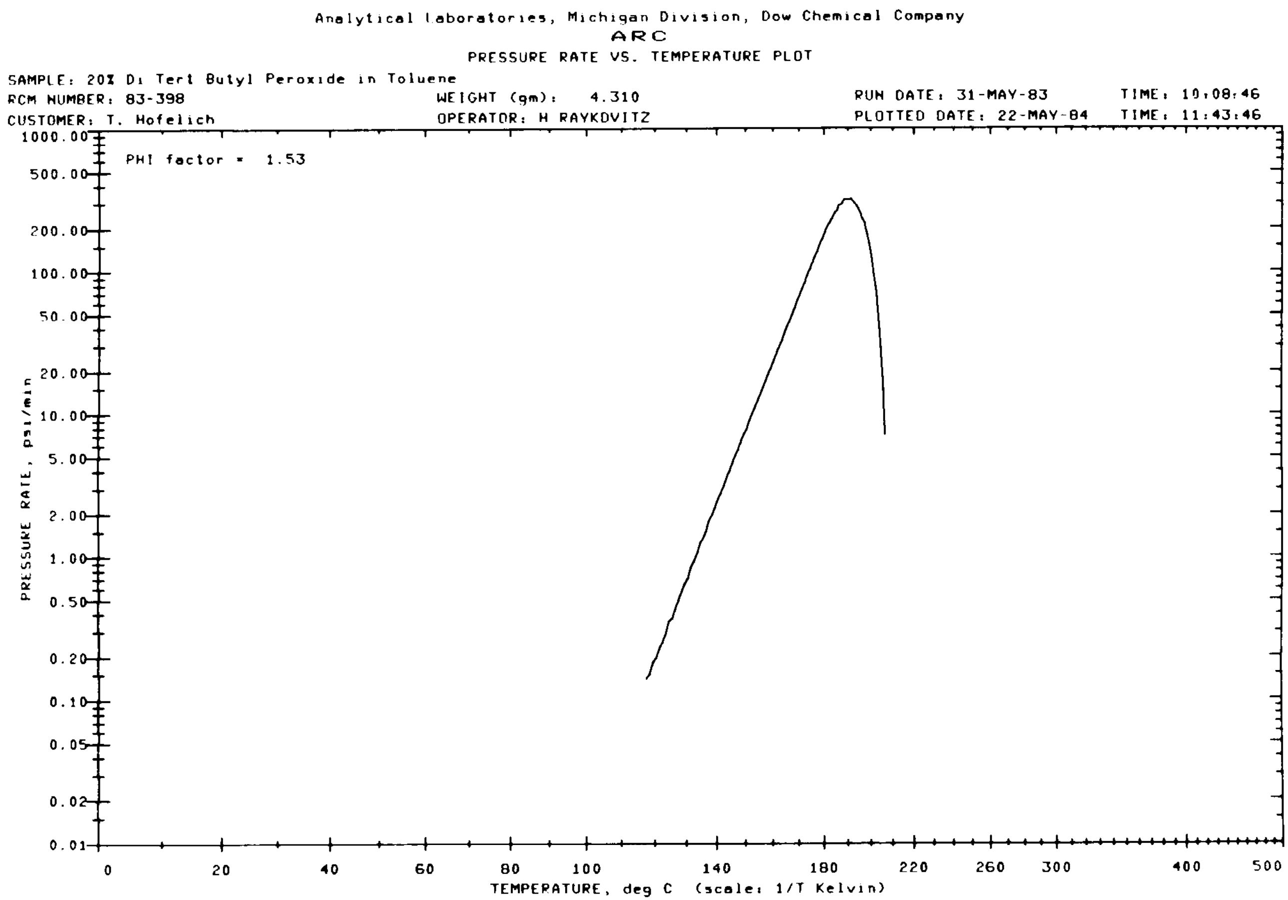

Fig. 6. Graph of pressure rate in psi min^{-1} vs. temperature in °C plotted as log of pressure rate vs. $1/T$ in K.

The cover page, all of the above plots, and the data list are generated with the absolute minimum amount of operator interaction with the computer. For the majority of the ARC work generated in our laboratory, these pages are sufficient to product a report. Other programs have been developed to take care of the special cases when additional plots are requested or kinetic data are to be generated. These programs cover the full range of plotting options available on the Columbia Scientific ARC with the added coveni-ence of previewing the plot on the Hewlett-Packard 2648A graphics terminal before a permanent copy is made. The programs are available from an options list titled the ARC Background Processing Menu.

The ARC Background Processing Menu is available through option 5 of the master menu. When this option is chosen, the following menu appears:

Enter 1 if this was the last sample on DSC-A
2 if this was the last sample on DSC-B
3 if this was the last sample on DSC-C
4 if this was the last sample on ARC-1
5 if this was the last sample on ARC-2
6 if this was the last sample on ARC-3
7 if this was the last sample on ARD
8 if none of the above or don't know

If the experiment was the last one run on an instrument, time is saved in searching for the data file. If numbers 1–7 are chosen, the program immediately proceeds to search for the file (the work "Working..." is displayed on the screen). When found, the computer displays the ARC Background Processing Menu. If number 8 is chosen, additional information is needed in order to locate the data file. The program first needs a sample number to search the Index for the actual data file name (which is never needed by the operator).

Upon obtaining this number, the program searches the Index file. If the file cannot be found, the operator is informed and given the option of entering another sample number or exiting the program.

Once found in the Index file, the program uses the actual data file name to search for the data on the hard disk. If not found on the hard disk, the operator is informed which backup floppy diskette contains the file. The operator is then given the choice of placing the proper floppy diskette in the drive, or exiting the program (if the diskette is unavailable).

When the file has been found, the computer places the data in its memory, and displays the ARC Background Processing Menu:

ARC Background Processing Menu

Enter 1 to change the descriptive information
2 to plot Self-heat rate versus Temperature
3 to plot Temperature versus Time
4 to plot Pressure versus Time
5 to plot log Pressure versus Temperature
6 to plot Pressure rate versus Temperature
7 to plot Pressure versus Temperature
8 to plot Pressure rate versus Temperature rate
9 to plot Reaction order: Rate Constant versus Temperature
10 to plot Time to Maximum Temperature Rate
11 to plot Predicted Self-heat rate versus Temperature
12 to list the data
13 to draw two plots on the same graph
14 to return to the master menu

The following summarizes the options available through the ARC Background Processing Menu.

Option 1 allows the operator to change any part of the descriptive information in the file. The information is presented in three successive "pages" and the operator has the option to change any entry. When finished, the operator is asked if these changes are to be permanent. If yes, the file itself is opened, and the descriptive information is rewritten. A new copy of the descriptive cover page (Fig. 1) is also printed on the Hewlett-Packard 7245B plotter/printer. If the changes are not permanent, no copy is made, but the changes will be in effect as long as the operator is using the ARC Background Processing Menu. This is useful for viewing the effect that a change in sample heat capacity might have on heat calculations, without making the change a permanent part of the file.

The plotting options (2–11 and 13) allow the operator to graph a specific plot on the terminal screen. After the data are plotted on the screen, a software "key" menu appears at the top of the screen in inverse video (dark on light). For plot options 2–8 and 10, this menu is:

f1–Unused	f2–Hard copy	f3–Change plot	f4–Exit to menu

These f keys are located at the top right-hand side of the Hewlett-Packard 2648A graphics terminal. Key f2 plots the graph on the plotter/printer making a permanent copy of the plot. Key f3 allows for changes in the plot maxima, minima and axes labels, and automatically allows for replotting the graph with the changes in effect.

The plotting programs are as follows.

Option 2. Self-heat rate in °C min^{-1} versus temperature in °C plotted as log of rate versus $1/T$ in K (Fig. 2).

Option 3. Temperature in °C versus time in min (Fig. 3).

Option 4. Pressure in psia versus time in min (Fig. 4).
Option 5. Pressure in psia versus temperature in °C plotted as log of pressure versus $1/T$ in K (Fig. 5).
Option 6. Pressure rate in psi min^{-1} versus temperature in °C plotted as log of pressure rate versus $1/T$ in K (Fig. 6).
Options 2–6. Duplicate the automatic plots that are generated for every run.
Option 7. Pressure in psia versus temperature in °C (Fig. 7).
Option 8. Pressure rate in psi min^{-1} verus temperature rate in °C min^{-1} plotted as log of pressure rate versus log of temperature rate (Fig. 8).
Option 9. Reaction order plot: pseudo rate constant, K^*, versus temperature in °C plotted as log of pseudo rate constant versus $1/T$ in K (Fig. 9).

This plot differs from the others in that the operator must enter some of the plot parameters before plotting can begin. When this option is chosen, the operator is asked which exotherm is to be plotted (if there is more than one available). The operator indicator indicates the choice through a numbered list, such as:

1 87.0 degrees C
2 215.0 degrees C

Enter the number of the starting exotherm temperature you want for the plot

(If only one exotherm is available, the program automatically uses that one.)

The operator is then asked if the reaction is autocatalytic or if it is a regular model (this is the sigma value in the equation).

The operator is then asked to enter the reaction order for the plot. Up to five different reaction orders may be plotted on the same graph. Figure 9 is a hard copy of a reaction order plot with no energy calculations. The plotting equation for this graph is [1]

$$K^* = \frac{\text{RATE}}{T_{\text{adiabatic}}\left(\dfrac{T_{\text{end}} - \text{TEMP}}{T_{\text{adiabatic}}}\right)^n \left(\dfrac{\text{TEMP} - T_{\text{initial}}}{T_{\text{adiabatic}}}\right)^\sigma} \tag{1}$$

where T_{end} is the exotherm end temperature, T_{initial} is the exotherm start temperature, $T_{\text{adiabatic}}$ is the difference between the exotherm end and start temperatures, RATE is the heat rate at a specific TEMP (temperature) from the experimental data, K^* is the pseudo rate constant, n is the reaction order, and the σ is 1 if autocatalytic and 0 if not.

This plot has a different f key menu than the others because of the large number of parameters the operator may change. The menu is:

f1–Change *rxn* order	f2–Hard copy	f3–Change plot	f4–Exit of menu
f5–Change temp start	f6–Change temp end	f7–Unused	f8–Calculate *E*

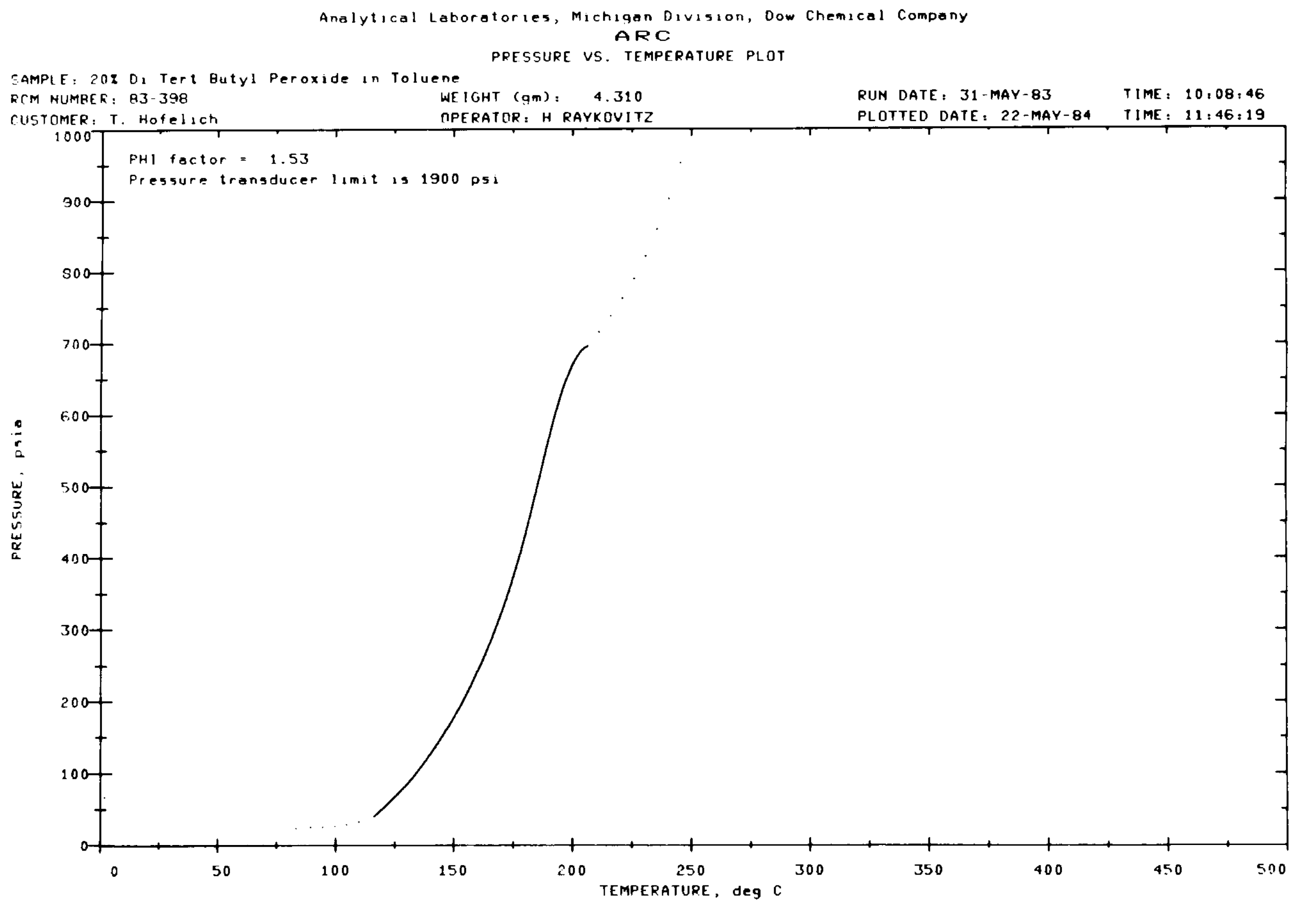

Fig. 7. Plot of pressure in psia vs. temperature in °C.

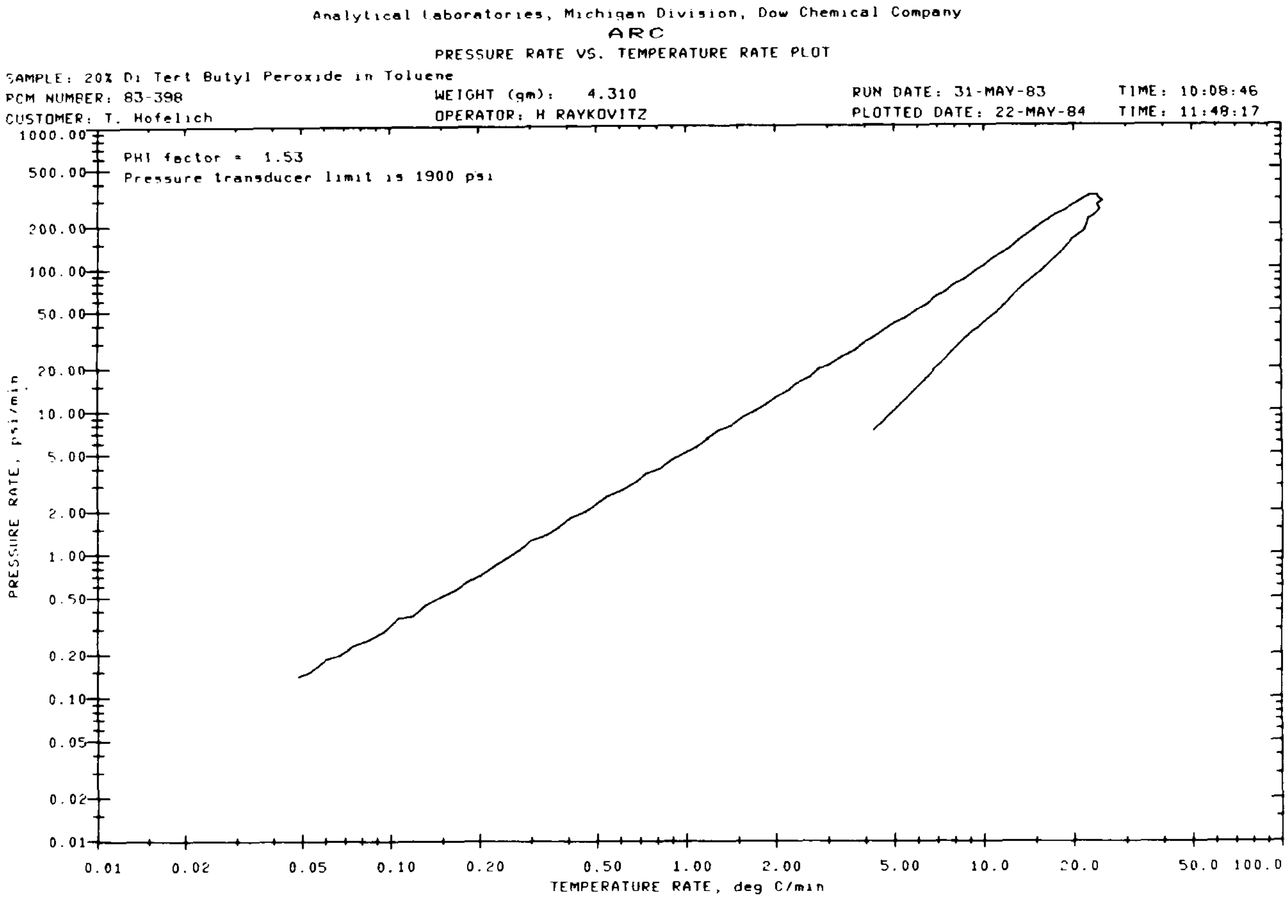

Fig. 8. Graph of pressure rate in psi min^{-1} vs. temperature rate in °C min^{-1} plotted as log of pressure rate vs. log of temperature rate.

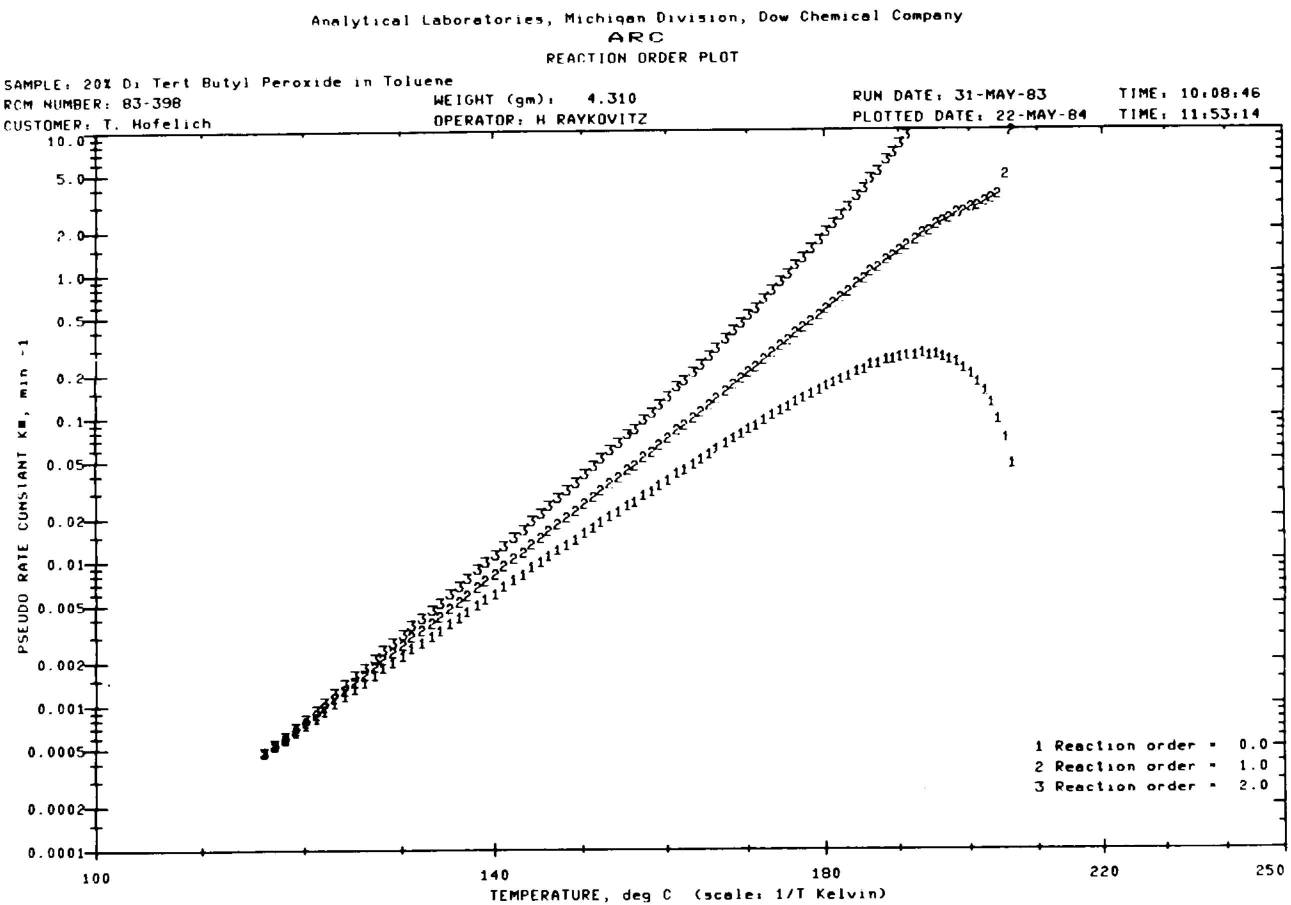

Fig. 9. Reaction order plot, graphed as log of pseudo rate constant in min^{-1} vs. temperature in °C plotted as $1/T$ in K.

Key f1 allows the operator to see the rate constant plot for any reaction order (up to five on a graph). Keys f2, f3, and f4 are the same as in previous plots. Keys f5 and f6 allow the operator to change the T_{end} and $T_{initial}$ used in the plot calculation above. Key f8 is used to calculate the activation energy of the reaction order plots.

When key f8 is chosen, the operator is asked to enter the temperature of the two points to be used in the least-squares determination of the activation energy. These points are required to be within the range of the exotherm. The calculation of activation energy is given by the following equation [1]

$$\Delta E = \frac{R \ln \dfrac{K^*(2)}{K^*(1)}}{1/T(1) - 1/T(2)} \tag{2}$$

where the rate constant, K^*, is as defined above at a particular temperature $T(1)$ or $T(2)$, and R is the gas constant, 0.001987 kcal mol^{-1} K^{-1}.

The value of the constant from the Arrhenius equation, $\ln A$, is found from the intercept of the least-squares calculation.

If a calculation is requested, values for activation energy, $\ln A$, and the least-squares correlation coefficient are returned for every reaction order on the plot. The two points chosen for this calculation are indicated on the plot in expanded type (Fig. 10).

Option 10. Time to maximum temperature rate plotted as $1/T$ in K versus log of time in s, labeled in s, min, and h (Fig. 11).

Option 11. Predicted self-heat rate in °C min^{-1} versus temperature in °C plotted as log of rate versus $1/T$ in K. This is plotted over an actual self-heat rate versus temperature curve (Fig. 12).

For Option 11, as in the reaction order plot (Option 9), the operator is required to enter the starting parameters. The necessary information includes which exotherm is to be plotted, whether or not the exotherm was autocatalytic, a reaction order, and a value for the activation energy in kcal mol^{-1}. The values can be determined by using the reaction order plot (Option 9). The plotting equation for this graph is [1]

$$\text{RATE} = \left(\frac{T_{end} - \text{TEMP}}{T_{adiabatic}}\right)^n \left(\frac{\text{TEMP} - T_{initial}}{T_{adiabatic}}\right)^\sigma (\text{Initial Rate}) \times \exp\left\{\frac{\Delta E}{R}\left[\left(\frac{1}{T_{initial}} - \frac{1}{\text{TEMP}}\right)\right]\right\} \tag{3}$$

where the parameters are the same as defined before in eqn. (1) and Initial Rate is the experimental rate at $T_{initial}$.

This plot also has a different f key menu:

f1–Unused	f2–Hard copy	f3–Change plot	f4–Exit to menu
f5–Change *rxn* order	f6–Change *E*	f7–Unused	f8–Unused

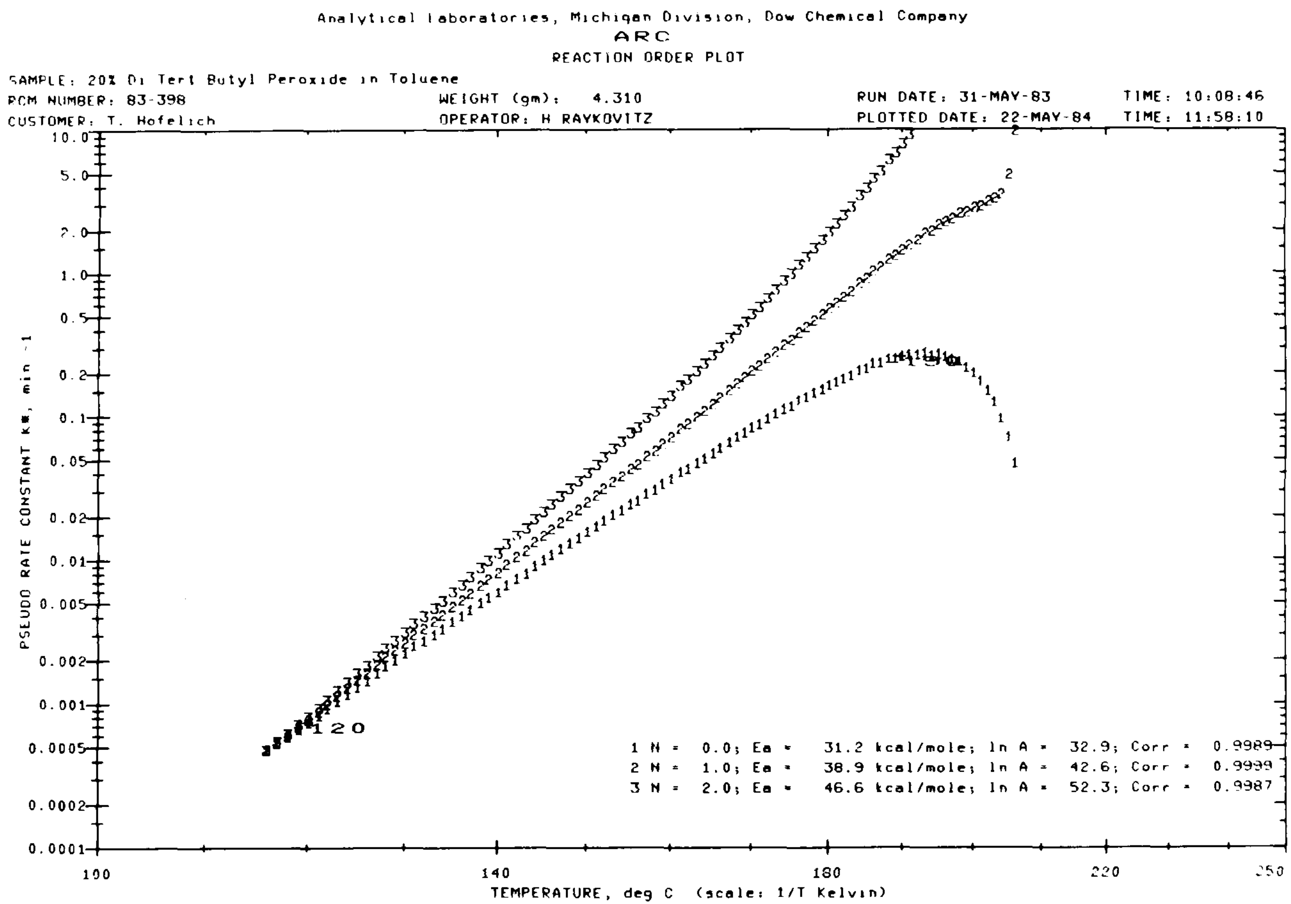

Fig. 10. Reaction order plot, graphed as log of pseudo rate constant in min^{-1} vs. temperature in °C plotted as $1/T$ in K. The expanded type numbers 120 and 190 are the operator entered temperatures in °C that bound the energy calculation. The results of the calculations are seen in the lower right of the graph, where N is reaction order, E_a is activation energy, $\ln A$ is the constant from the Arrhenius equation, and corr is the least-squares correlation coefficient.

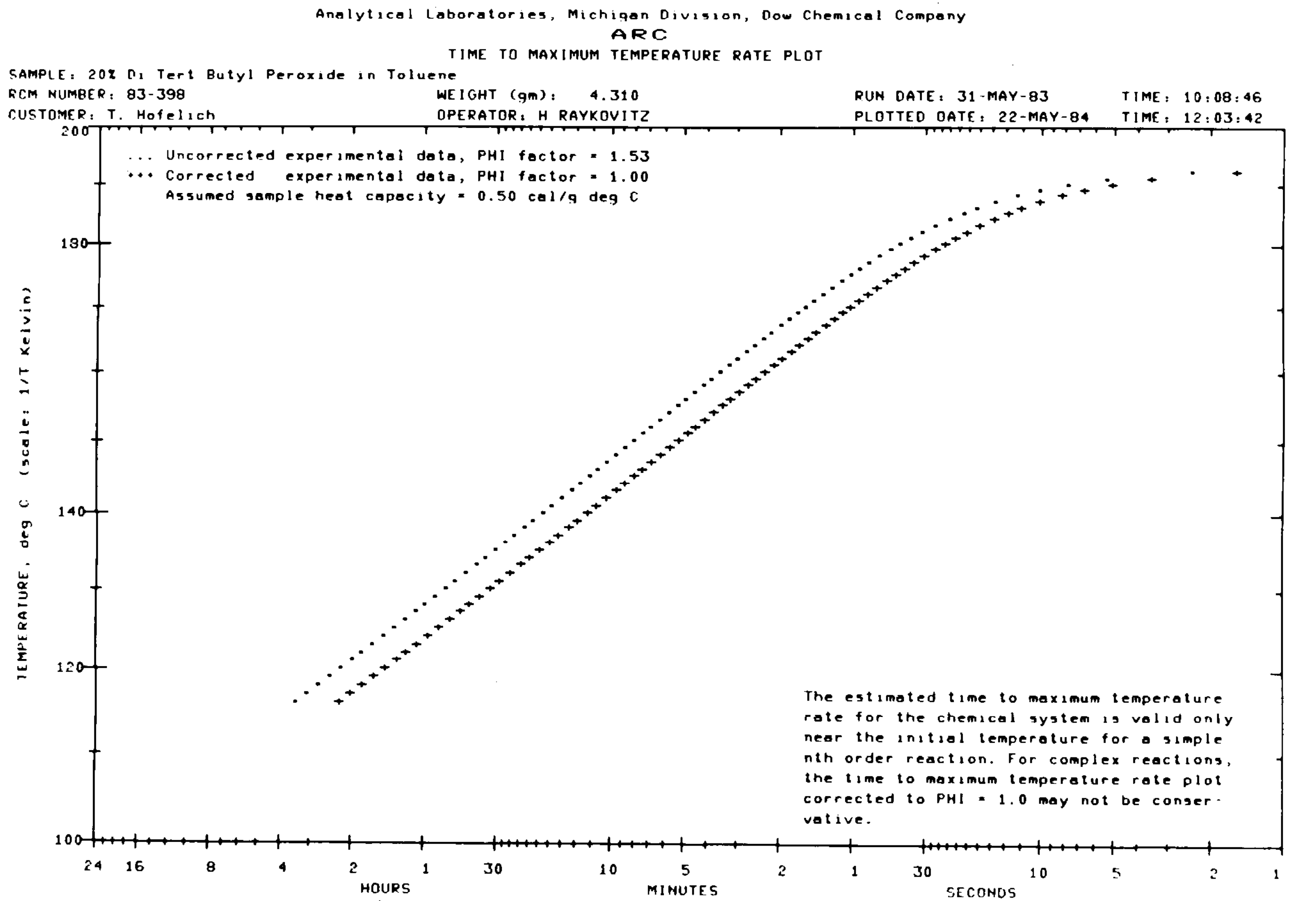

Fig. 11. Graph of time to maximum temperature rate plotted as $1/T$ in K vs. log of time in s, labeled in s, min and h.

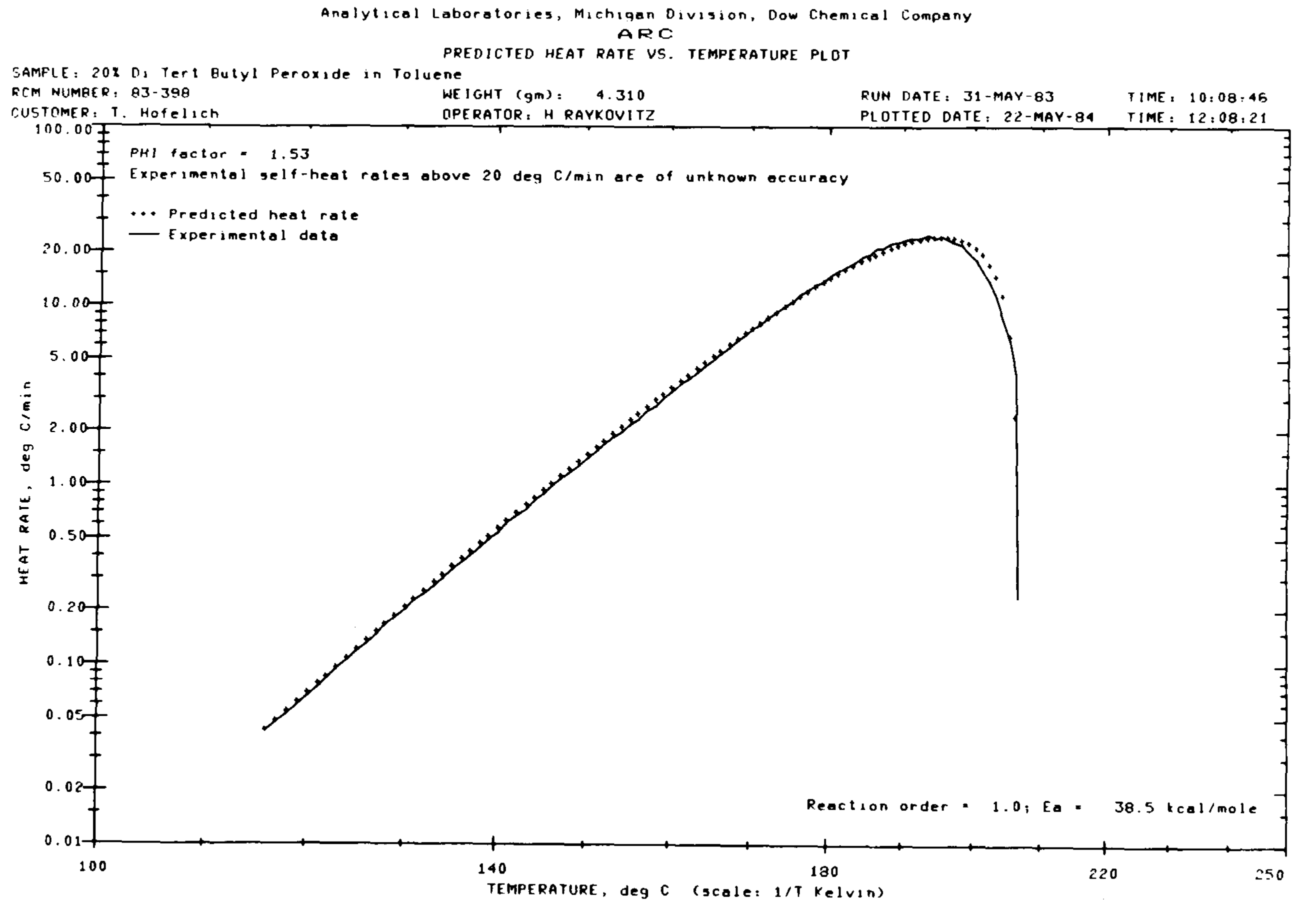

Fig. 12. Graph of predicted self-heat rate in °C min^{-1} vs. temperature in °C plotted as log of rate vs. $1/T$ in K, plotted over the experimental self-heat rate vs. temperature curve.

Accelerating Rate Calorimetry

Analytical Laboratories, Michigan Division, Dow Chemical Company

RCM 83-398 ARC run on 31-MAY-83 at 10:08:46

20% Di Tert Butyl Peroxide in Toluene

Submitted by: T. Hofelich
Phone number: 6-5960
Run by: H RAYKOVITZ

From: 438 Building
Charge number:
ARC # 2

DATA LIST

TYPE	TIME	TEMPERATURE	RATE	PRESSURE
HEAT	0.0	80.0	0.654	23.4
HEAT	26.7	85.3	5.225	24.3
WAIT	41.7	83.3	-0.001	24.5
SEARCH	52.2	83.3	0.000	24.4
HEAT	57.3	90.0	0.123	26.1
WAIT	72.3	89.5	0.002	25.8
SEARCH	82.7	89.5	0.003	25.6
HEAT	87.0	95.0	0.120	26.8
WAIT	102.0	94.5	0.006	26.4
SEARCH	112.2	94.6	0.005	26.2
HEAT	116.9	100.1	0.164	27.5
WAIT	131.9	99.7	0.007	27.3
SEARCH	142.2	99.8	0.006	27.3
HEAT	146.5	105.0	0.222	29.2
WAIT	161.5	104.5	0.010	29.2
SEARCH	171.9	104.6	0.010	29.6
HEAT	176.3	110.0	0.185	32.0
WAIT	191.3	109.8	0.024	32.7
SEARCH	201.4	109.9	0.017	33.1
HEAT	205.9	115.0	0.137	35.7
WAIT	220.9	115.1	0.000	37.3
EXOTHERM	244.4	116.1	0.043	40.2
	265.6	117.2	0.048	43.2
	285.3	118.2	0.053	46.2
	302.5	119.3	0.060	49.4
	317.4	120.3	0.067	52.4
	331.5	121.3	0.075	55.7
	341.3	122.2	0.084	58.2
	351.9	123.2	0.095	61.3
	361.9	124.2	0.106	64.9
	370.4	125.3	0.119	68.1
	378.2	126.3	0.131	71.6
	385.2	127.3	0.148	75.2
	390.3	128.2	0.166	78.1
	395.9	129.2	0.182	81.8
	401.2	130.3	0.202	85.6
	405.2	131.2	0.228	89.0
	409.6	132.3	0.248	93.2
	413.6	133.4	0.274	97.5
	416.5	134.2	0.300	101.1
	419.6	135.3	0.338	105.4
	422.3	136.3	0.369	109.6
	424.5	137.2	0.407	113.5
	426.9	138.3	0.455	118.4
	428.6	139.1	0.497	122.2
	430.7	140.2	0.542	127.3
	432.1	141.1	0.610	131.5
	433.8	142.2	0.674	136.7
	435.3	143.3	0.731	142.2
	436.4	144.2	0.825	146.6
	437.5	145.3	0.897	152.0
	438.4	146.1	0.988	156.5
	439.4	147.2	1.083	161.9
	440.2	148.2	1.183	167.5
	441.0	149.3	1.283	173.4
	441.8	150.3	1.422	179.0
	442.4	151.3	1.552	185.1
	442.9	152.2	1.700	190.1
	443.5	153.2	1.862	196.6
	444.0	154.3	2.000	203.1
	444.5	155.3	2.208	209.8
	444.9	156.2	2.324	215.5

Fig. 13. First page of the data list generated for a 20% di-*tert*-butyl peroxide in toluene experimental ARC run.

Keys f2, f3, and f4 are the same as before and f1, f7, and f8 are inactive. Keys f5 and f6 allow the operator to vary the reaction order and activation energy until the predicted plot is the same as the plot of the experimental data (or as close as possible).
Option 12. List the data on the plotter/printer. The data are listed on the printer in table form. Figure 13 is an example of the first page of this list.
Option 13. Draw two plots on the same graph. This option allows for up to six sample results plotted on the same graph. The self-heat rate vs. temperature, log pressure vs. temperature, and time to maximum temperature rate plots are those for which overplotting is available.
Option 14. Return to the master menu. This option returns the operator to the master control menu, exiting the ARC Background Processing menu.

Finally, in order to put the above plots and lists into a nice, neat package, we have designed a report cover sheet. This cover sheet contains a brief summary of the descriptive information and some analysis of the exothermic data for one or more ARC experiments.

In order to create a report cover sheet, the operator first selects Option 4 of the master menu. After clearing a space in computer memory, the computer responds with a request for a report number. After the operator enters a number, the computer then requests a sample number. This number is used by the computer to find the corresponding data file associated with that number. If the file is not found on the hard disk, the computer will inform the operator which floppy diskette it is stored on and wait for the disk to be put into the floppy disk drive. If the file cannot be found on any storage device, the operator is informed, and control returns to the master menu. The computer will then ask the operator if only a brief report is needed or if there is to be full data analysis (vide infra). The brief report contains only descriptive information from the report page: sample number, description, sample weight, ARC bomb type, sample heat capacity, sample atmosphere, programmed step heating, and a calculation of the thermal ratio, phi.

The computer cycles through the sample number request and brief vs. full analysis questions until the operator indicates that there are no more sample numbers to be included in the report. The computer will then indicate that a copy of the report is to be sent to the customer(s) of the first sample number entered. If there are any other people who should get a copy of the report, the operator indicates this, and the computer asks for the name(s), address(es), and if only a cover page is to be sent. When the list is complete, the computer then proceeds to print out the entire cover page (Fig. 14).

If the operator has indicated that a full report is needed, the computer sends control to the data calculation program. This program begins to search the data file to see if there are any exotherms. The computer also differentiates between regular ARC experiments and isothermal age experiments. If no exotherm was found during an isothermal age, the following is printed:

"No exothermic reaction was detected during the isothermal age test. Programmed step heating of the sample was initiated at *XX* degrees C using a heat step of *YY* degrees C." (where *XX* and *YY* are variables obtained from the data).

If no exotherm was found in an ARC experiment or in the subsequent heating of an isothermal age experiment, the following is printed:

"No exothermic reaction was detected up to *XX* degrees C using a detection threshold of *YY* degrees C/minute".

If an exotherm has been found, a check is made to see if the sample was in isothermal age. This difference is noted in the statements printed out on the report:

"Isothermal aging of the sample was begun at *XX* degrees C. An exothermic reaction was detected after *YY* minutes in isothermal age at a temperature of *XX* degrees C".

Or:

"An exothermic reaction was detected at *XX* degrees C with a self-heating rate of *YY* degrees C/minute and a pressure of *ZZ* psi".

The program will indicate if the exotherm did not meet the temperature rise criterion:

"An exothermic reaction was detected at *XX* degrees C with a self-heating rate of *YY* degrees C/minute and a total temperature rise of less than 5 degrees C".

ANALYTICAL REPORT AL 84-9999
23-MAY-84

TO: I. Hofelich 438 Building Charge

TITLE:

AUTHORS: Reviewed by

SUMMARY

The following results have been obtained by Accelerating Rate Calorimetry (ARC). Refer to data plots contained within this report for more detail.

Caution: The following data were generated under specific phi factor, ø, conditions. These data should not be applied to larger scale operations without considering the effect of ø on the ARC results. Please contact Reactive Chemicals personnel for further interpretations and applications of these data.

RCM 83-398 20% Di Tert Butyl Peroxide in Toluene

A 4.310 g sample was loaded into a No. 1, .032" wall, 1" Titanium container which yields a ø factor of 1.53 assuming an average sample specific heat of 0.500 cal/g deg C. The sample atmosphere was air.
The programmed step heating was initiated at 80 deg C with a heat step of 5.0 deg C.

Fig. 14. Report summary sheet containing only descriptive information (a brief report).

No calculations are done for exotherms of less than 5 degrees temperature rise.

If the self-heating rate should exceed 20°C min^{-1} and/or if the pressure was above the transducer limit of accuracy, the following are printed:

"Self-heating rates above 20 degrees C/minute are of unknown accuracy".

"The pressure of *XX* degrees C was above the pressure tranducer limit (1900 psi)".

The program will then go on to determine if the exotherm contained more than one maximum. If more than one was found, the temperatures of these maxima are reported, for example:

"Relative maxima in the self-heat rate curve were observed at *XX* and *YY* degrees C. These results suggest that multiple physical or chemical processes are occurring".

If only one maximum was present, the program would then print out the heat rate, temperature, and pressure at that maximum:

"The maximum self-heat rate observed during this exotherm was *XX* degrees C/minute at *YY* degrees C with a pressure of *ZZ* psi".

The program can also determine if an exotherm had been cut off due to the preset end temperature of the experiment. The following message is printed if this was the case:

"This experiment was terminated at *XX* degrees C. If the sample had been allowed to continue to generate heat, it may have reached significantly higher temperatures. Therefore, these data may not represent the full potential of this exothermic reaction".

Finally, if any exotherm was completed during the experiment and also met the criterion of a temperature increase of more than 5 degrees, the adiabatic temperature rise and heat of reaction would be calculated. The adiabatic temperature rise is equal to the difference of the final and starting temperatures of the exotherm multiplied by phi. The heat of reaction is the adiabatic temperature rise multiplied by the sample heat capacity. The following is printed for this calculation:

"The observed temperature rise for this exotherm was *XX* degrees C. Using a phi factor of *YY* the estimated adiabatic temperature rise is *ZZ* degrees C and the heat of reaction is *WW* cal/g of total sample. This calculation assumes that any *PV* energy change during the reaction was negligible".

Figure 15 is a cover sheet for a full analysis report consisting of only one experiment. After the basic descriptive information was listed, the exotherm summary was printed. In this case (20% di-*tert*-butyl peroxide in toluene, an ARC standard) there is only one exotherm that started at 116°C and had a maximum at 193°C. It was noted that the self-heat rate at the maximum was above the accuracy of the instrument. A calculation was made based on an assumed heat capacity of 0.5 cal g^{-1} $°C^{-1}$ for the sample.

ANALYTICAL REPORT

AL 84-7333
23 MAY-84

TO: T. Hofelich 438 Building Charge #
* S. Hankin 1707 Building

* cover sheet only

TITLE:

Reviewed by

AUTHORS:

SUMMARY

The following results have been obtained by Accelerating Rate Calorimetry (ARC). Refer to data plots contained within this report for more detail.

Caution: The following data were generated under specific phi factor, ø, conditions. These data should not be applied to larger scale operations without considering the effect of ø on the ARC results. Please contact Reactive Chemicals personnel for further interpretations and applications of these data.

RCM 83-398 20% Di Tert Butyl Peroxide in Toluene

A 4.310 g sample was loaded into a No. 1, .032" wall, 1" Titanium container which yields a ø factor of 1.53 assuming an average sample specific heat of 0.500 cal/g deg C. The sample atmosphere was air.
The programmed step heating was initiated at 80 deg C with a heat step of 5.0 deg C.

An exothermic reaction was detected at 116 deg C with a self-heating rate of 0.04 deg C/min and a pressure of 40 psi.
The maximum self-heat rate observed during this exotherm was 25.00 deg C/min at 193 deg C with a pressure of 609 psi.
Self-heating rates above 20 deg C/min are of unknown accuracy.
The observed temperature rise for this exotherm was 90 deg C. Using a phi factor of 1.53, the estimated adiabatic temperature rise is 137 deg C and the heat of reaction is 68 cal/g of total sample. This calculation assumes that any PV energy change during the reaction was negligible.

Fig. 15. Report summary sheet containing a full analysis for the experimental run.

The computer will print out each sample number summary in the order in which the operator entered them. A maximum of twelve ARC experiments may be summarized in this manner. Extra space is left on the cover sheet between summaries so that additional comments may be added by the reviewer.

CONCLUSION

The convenience of the ARC data acquisition system makes it attractive for operator use. The ability to generate a cover page and five plots automatically has eliminated the need for the operator to do the plotting on the ARC units. This not only saves time, but produces plots in 8 1/2 × 11 inch format (easier to copy than the oversize ARC plots).

The ARC Background Processing Menu is an easy-to-use method for generating the ARC graphs that are not automatically made when an experiment is processed. The options allow for changing plot parameters, which in many cases can make the graphs easier to read and interpret. Reaction order plots are useful in kinetic studies and aid in mechanistic interpretations.

Finally, the creation of a Report cover page for ARC experiments is a very simple task requiring only the sample numbers of the experiments to be included on the summary page. The software improves the accuracy of the report, makes a more complete (and neater) report, and saves considerable time that was normally needed for doing simple heat calculations by hand.

Note

Inquiries regarding specific software may be made to the author.

ACKNOWLEDGMENT

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REFERENCES

1 CSI ARC, Accelerating Rate Calorimeter, Operating Manual, Columbia Scientific Industries, P.O. Box 9908, 11950 Jollyville Road, Austin, Texas 78755.
2 H. Raykovitz, private communication, 1983.