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The temperature scanning reactor
I: Reactor types and modes of operation

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Abstract

New analytical instruments and experimental techniques can have a profound influence on research methodology and effectiveness. At times, their introduction supports a step change in the rate of progress in a field of research; such radical innovations are usually preceded by a new theoretical insight, one which may require breaking with an established paradigm. Such a time appears to have come in the study of reaction kinetics, with the introduction of the temperature scanning (TS) methods and technology. The TS methodology makes it possible to perform kinetic experiments conveniently and rapidly, in fully-automated reactors, with software that simplifies data reduction to a point where temperature scanning reactors (TSRs) could become the first "kinetics instruments". The TS technology has the potential to influence and change the way research is done in chemical kinetics, in much the same way that the advent of gas chromatography changed the ease and procedures of analysis. Temperature scanning methods, although new in kinetics research, have already been proven effective in other areas. They follow the lead of earlier transient operations, and of non-steady-state procedures, that are now well-established in thermal analysis (TA) and enzyme kinetics. The temperature scanning methods can be used to extract meaningful kinetic data from batch reactors (BRs), stream-swept reactors (SSRs), continuously-stirred tank reactors (CSTRs) and plug-flow reactors (PFRs). TS methods are broadly applicable to the study of chemical rate processes in all three phases of matter, with and without catalyst. They are applicable in all reactor configurations, because they deal with fundamental aspects of data-gathering, not with reactor-specific aspects of configuration or operation. Reactor-specific operating requirements, such as efficient mixing in the case of the CSTR, are no different in TS-CSTRs than they are in the corresponding conventional CSTR reactors. Conversion to the new TS technology is easy and rapid; TSRs are easy to operate and significantly more cost-effective than any of the research reactor types currently in use. Round-the-clock fully-automated TSR operation can provide R and D laboratories engaged in kinetic studies and/or catalyst development with unprecedented volumes of kinetic data, quickly and reliably. As the TS technology becomes widely available, research in reaction kinetics, reaction mechanisms and catalyst development should enter a period of renewal and rapid growth.

Keywords: Reactor operation; Reactor design; Temperature scanning; Transient kinetics; Catalyst evaluation

1. Introduction

1.1. Research in heterogeneous catalysis

Catalytic processes are essential for the production of most liquid fuels, and for about 75 percent of all chemical and petrochemical products; for newer processes, this figure rises to 90 percent. These industrial processes are constantly undergoing improvement, including the development of new or improved catalysts. Over many years, advances in catalyst formulation

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have helped to control the costs of production of chemicals and fuels by increasing the rate of conversion, improving selectivity, controlling undesirable by-products and decreasing the energy requirements of a broad range of chemical conversion processes. However, industrial catalyst research has decreased sharply in the past decade, and improvements in catalyst selectivity and activity have tended to be incremental. A study commissioned by the US Department of Energy has called for increased research to provide improved understanding of catalyst capabilities with respect to new materials, removal of pollutants and other new industrial applications [1].

Up to the present, most advances in this field have been achieved by an empirical approach to catalyst formulation, guided by incomplete studies of catalyst capabilities and the effects of reaction conditions. Many commercial reactors operate with the aid of catalysts whose formulation is a secret which constitutes a valuable commercial property. In most industrial processes, the mechanisms of the conversion reactions are poorly understood, and the significance of the physical condition of the catalyst is in dispute. Catalysis by enzymes in living systems is often better understood than industrial heterogeneous catalysis, despite the fact that heterogeneous catalysis has been an essential part of the chemical industry for almost a hundred years, while enzymes are only now being identified and considered for industrial applications (beyond brewing and such other traditional fermentations).

At present, the understanding of the fundamental mechanisms of reactions dependent on heterogeneous catalysts is incomplete and unsatisfactory. This situation can be ascribed in part to a rush to achieve improvements in highly competitive industrial processes, with little attention paid to the underlying causes responsible for improvements. Another constraint has been the difficulty of identifying the surface species present on heterogeneous catalysts, species presumably representative of the intermediates or even the transition state during the act of catalysis. Recent improvements in analytical techniques of surface studies have helped to reduce the extent of this problem.

A major stumbling block still remains: the problem of obtaining enough kinetic data, at realistic reaction conditions, for a thorough understanding of the reaction mechanisms and the kinetics pertinent to industrial reactors. With the laboratory reactors presently in use, this requires a great many kinetic runs over a wide range of reaction conditions, catalyst formulations, conversions and feed compositions. Thorough mechanistic rate studies are difficult, tedious, time-consuming and expensive, and catalyst research laboratories charged with seeking timely commercial success tend to avoid them. Their catalyst development efforts are commonly guided by one or a few "standard runs" on each sample. The resulting inadequate kinetic data lead many workers to resort to empirical correlations which describe kinetic behaviour over a narrow range of conditions, using unrealistically simple and uninformative rate expressions.

1.2. The temperature scanning technology

The Temperature Scanning (TS) technology was developed and patented in the author's laboratories in the Department of Chemical Engineering at Queen's University at Kingston. The theoretical underpinnings were put in place in collaboration with Norman M. Rice of Queen's Department of Mathematics and Statistics. This technology promises to bring to reaction studies and catalyst development the kind of leverage that new analytical techniques are bringing to the study of material properties, chemistry and biochemistry. TS can increase rate-data output per person-hour to an extent commensurate with that made possible by the introduction of gas chromatography in gas analysis.

There are established precedents for the TS methodology. Some thirty years ago, temperature ramping was applied to the study of desorption. From this beginning, a variety of thermal analysis (TA) methods have evolved that today provide powerful semi-quantitative techniques for the study of a wide range of solid-phase processes. In biochemistry, transient operation of reactors has long been used in studies of enzyme kinetics, in the form of "stop flow" experiments. TS methodology follows along the path of these earlier transient methods of operation, and applies non-steady-state thermal methods to various types of reactors, including those based on existing TA instruments.

TS methodology can be applied to a batch reactor (BR), a plug-flow reactor (PFR), a continuously-stirred tank reactor (CSTR) and a stream-swept reactor (SSR) — the latter is a reactor type based on the mode of operation used in TA instruments. There is no theoretical reason why TS methodology should not be applicable to additional reactor types as well. Within each of these four reactor types, a variety of options for effluent analysis, reactor size and configuration, and other specifics, can be used to suit the phase, composition and other requirements of the system under study. The only requirement of the TS reactor is that analysis of the product mixture must be frequent in relation to the temperature-ramping rate being used. Beyond that operational requirement, the TS methodology deals with fundamentals with broad applicability.

The operation of a temperature scanning reactor (TSR) is simple. There are no complicated demands on the ramping procedure in the case of the BR, CSTR or SSR configurations. Only in the PFR are there strict requirements regarding the method of operation of the reactor, but these are easy to accommodate in an automated laboratory reactor. All the TSRs, but in particular that of the "open" CSTR and PFR types, are easy to automate, so that continuous round-the-clock operation is not only possible but desirable and readily implemented.

All TSRs automatically produce rate data which cover a wide range of output conditions. These data are easily collated in the form of standard sets of isothermal or isokinetic results, at a pace many times faster than any method presently available. For example, one 8-hour period of TS-PFR operation will produce many thousands of conventional reaction rates over a broad range of temperatures and conversions. Over a 24-hour period of automated operation, three feed compositions or pressures can be investigated at this level of detail. In just two days, catalyst performance can be examined in greater detail, and over a broader range of operating conditions than is normally available for an established catalyst.

1.3. A fundamental look at data acquisition

As with many innovative concepts which break with tradition, the TSR technology is simple and even obvious. However, the transient mode of data acquisition of the TSR is unconventional, and may appear to be suspect to those schooled in the isothermal mode of operation. We, therefore, begin by re-examining the nature of data acquisition and interpretation in the physical sciences, and apply these insights to chemical reactor operations.

Most data are acquired as signals, which may be considerably removed from the quantity being measured. For example, a voltage or current is a signal which can be interpreted as a concentration or a temperature only by means of calibration, often involving a long chain of connections. This is done so commonly that we may fail to remember that calibration is a method of deciphering raw readings into quantities of interest.

Using current isothermal experimental techniques, after decoding a voltage signal from an analytical instrument to yield a temperature and a concentration, the output temperature and conversion from a reactor are then further decoded to yield the reaction rates. Once the conversion, the reaction rate and the temperature are established, we can proceed to fit proposed rate expressions to this data. This is a still-higher level of decoding, one which requires us to find the proper rate expression and yields estimates of the parameters of this expression, as signals for the next stage of interpretation.

The final stage of decoding involves interpreting the behaviour of the estimated parameters of the proposed rate expression as being due to changes in reactor operating conditions or in catalyst formulation. We see then that the data collected under well-defined "boundary conditions" constitute an interpretable signal. This signal contains the information required to decipher a plausible form of the kinetic rate expression which governed the reaction as it was taking place in the reactor and in turn suggests the chemical mechanism which is responsible for the conversion of the feed.

Currently, the dominant method of experimentation requires that the data be obtained in an isothermal reactor under well-defined conditions. We know how to read that signal. Data collected under other (i.e., non-isothermal) conditions will still contain all the information about the kinetics of the reaction; however, that data will be in an encrypted form, and therefore cannot be interpreted (deciphered) to yield a rate expression unless we possess the key required to break the code.

Another way of making this point is to say that the behaviour of the concentration and temperature at the output of a reactor, as functions of reaction conditions, reactor configuration, etc., contains all the information one needs to decipher the kinetics of a reaction. Any type of reactor configuration or operation will yield a unique and reproducible result which contains all this information. The key to the code required to interpret this signal requires that the data (the signal) be generated (encrypted) under certain strictures — the boundary conditions. These must be obeyed in order to generate an interpretable signal and make the "message" understandable. If we are not able to extract the information necessary to establish the kinetic rate expressions from a given signal, it is because we do not know the applicable boundary conditions, or because we do not know how to use them to interpret the data; it is not that the signal does not contain the information.

The TS methodology defines the operating conditions required to generate interpretable signals from chemical reactors operating under new boundary conditions. It then uses published and patented algorithms to decipher the resulting signals. These methods are different from the conventional procedures now in use, but are no less valid. They yield conventional reaction-rate data much faster than isothermal methods: because of the inherent nature of the TS algorithms and methods of operation; because TSRs are much more adaptable to automated operation; and because TSR boundary conditions are easier to implement than isothermal operation. The TSR is eminently suited to automated data-logging and statistical data analysis.

The output of a TSR experiment, in the case of a TSR built to operate as a "kinetics instrument", could simply be the values of the rate parameters of a previously established rate expression, perhaps with their temperature dependencies, treating all intervening stages of data reduction as background information. A kinetics instrument could therefore report, for example, changes in the estimates of the reaction-rate parameters as catalyst formulation is incrementally varied in the course of catalyst development. The next stage of decoding would then interpret the behaviour of these parameters as a function of the changes in the catalyst formulation.

2. The TSR operating procedure

The operation of a TSR involves ramping the feed temperature while collecting composition and temperature data at the output of the reactor. In order to make such data interpretable, the temperature ramping rate must be such that the time between successive analyses is much shorter than the time required for a kineticallysignificant increment of temperature to be induced in the feed to the reactor.

Temperature scanning is already applied in a much simplified form in some long-duration experiments in pilot plants. In these cases, space time is kept constant and the reaction is maintained at isothermal conditions for extended periods of time. In some instances, however, the temperature is ramped very slowly, or periodically increased in small increments, and analyses continue to be made on a regular schedule. The results yield multiple isothermal conversion data, from which multiple rates can be calculated at various conversions and temperatures. There are normally no two data points resulting from this procedure that occur at the same temperature. The results of such an operation therefore cannot be assembled into an isothermal data set (i.e. conversion–rate–temperature) suitable for determining the rate equation unless one is certain that during the ramping the whole bed of the reactor was at the same temperature as the feed. It is in order to make such isothermal data sets available from non-isothermal operation, and in this way to speed up the collection of the wide range of data necessary for the determination of the kinetics of a reaction, that the TS technology was developed.

In the following discussion we will illustrate the uses and the results of temperature scanning by means of plots obtained using a simulation program. The program takes into consideration the kinetics of the reaction, heat transfer to the catalyst, to and through the walls of the reactor, and on to the surroundings. It includes heat capacities for all these components, pressure drop calculations and the effects of volume expansion. Furthermore, it includes the effects of variation of heat transfer coefficients as a function of Reynolds number. The simulation software represents the best available method of examining the behaviour of temperature scanning reactors until such time as the various TSR configurations described below become available for experimental work. Even then, it is unlikely that any one reaction can be studied experimentally in all of the reactor types we consider below.

2.1. The TS-batch reactor

The temperature-scanning batch reactor (TS-BR) presents the most straight-forward application of the TS approach. Consider the following five steps, which together constitute a series of TS-BR runs which comprise one TS-BR experiment.

1. Load the reactor at a conveniently low temperature.
2. Begin monitoring the composition of the reactant charge.
3. Begin to raise the temperature of the reactants in any fashion desired.
4. End all procedures when predetermined conversion or temperature limits are attained.
5. Repeat steps 1 through 4 a sufficient number of times (say 10) to constitute the desired experiment, making sure that the temperature ramping history is not repeated in any run of the experiment.

Curves of composition versus clock time (C versus t) in the reactor can be recorded during each run. These composition data are converted to yield curves of fractional conversion versus clock time (X versus t). An example of such a result is shown in Fig. 1.

A second plot, which is logged at the same time as that for conversion shown in Fig. 1, is reaction temperature versus clock time (T versus t), as shown in Fig. 2. Notice that we have

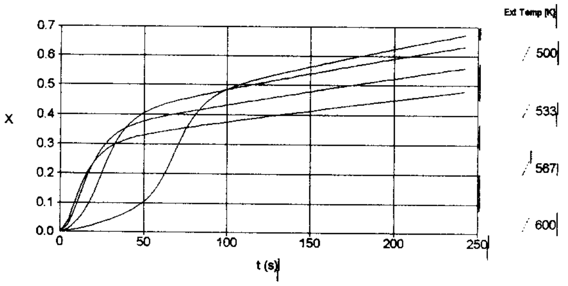

Fig. 1. Conversion versus clock time for various external temperatures.

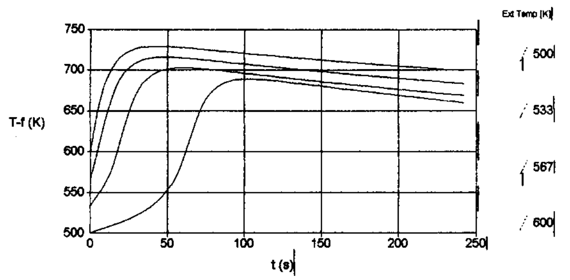

Fig. 2. Fluid temperature versus clock time for various external temperatures.

shown no concern about any exo- or endothermal effects of the reaction; we merely record the temperature at each instant and the corresponding composition. The change in temperature need not be confined to a specific trajectory.

This procedure yields many couplets of data points, consisting of conversion and temperature, each at the same clock time. There will be as many such couplets in each run of the series as we may wish to collect using the available instrumentation — thousands, in most cases. The only constraint is that the analysis be performed often enough so that well defined curves are produced in the X and T versus clock time planes.

The slope of the curve of conversion versus clock time shown in Fig. 1, is by definition the rate of the reaction $(\mathrm{d}X/\mathrm{d}t)$ at that clock time and at the corresponding conversion. Fig. 3 shows the rate of reaction as a function of clock time as calculated from Fig. 1.

By cross-reading on the curve of temperature versus clock time (Fig. 2) we can find the temperature which applies to this clock time, and hence the temperature at which this rate was occurring. Thus, we now have triplets of conversion, rate and temperature $(X\text{–}r\text{–}T)$ all collected at the same clock time, just the data required for fitting with rate expressions.

Each run, in principle, yields an infinite number of such triplets. Subsequent runs in the series are done with different temperature histories during the ramping. If the experiment is so arranged that the temperature history (i.e., the shape of the curve in Fig. 2) is different for each run, we will obtain one triplet from each run of the series in which the reaction temperature is at the same value but the clock time, rate of reaction and the conversion are not the same. This selection of data represents a set of isothermal data points at various conversions and rates. We can select as many such triplets at each temperature covered by the ramping as there were runs in the experiment. We can then repeat this selection at any number of temperatures within the range traversed by the temperature ramping. In some cases we may be able to safely interpolate values between the highest and lowest curves observed in Fig. 1 and Fig. 2. In those cases we will have an unlimited number of rates at each temperature from Fig. 3, lying between the limits set by the highest and lowest observed rates.

Two paths are now open for the evaluation of this data.

(1) Fit the selected isothermal data sets with rate expressions, one temperature at a time. If the same rate expression fits at all temperatures, then determine the temperature dependence of the rate parameters.

(2) Alternatively, fit both the temperature and the conversion dependencies simultaneously to a preferred or mechanistic rate expression in which the rate parameters are explicitly expressed as functions of temperature.

The choice of procedure will depend on many factors, including the availability of a suitable

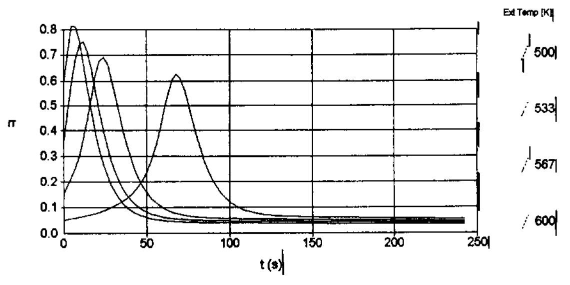

Fig. 3. Reaction rate versus clock time for various external temperatures.

kinetic expression and an expression for the temperature dependence of the parameters, and on the nature of the mathematical relationships involved. Most kinetic equations will have to be rearranged in some way if they are to be solved for their temperature and conversion dependence simultaneously. Fortunately, procedures have been formulated for the rearrangement of kinetic rate equations to ameliorate the difficult problem of statistical correlation among parameters.

It is in this last context that the TS methodology is particularly useful. The number of data points obtained from a TSR experiment is, in principle, unlimited. Because so many points are obtained from a single series of rampings, the data are also less likely to be subject to random error than data from conventional single-point studies. Rather, it is systematic error that is potentially troublesome in the TS mode, but such errors are usually due to known and easily-identifiable causes. A careful experimenter should be able to eliminate such errors by performing appropriate tests. The wealth of data available from as few as ten rampings of a TS-BR should satisfy the most demanding statistical analysis and data fitting procedures. A further advantage of this type of operation is that all the data, starting at the temperature at which the reactor is filled, are available for evaluation. Conventional isothermal batch reactor experiments lose all the information on the way up to the desired isothermal condition. Low-conversion data are therefore routinely lost, data which are most useful in determining the behaviour of a reaction under initial conditions, before back reactions or secondary reactions confuse the picture. Moreover, maintaining isothermal operation in a batch reactor in the presence of thermal effects due to the ongoing reaction can be difficult, and can lead to random errors as the temperature controller struggles to maintain isothermality.

In operating the TS-BR, the required temperature changes may be caused by an internal heater, an external heater, the heat of reaction, or any combination of such agencies; there are no restrictions on the trajectory that the temperature must follow in clock time, and thus the trajectories of the ramps require little control. If the operator wishes to impose a specific ramping behaviour, say a linear ramp, there will be a need for more careful temperature control. However, this type of complication does not satisfy any theoretical requirement or improve the quality of the data.

Finally, conventional isothermal operation requires many runs to yield a reasonably valid estimate of the temperature dependencies of the kinetic parameters. A number of isothermal runs are needed, each at a selected reaction temperature. This procedure is repeated at various temperatures. Since the analysis normally occurs at the end of a run, i.e., at one level of conversion, many runs of different duration may have to be performed at each temperature in order to investigate the course of the reaction as a function of conversion.

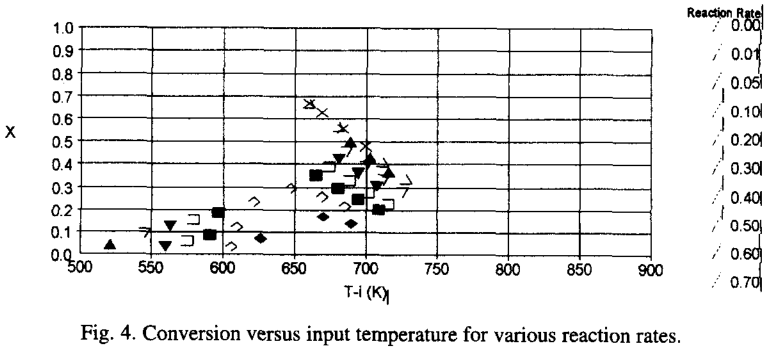

Fig. 4. Conversion versus input temperature for various reaction rates.

Fig. 4 shows several isokinetic data sets recovered from the temperature scanning operation of a batch reactor whose results were shown in Fig. 1 and Fig. 2.

This illustrates an alternative to the conventional isothermal data set: an alternative mapping of the data set made available by a TS-BR. Various other mappings can be assembled by repeating the above series of runs at various feed concentrations, pressures, or other reaction conditions. The total data set, with a reasonably sure interpolation to fill in the gaps due to limitations in sampling rates, etc., will allow an examination of the performance space of a given system in two or three dimensions of the operator's choosing. The addition of this and other user-friendly data-manipulation and interpretation software features can transform any TSR into a research instrument, not just a reactor.

TS data-gathering and data-handling operations are ideally suited for computer involvement at all stages of operation. The proposed kinetic instrument will, therefore, be capable of presenting the data in any desired graphical form in two or three dimensions, just as other contemporary instruments do. By contrast, most autoclave reactors presently in use consist of home-made assemblies, or commercial versions of such assemblies, requiring "point by point" data gathering and subsequent off-line processing of the data.

Unfortunately the TS-BR will require recharging after each run, thus denying us the advantages of full automation; a batch reactor is not an "open" system.

2.2. *The TS-stream-swept reactor*

The temperature-scanning stream-swept reactor (TS-SSR) requires the same type of configuration as that presently being used for the semi-quantitative evaluations involved in temperature-programmed desorption and other such TA techniques, all of which rely on temperature ramping during data collection. In this sense, a potential TS-SSR is already commercially available from various vendors. However, to our knowledge, none of these commercial TA instruments make temperature-scanning operation available as an option, nor is there any indication that TA instruments have been used in this manner to study kinetics.

Just as the BR has its special merits and uses which make it the preferred reactor configuration in some instances, such as for studies of the reactions of limited quantities of liquids, the SSR can be the optimum configuration for other studies, such as ore roasting, solids decomposi-

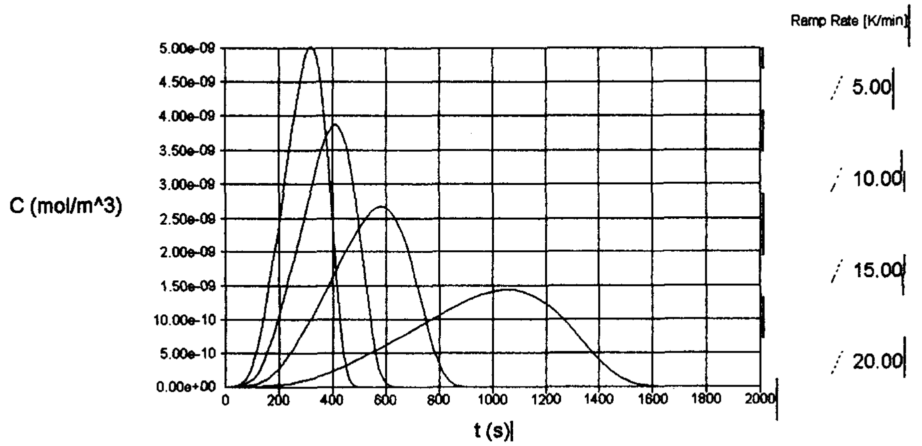

Fig. 5. Concentration versus clock time for various external temperature ramp rates.

tion, desorption kinetics and a wide range of other rate processes, mostly involving solids.

The underlying operating requirements of the TS-SSR are simple: the static sample must be ramped in temperature at the same rate as the stream of sweeping fluid, which can be a gas or a liquid. In the simplest configuration, the temperature and composition of the sweeping fluid must not change significantly during passage over the solid sample; otherwise, we may not be observing the forward rate of reaction, free of complications due to a back reaction or secondary reactions. Operation of this reactor therefore involves the following steps.

1. Load the sample cell with the sample.
2. Begin the flow of the sweeping fluid at a velocity that is adequate to assure that no significant back reaction will take place.
3. Begin collecting composition data at the outlet of the reactor or at the sample (e.g., by gravimetry).
4. Begin ramping the temperature of the fluid and sample at the same rate.
5. End the procedure when the sample has achieved 100% conversion.
6. The TS-SSR is also not an open reactor, and in general we must repeat steps 1–5 with a fresh sample, making sure that the temperature trajectory does not repeat any of those used previously.

Fig. 5 shows the result of such an experiment in terms of signal versus clock time. The signal could represent, for example, the water content in the exit stream in a study of the rate of desorption or dehydration of a solid. The area under each curve in Fig. 5 represents the total amount of water released. If one calculates this total area and then, at each clock time during the run, calculates the fraction of that total area which has accumulated up to that point, one obtains the fraction of reaction completed at each clock time.

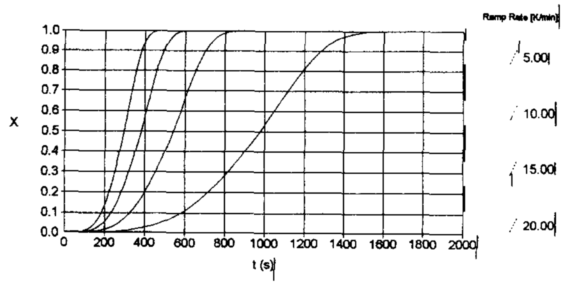

Fig. 6. Conversion versus clock time for various external temperature ramp rates.

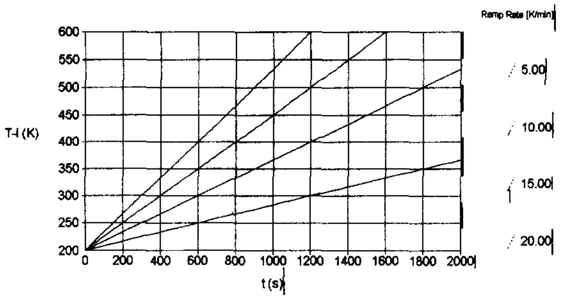

Fig. 7. Input temperature versus clock time for various external temperature ramp rates.

This produces curves such as those shown in Fig. 6, which represent data analogous to that shown in Fig. 1.

Fig. 7 shows the behaviour of temperature versus clock time in the SSR operation, and is analogous to Fig. 2 for the batch reactor. In Fig. 7 the curves are simply the linear ramping trajectories employed in this experiment; there are no heat effects large enough to distort the temperature ramps in this simulation. Fig. 6 and Fig. 7 show that the SSR can yield the same type of data as the batch reactor. Calculation of the rates and the consequent collection of conversion–rate–temperature $(X–r–T)$ triplets, therefore, proceeds in exactly the same manner as that described for the batch reactor. In effect, the SSR is simply a batch reactor with operating advantages, in some cases, over a conventional autoclave.

Notice a very useful relationship between Fig. 5 and Fig. 6. Fig. 6 represents the fraction converted as a function of clock time; its derivatives therefore yield the rate of reaction as a function of clock time. But the derivatives of Fig. 6 will give us a plot exactly like Fig. 5, scaled by the total area under the curve in Fig.

5. We see, therefore, that the raw signal recorded in Fig. 5 presents us directly with a number which is related to the rate of reaction. This will be true no matter how complex the shape of the curve in Fig. 5. This curve may in fact be very complex if a number of overlapping processes take place, for example due to desorption of a material from sites of differing strength. Notice also the similarity between Fig. 3 and Fig. 5. In both cases these are rate curves resulting from batch operation. Fig. 8 shows some isokinetic rates recovered from data in Fig. 5 and Fig. 6.

Although the BR and the SSR produce identical forms of data, they differ greatly as to where and how they may be used in practice, and therefore occupy distinct and rarely overlapping niches in the study of reaction kinetics. It is also clear that TS procedures can be readily implemented in many existing TA instruments, and will eventually constitute an integral feature of most if not all future TA configurations. Such devices, combined with convenient data-fitting algorithms and user-friendly presentations of the results, will make available a kinetic instrument for quantitative kinetic studies of solid reactions. The kinetics of these reactions will thereby be made much simpler and accessible than they have been to date.

There are advantages in making the several TS-SSR samples that are required to complete a TS-SSR experiment of uniform size. First, this means that the area under each of the curves in Fig. 5 will be the same, so that the "raw" experimental readings which yield Fig. 5 will report a number directly proportional to the rate of the reaction, without any further processing or scaling. We can therefore omit the process of integration used to scale the rates from the raw TS-SSR data, and avoid any errors which are introduced by this procedure, which is required to provide a scaling factor for the raw TS-SSR data when the samples are not of the same size. Second, with uniform-size samples it will not be necessary to drive the reaction to completion in all runs in order to obtain the absolute rates of reaction. In fact, one does not need to take even one run to completion in order to measure relative reaction rates from incomplete curves on Fig. 5, as long as one is sure that the sample sizes were the same. On the other hand, if the samples are not of the same size, the results must be gathered in the manner described in the first instance and the rates are available only after the whole peak has passed in each sample and its scaling factor has been evaluated.

If the gas–solid reaction is reversible and the net rate of reaction depends on the gas phase concentration of one of the reactants, the TS-SSR will still give the correct net rates of reaction. By changing the rate of flow of the sweeping stream in successive scannings, one can determine both the forward and reverse rates of reaction using TS methods. Furthermore, if there are multiple overlapping peaks in

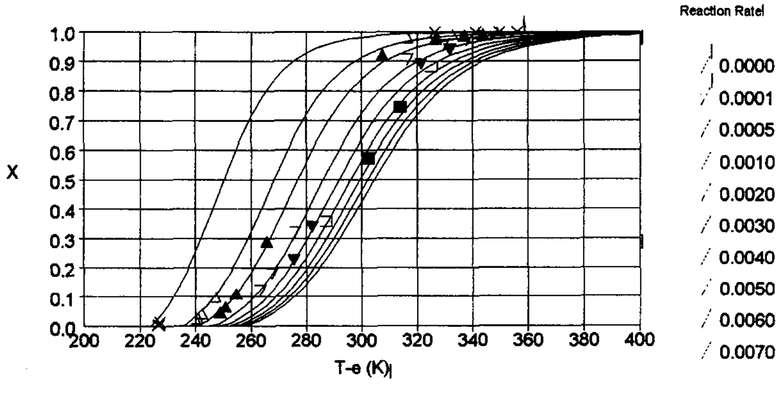

Fig. 8. Conversion versus exit temperature for various reaction rates.

the curve on Fig. 5 (or Fig. 3, for that matter), peak deconvolution precedes the evaluation of the successive rates of reaction when one is using conventional methods. However, with TS-SSR data, the techniques described will yield the total rate of reaction at each temperature: i.e., at each point along the curves in Fig. 5. This fact may be useful in guiding the deconvolution process by applying postulated kinetic expressions to describe each of the underlying rates (i.e., each rate corresponding to a process responsible for one of the peaks), and synthesizing the overall curve from the sum of the rates, rather than by deconvolving the curves in Fig. 5 into a sum of idealized (often assumed) peak shapes.

The TS-SSR techniques are not limited to the measurement of rates in chemical kinetics in static circumstances. Similar procedures can be implemented in the study of rate processes such as adsorption/desorption, physical transformations, heat flows and other time/temperature-dependent processes. In some of these applications, for example in calorimetry or gravimetry, there may be no need for a sweeping stream of fluid, reducing the TA apparatus to a simple TS-BR.

2.3. The TS-continuously stirred tank reactor

2.3.1. Steady state operation

The Continuously Stirred Tank Reactor (CSTR) is also an unusual reactor. Like the SSR, in steady-state operation it yields reaction rates directly from an analysis of the output composition, without differentiation, although in this case the reading of output conversion has to be deciphered to yield the rate of reaction using the "design equation" for the CSTR. It is also a continuous or "open system" reactor, capable of being operated either at steady state or in the TS mode without changing the sample of reactant between runs. This is in contrast to the two previous reactors where the reactant sample has to be replaced, or restored in some fashion, after each run. In many ways the CSTR is the most attractive reactor for fundamental kinetic studies of the reactions of fluids, and in particular for studies in heterogeneous catalysis. Only its mechanical awkwardness has kept it from being the preferred configuration for laboratory studies.

The steady state "design equation" relating conversion in a CSTR operating at isothermal conditions to the rate of reaction is simply:

$$\tau = C_0(X_f - X_0)/(-r_f), \tag{1}$$

where τ is the space time, and is defined as the weight of catalyst divided by the volumetric flow rate of the feed; C_0 is the concentration of the reactant at zero conversion; X_f is the fraction converted at the output of the reactor; X_0 is the fraction converted at the input to the reactor; $-r_f$ is the rate of conversion of the feed at the output concentration.

In most laboratory experiments X_0 is zero, leading to the simplified form of the design equation:

$$\tau = C_0 X_f/(-r_f). \tag{2}$$

The conventional CSTR is much easier to maintain at an isothermal condition than a BR or a PFR and, as Eq. (1) shows, yields the desired (X–r–T) triplets directly from measurements of the conversion and the temperature of the output stream. However, it suffers from the same problems as the BR if one means to collect data at a selected temperature. Any heat evolved by the reaction must be taken into account in achieving a specific temperature, making temperature control conversion-dependent. Much trimming of temperature control is necessary in order to collect a set of isothermal data at various conversions and the same temperature. Typically, it may take a day or more to tune the reactor to the desired temperature at a new conversion, by adjusting flow rate and/or temperature control.

2.3.2. Transient operation

In the TS mode of operation the reactor is never at steady state. As a result, the form of

Eq. (1) changes to include an "accumulation" term:

Curves of composition versus clock time (C versus t) in the reactor can be recorded during each run. These composition data are converted to yield curves of fractional conversion versus clock time (X versus t). An example of such a result is shown in Fig. 1.

$$\tau = C_0 X_f / \left[-r_f + \left[(C_0/\Phi) * (dX_f/dt) \right] \right], \quad (3)$$

where Φ is the catalyst load in grams of catalyst/volume of the reactor; τ is in grams of catalyst/volumetric feed rate; C_0 is in moles/unit volume; $-r_f$ is in moles of feed/gram of catalyst/time.

The operation and data collection in a TS-CSTR experiment proceeds as follows:

1. Load the reactor basket with catalyst.
2. Establish a feed rate at an initial low temperature.
3. Begin ramping the temperature of the feed.
4. Begin collecting the following data:
    - 4.1. output composition;
    - 4.2. output temperature;
    - 4.3. output volumetric flow rate (this can be obtained by calculation in many gas phase reactions, and is unimportant in liquid phase reactions)
5. Terminate the temperature ramping at a selected condition.
6. Repeat steps 2–5 at a new feed rate.

Complications such as volume expansion can also be taken into consideration here and lead to equations which yield the same X-r-T triplets from TS-CSTR operation as those obtained from conventional isothermal CSTRs.

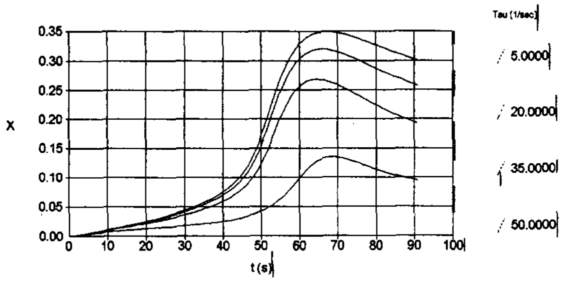

Fig. 9. Conversion versus clock time for various space times.

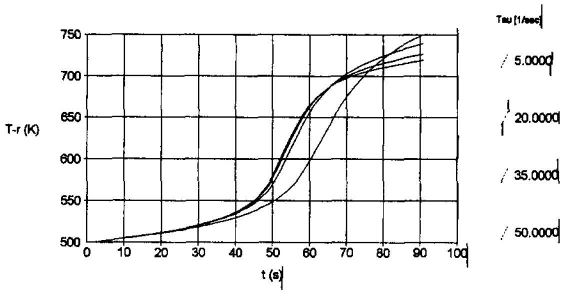

Fig. 10. Reactor temperature versus clock time for various space times.

Fig. 9 shows the data collected by a TS-CSTR operated in the following manner.

As clock time progressed, the temperature of the feed was ramped linearly, together with the exterior temperature of the reactor, in order to minimize heat losses through the walls of the reactor. This procedure was repeated at various feed input rates, keeping the temperature ramping rate the same in each run. Fig. 10 shows the effect of the exothermicity of the reaction inside the reactor (and at the outlet).

Since the output condition corresponds to the condition in the working volume of the CSTR, the rate is calculated at those conditions by using Eq. (3) and is shown in Fig. 11. The data from Fig. 9, Fig. 10 and Fig. 11, when collected at the same clock time produce the desired triplets of X–r–T data for kinetic model fitting.

Fig. 12 shows isokinetic rates extracted from the X–r–T data from Fig. 9 to Fig. 10 and overlaid on the true rates for the reaction. It is clear that the TS algorithm recovers the isokinetic rates very well. We can now fit these data to rate expressions derived from mechanistic considerations in any of the ways mentioned before.

Once again, there are no restrictions on how the temperature ramping is done. The only operating requirement is that the trajectory of the time-temperature plot be different for each feed rate. It is also possible to collect useful data

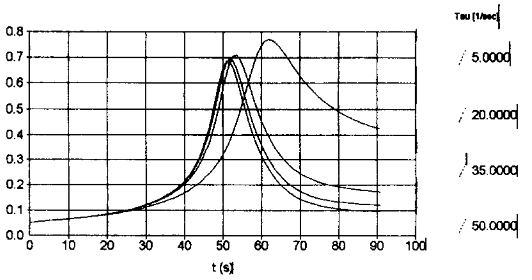

Fig. 11. Reaction rate versus clock time for various space times.

both on the up-ramp and on the ramp down, thereby speeding up data collection by a factor of more than two. To make this mode of operation even more productive, one could change the feed rate at the top of a ramp and then proceed to ramp down using the new feed rate. This procedure widens the hysteresis distance between the up-ramp trajectory and the down-ramp trajectory, allowing a broader range of reaction conditions to be investigated. Other, more esoteric, methods of TS-CSTR operation will be described elsewhere; these can enlarge the choice of useful operating modes to make the TS-CSTR the most flexible of the TSRs.

As a final bonus, one can imagine a control system for a TS-CSTR which consists of a "joy-stick", with motion in the X-direction controlling the rate of temperature ramping, while that in the Y-direction controls feed rate. By moving the joystick, one can move the reactor output on the X–T plane shown in Fig. 12. This can re-involve the under-utilized operator of a TS-CSTR by allowing him/her to explore various corners of the performance space by moving the operating point around the X–T plane using the joy-stick. Once a suitable X–T trajectory has been established by trial and error, it may be decided to use that trajectory to perform all routine tests in the testing program for a particular type of catalyst. By automating the desired trajectory (it is hardly a ramp anymore — more of a meander), detailed data can be collected over a broad range of interesting operating conditions, for each variation of the catalyst being developed. Unlike the traditional method of testing in a PFR at "standard conditions", this type of testing would be designed to examine various interesting regions of performance space of new catalysts, or even to re-examine the performance of existing catalysts. To those experimentalists used to the struggle to achieve isothermal steady-state operation in a CSTR, the idea of roaming the X–T plane using a joy-stick, unconstrained by the usual strictures, should be rather tempting.

2.4. The TS-plug flow reactor

2.4.1. The uniqueness of the TS-PFR

The Plug Flow Reactor (PFR) in its conventional isothermal or adiabatic mode of operation is the preferred configuration in both laboratory and plant scale reactors. At the same time the temperature scanning version of the PFR is the most difficult of the TSRs to understand and to operate. However, it is the most productive in

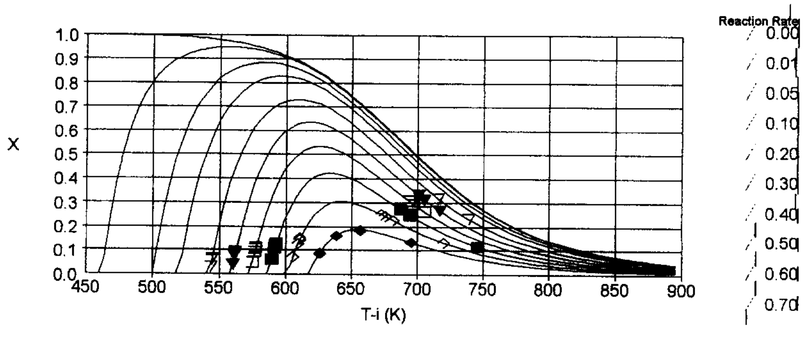

Fig. 12. Conversion versus exit temperature for various reaction rates.

terms of the quantities of data it yields per unit time and must not be ignored. Fortunately, once TS-PFR operation is understood and correctly implemented, even this reactor is more forgiving and easier to control as a TS reactor than when it is operated in the conventional isothermal or adiabatic mode. More importantly, the TS-PFR offers a method of inherently rapid data acquisition which is a consequence of the need for interpolation at all stages in the processing of raw data. The bottom line is: the TS-PFR produces much larger quantities of data, much faster, than any other reactor type.

The mode of data handling required for the TS-PFR is more difficult to understand because of its very different contacting pattern, as compared to the BR, CSTR and SSR, where both temperature scanning and isothermal operation ensure that the whole reactant charge is at all times at a uniform temperature. Not so for the PFR, which, if the reaction is not strictly thermoneutral, or heat transfer is not perfect, has a temperature profile along the axial direction. The profile develops as a result of thermal effects due both to the reaction itself and to the ramping of the input temperature. This makes it necessary to ensure a well-conditioned temperature profile from run to run if interpretable data is to be obtained. Only by the application of certain ''boundary conditions'', involving the method of temperature ramping and other features of operation of the reactor, is it possible to establish the profiles that permit our algorithms to interpret correctly the data from a PFR operated in the TS mode. This means that, unlike the cases of the other reactor types, in the TS-PFR careful temperature control during ramping, and other strictures relating to the temperature, must be observed.

2.4.2. Operation of the TS-PFR

The operating procedure for a TS-PFR requires careful attention to the details of how each run in an experiment is performed. Each experiment proceeds as follows:

1. Load the reactor with catalyst.
2. Establish a feed rate at an initial temperature.
3. Begin ramping the temperature of the feed.
4. Begin collecting the following data:
    4.1. output composition;
    4.2. output temperature;
    4.3. output volumetric flow rate (this can be calculated in many gas phase reactions and is unimportant in liquid phase reactions).
5. Terminate the ramp at a preselected condition.
6. Repeat steps 2 to 5, using exactly the same ramping procedure for a number of selected feed rates. There is no need to reload, as the PFR is an open system.

In performing the above experiment, more than just the ramping rate must be regimented; four boundary conditions must be observed.

Boundary condition 1: this is the stricture in step 6 — exactly the same ramping procedure must be used in each run of an experiment. This makes TS-PFR operation less flexible than that of the other configurations. However, implementation of this condition ensures that the thermal history of an increment of feed, as it exits the reactor, is properly conditioned. Although this history is not known in detail, the fact that it is well defined and conforms to the requirements of the theoretical equations will allow the output signal to be translated into rates of reaction at a known temperature. There is an interesting extension of the TS-PFR temperature ramping procedure which we will mention only in passing. One can minimize the time wasted in cooling the PFR after each run before starting the next ramp-up, as per steps 3 to 5. Instead, one can ramp up to a pre-set inlet temperature at one ramping rate, change the feed rate by a pre-selected factor and ramp the temperature down to the initial condition at a different ramping rate. The two sets of rampings, up and down, produce two sets of data, both of which can be interpreted by an expanded version of the algorithms we are about to describe. In this way one can save all of the time otherwise idled by the cool-down between up-ramps. Only the time used to achieve isothermality at the low temperature, before the next ramp up, is spent without producing data.

Boundary condition 2: the reactor must be of uniform effectiveness along its length (i.e., uniform in diameter, uniformly packed with catalyst, etc.). This ensures that the rate of reaction is not distorted by physical effects. This condition is also necessary in isothermal PFR operation.

Boundary condition 3: each run must begin with the reactor at the same condition throughout the bed; usually isothermal. This ensures that the subsequent evolution of the axial temperature profile starts on the same basis in each run.

Boundary condition 4: the temperature of the surroundings with which the reactor exchanges heat (i.e., the exterior of the reactor) must be ramped in the same way, from the same starting temperature, in each run. This ensures that the driving forces for heat flows between the reactor and its surroundings are the same from run to run.

We can readily see the effect on the physical setup of imposing the above boundary conditions. Condition 2 requires uniformity of the reactor ''effectiveness'' and guarantees that all heat transfer coefficients, heat capacities, and catalyst amounts are independent of position along the reactor. This condition must be carefully implemented in TS operations, as it should be in any PFR. Some of the requirements of condition 2 are less obvious than the simple requirement for homogeneity in the packing of the catalyst. For example, the reactor must always be in the turbulent-flow regime so that plug flow is maintained under all experimental conditions employed in the TS-PFR experiment. The heat transfer coefficients must also be relatively insensitive to the linear velocity of the reactant fluid; preferably, they should be minimized by the choice of the materials of reactor construction, or by active means. Among the active means available is the technique of ramping the temperature of the reactor surroundings at the same rate as that of the feed. This will minimize heat transfer from the inside of the reactor to the surroundings.

Condition 3 defines the same starting point for the subsequent evolution of the temperature profiles from run to run. Condition 1 then imposes the same temperature ramping program for each run. Finally, condition 4 guarantees that, during the evolution of the temperature profiles as a consequence of ramping, the driving potentials for heat transfer, and hence for changes in reactor temperature, are the same from run to run in an experiment.

Conditions 1 to 4 are the ''boundary conditions'' that are necessary and sufficient to define the operating regime required for correct TS-PFR operation. Additional conditions are required to assure plug flow operation and must also be obeyed, but these are identical to those required to assure proper isothermal PFR operation.

2.4.3. *The raw results obtained by operating a non-adiabatic non-isothermal TS-PFR*

Fig. 13 shows the conversion data collected in the manner described above, at the output of a fixed-length TS-PFR, as a function of clock time. The several lines correspond to separate runs at a series of constant feed rates, each run using the same boundary conditions. This set of runs constitutes one non-adiabatic non-isothermal TS-PFR experiment on a reaction with a volume expansion factor of 2. The corresponding output temperatures are shown in Fig. 14.

Nothing much can be done with any one

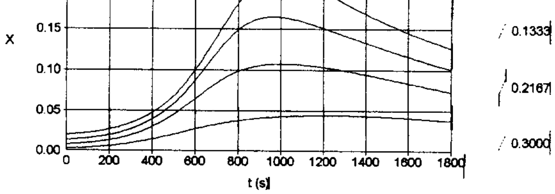

Fig. 13. Conversion versus clock time for various space times.

point, or any one line, or even any two lines on Fig. 13 and Fig. 14. Even if the boundary conditions have been correctly applied, these raw data are uninterpretable in terms of rates of reaction without applying the algorithms developed for TS operation in the PFR. The requisite mathematics is presented elsewhere [2–4]. To gain an intuitive understanding of the principles underlying these algorithms, without resorting to a simple re-statement of the defining equations, we must remind ourselves of the processes taking place in PFRs and the method of collecting kinetic data from various modes of PFR operation. We do this by first considering the behaviour of an adiabatic PFR at steady state.

2.4.4. *The observations expected from a long adiabatic PFR*

In an arbitrarily long adiabatic PFR, the temperature profile along the reactor at steady state is defined by the exo- or endothermicity of the reaction, the reactant flow rate, the degree of conversion and various heat capacities. By measuring the output temperature and composition of the product stream, we can calculate the conversion and the thermal effects of the reaction. Once we have this information we can measure the conversion at other input conditions simply by measuring the output temperature at steady state. In most cases we can do this with some assurance without knowing the heat capacities of the reactants and products because the "adiabatic operating lines" of most systems are straight and all have the same slope in the X–T plane, regardless of the input temperature. It will be important to remember that in our discussion the term "operating line" is reserved for all lines which are generated by plotting conversion against temperature, using data gathered from a long PFR whose feed temperature is kept constant; or by any other means which will give identical results. Fig. 15 shows a set of segments of adiabatic operating lines for the same reaction as that shown in Fig. 13 and Fig. 14. These are not the operating lines for the non-adiabatic TS-PFR, which produced the results shown in Fig. 13 and Fig. 14.

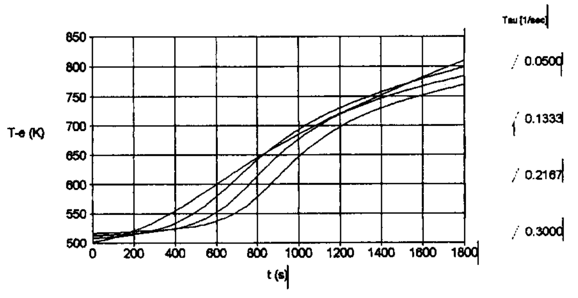

Fig. 14. Exit temperature versus clock time for various space times.

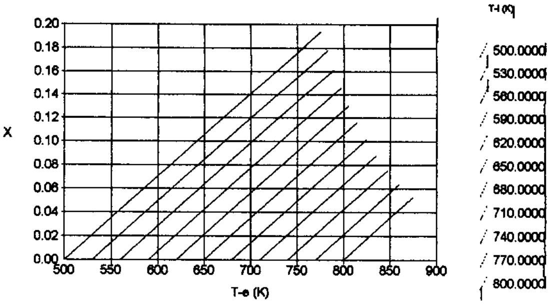

Fig. 15. Conversion versus exit temperature for various input temperatures.

Points along a single adiabatic operating line in Fig. 15 correspond to those one would observe by reading the conversion and temperature at various distances from the entrance of a long adiabatic PFR, i.e., at various space times, τ. Clearly an adiabatic operating line could also be constructed by measuring the output X and T of a fixed-length adiabatic reactor operated at a series of different feed rates. By doing the latter we would be synthesizing the behaviour of a long adiabatic PFR from data obtained using a short fixed-length reactor.

From either set of observations one could plot conversion against space time (X versus τ) at the constant input temperature we used, as shown in Fig. 16.

A corresponding plot of output temperature against space time (T versus τ shown in Fig. 17) would complete the set of observations from either a long or a fixed-length adiabatic PFR.

If the data are gathered at steady state then the clock-time dimension is unimportant, but if the reactor is not at steady state, then the X–τ and T–τ pairs would have to be collected at the same instant in the evolving condition of the reactor (i.e., at the same clock time), and we would have the many curves on Fig. 16 and Fig. 17, each corresponding to a different clock time during the evolution of the transient. We will consider this case later; it forms the basis for understanding the consequences of temperature scanning in a PFR.

As discussed previously, from each X–τ curve in Fig. 16 we can measure the rates of reaction by taking slopes, and read the corresponding temperatures from the T–τ curve on Fig. 17, at the same position along the reactor, i.e., at the same τ. This will give many X–r–T triplets from each operating line. Notice that each output temperature is encountered only once in the set of triplets from a single operating line. By repeating this procedure using several operating lines, each with a different input temperature, we would encounter a given output temperature on a number of the operating lines and thus obtain the variety of triplets required to sieve out isothermal or other sets of rates. Alternatively, we could proceed directly to data fitting, as was suggested in the case of the other TS-BR. We see that the signal from a long adiabatic steady-state PFR is readily interpreted to yield valid X–r–T triplets and that the required variety of triplets, suitable for use in determining the form of the rate equation, can be obtained if data are collated from several operating lines.

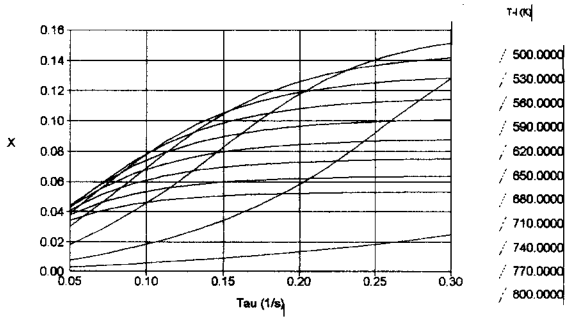

Fig. 16. Conversion versus space time for various input temperatures.

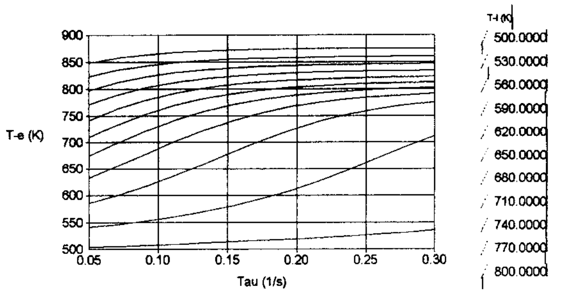

Fig. 17. Conversion versus exit temperature for various space times.

2.4.5. *The idea of re-mapping data sets from adiabatic reactors*

What may not be immediately obvious is that appropriate interpolation and an alternative sieving of the same data sets from the several adiabatic operating lines, each with a different input temperature, will also yield data sets of output conversion versus output temperature at constant τ. Many such re-mapping procedures are commonly used to make data easier to understand in conventional data handling; it is also a procedure which is at the heart of interpreting the data from a TS-PFR. In the case under consideration, this means that operating the long adiabatic PFR at steady state at a series of inlet temperatures (i.e., observing a series of adiabatic operating lines) can be made to yield X–T data at various sampling points (i.e., various values of τ), from which X–T lines at constant τ can be plotted, as shown in Fig. 18.

The X–T plots in Fig. 18 are not operating lines in our terminology; instead, each line presents the conversions and temperatures which would be observed at a given position along a long adiabatic steady-state PFR if we were to keep the feed rate constant and vary the inlet temperature. On the other hand, if we operate a fixed-length adiabatic reactor at a constant space velocity (i.e., feed rate, or space time τ) and at steady state, and ramp its input temperature, we

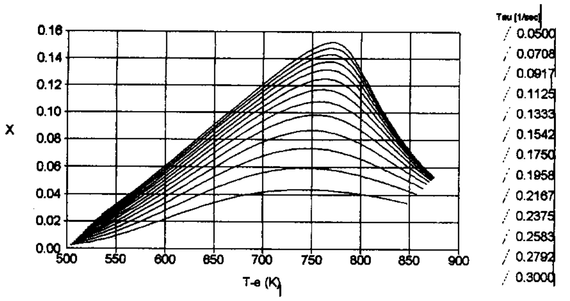

Fig. 18. Conversion versus exit temperature for various space times.

would generate the same lines as those on Fig. 18, each corresponding to the feed rate used. Now we have a further clue to interpreting temperature scanning, but we are still talking about adiabatic operation of the PFR, though by now we are considering temperature scanning the adiabatic fixed-length reactor.

The effect of ramping the input temperature of a long adiabatic reactor, while operating at a constant feed rate, is, therefore, to move the readings of X and T at each sampling point of the reactor along the corresponding curve of X versus T shown in Fig. 18. Motion along this curve would normally be induced by changing the feed temperature as a function of time, and, hence, would correspond to changes in clock time. Clearly in this ramping operation there will be as many curves on Fig. 18 as there were points monitored in the long adiabatic PFR. We have also shown that each curve in Fig. 18 could also be generated by the output of a fixed-length adiabatic reactor whose feed temperature is ramped in runs at various feed rates.

Notice also that Fig. 18 shows the same dependencies as the one we could have constructed by an appropriate re-mapping of the raw experimental data used to plot Fig. 13 and Fig. 14. The key to constructing a figure such as Fig. 18 from the experimental TS-PFR data is to select data from Fig. 13 and Fig. 14 at the same clock time. This requirement for the collation of data will prove to be the key to deciphering the message contained in the signal at the outlet of either an adiabatic or a non-adiabatic TS-PFR; we must assemble TS-PFR data into triplets collected at the same clock time.

2.4.6. Re-mapping of data sets from non-adiabatic non-isothermal reactors

Consider now the same long PFR, operating on an exothermic reaction with constant feed rate and temperature but, unlike the long adiabatic PFR, with some finite rate of heat transfer between the reactor and the surroundings. In the presence of a finite rate of heat transfer, a temperature profile will develop along the reactor, producing an operating line which can be observed by noting the conversion and temperature at points along this long non-adiabatic non-isothermal PFR. This will not be an adiabatic operating line, which has a slope dictated solely by the thermal properties of the system, nor an isothermal operating line, which we force to be vertical on the X–T plane by means of temperature control. This real operating line will lie between the two limits and is influenced by heat flows between the system components. It can be, but need not be, a straight line.

The point is that real data will still yield a valid operating line as previously defined. From this the curves of X versus τ and T versus τ at constant inlet temperature can be derived, just as they can from the operating lines of a long adiabatic PFR. The slopes of this X versus τ plot will still give valid reaction rates at the corresponding temperatures. Valid X–r–T triplets can, therefore, be collected from a series of runs at various input temperatures and made to yield isothermal selections of triplets, suitable for further processing, just as before. Adiabaticity and isothermicity are not important if we can gather data at many points along a non-adiabatic non-isothermal reactor of sufficient length. The problem now becomes: how can we obtain this same data from a PFR of fixed length by observing only the output values.

We know from the above discussion that the behaviour of a long reactor can be synthesized from results obtained at the output of a fixed-length reactor in two cases:

- if the long PFR and the fixed-length PFR are both isothermal and obey the same boundary conditions of homogeneity, etc;
- if the long PFR and the fixed-length PFR are both adiabatic, homogeneous in physical attributes, etc.

Other suitable strictures should therefore allow the synthesis of the behaviour of a long non-adiabatic non-isothermal reactor from output data obtained from a properly operated and constrained fixed-length reactor. This is exactly what the TS-PFR boundary conditions, together with the data collation and interpretation algorithms, provide. The appropriate algorithms use the four boundary conditions to regiment the required data gathering procedures and thereby allow us to synthesize the real non-adiabatic non-isothermal operating lines from data obtained at the outlet of a fixed-length non-adiabatic non-isothermal TS-PFR. The TS algorithms therefore allow us to interpret the raw data from real (and therefore non-ideal) operation into a usable form: the same *X*–*r*–*T* triplets that one would have obtained by operating an ideal isothermal reactor.

2.4.7. *Observations from a fixed-length non-ideal PFR undergoing temperature scanning*

Gathering data at many points along a long adiabatic reactor is not an easy matter. To begin with, it is much easier to build a reactor that is not strictly adiabatic nor, for that matter, strictly isothermal. Moreover, it is easier to measure conversion and temperature at the outlet of a reactor; otherwise, one has to face the problems of constructing a reactor with multiple sampling ports, then contend with the limited flexibility of sampling due to the fixed locations of the sampling points, and with the potential distortions in readings resulting from the presence of the temperature probes and from sample withdrawal. It is much simpler to measure temperature and conversion at the outlet of a fixed-length reactor, operating under non-adiabatic non-isothermal conditions, and then convert the data to a more familiar and usable form which would have resulted from operating an equivalent long reactor. A correctly operated TS-PFR, together with the data assembly algorithms, does this.

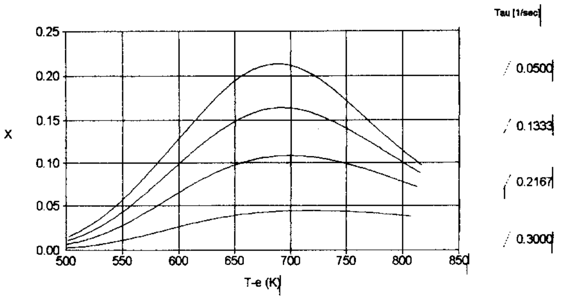

Fig. 19. Conversion versus exit temperature for various space times.

As was pointed out in previous discussion, data from Fig. 13 and Fig. 14 can be re-mapped to yield the experimental *X*–*T* lines at constant feed rate (τ), by taking pairs of experimental *X* and *T* values from Fig. 13 and Fig. 14, from curves at the same feed rate, at the same clock time. The resultant *X*–*T* lines for the real reactor are shown in Fig. 19. They are the real TS-PFR equivalent to those shown in Fig. 18 for the adiabatic TS-PFR experiment carrying out the same reaction. What we note is that if the four boundary conditions are observed, these real *X*–*T* curves at constant τ present data which would also have been observed: at a given τ in a long non-adiabatic non-isothermal PFR, with the same physical characteristics as the fixed-length PFR, while both undergoing the same temperature ramping procedure.

Another way of gaining an understanding of the required data-assembly procedure is provided by examining how one would obtain the rate of reaction from the outlet values of conversion and temperature from two separate runs, carried out in the same fixed-length reactor. The two runs differ by an incremental amount in feed rate and both runs are carried out at the same temperature ramping rate. We now consider the following: under what conditions do we have comparable outputs so that the correct differential $\mathrm{d}X/\mathrm{d}\tau$ can be interpreted as a rate at some temperature? Careful consideration will show that the comparable results will occur at the same point during the ramping process, i.e., at the same clock time and the same input temperature.

A final perspective may make this even clearer: imagine that the above readings are taken at two adjoining positions in a long non-adiabatic non-isothermal reactor undergoing temperature ramping. In this case, we should take data at the two positions, which must be very close together, at the same instant of clock time. If the ramping procedure and the other boundary conditions are fulfilled in both reactors, then these data will correspond exactly to the data from the two runs described in the previous paragraph.

Assembling the *X–T* couplets in this way (i.e., at the same clock time), from data gathered using a fixed-length reactor in the TS-PFR operating mode at constant feed rate, is the key to unlocking the kinetic message conveyed by the output conversion and output temperature of a TS-PFR. We assemble meaningful X versus T data from the output conditions of the fixed-length TS-PFR, operated using the boundary conditions described, when we choose values collected at the same clock time.

We know now how to construct valid curves of *X* versus *T* at constant feed rate from the two kinds of experiments, but not the operating lines. However, we have succeeded in synthesizing the correct behaviour of the long reactor undergoing a temperature scanning operation by the proposed re-mapping of real reactor output values. In order to construct the corresponding non-adiabatic non-isothermal operating lines, we must re-map the data once more, and bring in one more piece of data: the history of inlet temperature as a function of clock time. From the *X–T* curves at constant τ on Fig. 19 we pick *X–T* pairs which had arisen from the same inlet temperature (and therefore at the same clock time) and various values of τ. Observing boundary condition 1 has ensured that these pairs of *X–T* at constant clock time arose at the same inlet temperature.

Correlating data at the same clock time is the key to the collation of data so that the operating lines for a long non-adiabatic non-isothermal reactor can be assembled from data obtained using a real fixed-length PFR undergoing temperature scanning.

Once we have triplets of outlet conversion, outlet temperature and inlet temperature at various constant space times, i.e., the *X–T* data at constant inlet temperature — we can plot the real operating lines for this long non-adiabatic non-isothermal PFR. As we have already seen, with this information we can proceed to re-map the same data to produce $X\text{–}\tau$ and $T\text{–}\tau$ plots from the operating lines in the manner described above, and use these to obtain the *X–r–T* triplets we require for kinetic studies. Clearly, the actual application of the algorithms does not

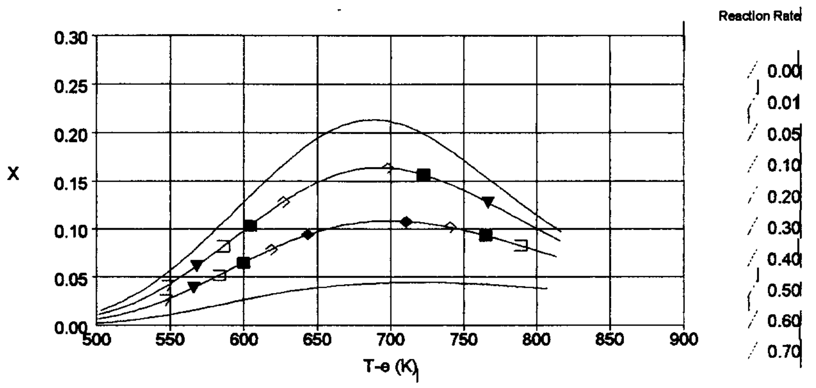

Fig. 20. Conversion versus exit temperature for various reaction rates: 4 runs.

have to be so roundabout, and is done automatically by a suitably programmed data-logging computer. Notice that we do not care just how non-ideal the actual fixed-length reactor is. Its proper operation in the temperature scanning mode will allow us to assemble the correct operating lines for a correspondingly non-ideal long reactor: all else follows. This means that the design requirements for the construction of a TS-PFR are less demanding than those for either of the conventional ideal PFRs.

Fig. 20 shows isokinetic points calculated from the TS-PFR data shown in Fig. 13 and Fig. 14. The four curves in Fig. 20 are the cross-plots from Fig. 19. Because we use spline functions to interpolate data for the various mappings, the lowest and highest feed rates in Fig. 19 were not used to yield kinetic rates.

Fig. 21 shows an extension of this procedure from four to ten constant-feed-rate runs using up-ramping only and a wider range of feed rates.

Only those points which coincide with both the theoretical constant rate of reaction curves and the experimental constant feed rate curves are shown. However, all the points lying between the highest and lowest experimental curves, along any of the theoretical constant reaction rate curves, can be recovered with the same accuracy. Experience with a laboratory reactor of this type indicates that a real experiment such as that which produced Fig. 21 takes no more than 8 hours. If up and down ramping is applied, this amount of data can be collected in a little more than half that time. There is, however a negative aspect to up and down ramping. This comes from the fact that the two extreme feed rate curves are used as the end points in the spline interpolations. Thus if ten up ramps are run, data are recovered from eight of the rampings. If five up and five down ramps are run, only six usable rampings are made available; the up and down rampings belong to separate sets for the purpose of rate recovery using the TS algorithms.

As Fig. 20 and Fig. 21 show, the data-handling procedure produces rates that correspond exactly to the actual rates used in the simulation. Moreover, because of the interpolations used to map the raw data onto the various coordinates, a satisfactory interpolation procedure will allow access to an infinite number of data points within the area delineated by the experimental X–T curves. In other words, the TS-PFR provides an unlimited amount of data, within a wide range of temperatures and conversions, at realistic reaction conditions, in a very short time.

2.4.8. *The scope of the temperature scanning technique in the PFR*

Consider the currently known methods of obtaining kinetic rate data. The best known and most commonly applied is the isothermal method, where the same temperature is maintained at all points along the axis of the PFR.

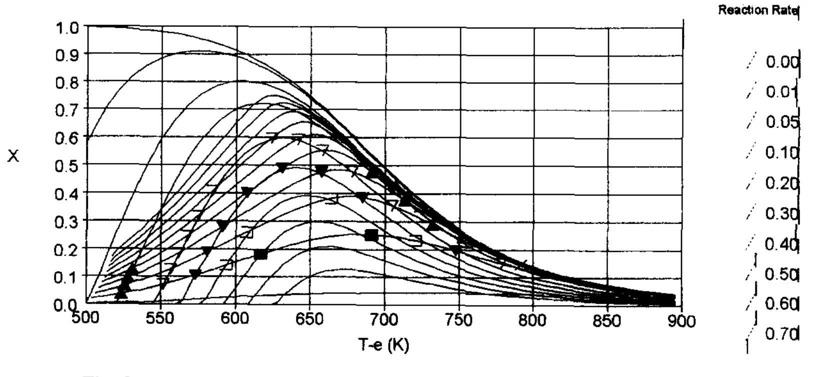

Fig. 21. Conversion vs exit temperature for various reaction rates: 10 runs.

This is easily achieved in a reactor system where all the heat transfer coefficients are infinite and heat is redistributed instantaneously so that temperature can be controlled by external heaters or coolers. The isothermal PFR therefore constitutes one idealized limit of a PFR. The other limit is encountered when all heat transfer coefficients are zero: in this limit we have no heat flow and therefore adiabatic operation.

These two limits are the two conditions of PFR operation used in current operations. They also define idealized conditions which are difficult — in some cases, impossible — to achieve. The TS-PFR fills the range occupied by real heat transfer coefficients which lie between zero and infinity. This makes TS methods readily-approachable by real reactor systems. Although the resulting raw kinetic data is uninterpretable by previously available procedures, by using the appropriate algorithms, this raw TS-PFR data can now be translated to a form which would have been observed at an idealized condition: normally, the isothermal condition. The TS-PFR includes as its own limits the adiabatic and isothermal mode of operation, and therefore encompasses the whole continuum of heat transfer regimes. The TS methods therefore represent a generalization of reactor thermal operating conditions. TS technology expands the range of thermal regimes where plug flow reactors may be operated, increases their productivity, and improves the quality of the data gathered.

3. Some constraints on temperature scanning techniques

The temperature scanning methodology will be widely applicable in kinetics research and catalyst development. However, it will not solve all problems immediately; some it may not solve at all. The TS-PFR, TS-CSTR and TS-BR are all unquestionably applicable to the study of the chemical kinetics of homogeneous reactions of fluids, where adsorption equilibria, catalyst decay, and induction periods are unimportant. However, in systems where such effects are important, there could be problems.

For example, if the rate of temperature scanning is such that the catalyst surface is not in adsorption equilibrium with the gas phase at each instant during the experiment, a more sophisticated understanding than that described above will have to be brought to the interpretation of the results. It is hard to say how such a problem, if it arises, will finally be resolved; there is not enough theoretical work, and certainly no experimental work, to act as a guide. On the other hand, the problem does not seem to be insoluble if one takes the position that the "signal" at the output of the reactor contains all the information about what goes on in the reactor. The solution should lie in the formulation of appropriate boundary or operating conditions.

A second, and less serious constraint involves variable heat transfer coefficients between the reactor and its surroundings, as well as between the fluid and the catalyst. Such problems may arise in the TS-PFR if the heat transfer coefficients are strong functions of flow rates; they are non-existent in the other reactor types under TS operation or in PFRs operating at steady state. There seems to be no reason to expect that such a heat transfer variability will prove to be an insurmountable problem. Solutions and ameliorations of this situation may include:

- the choice of materials of construction for the reactor;
- the policies and methods of heating the exterior of the reactor as the feed temperature is ramped;
- reduction of the ramping rate,
- accounting, by calculation, for the changing heat transfer coefficients as feed rate is changed.

In general this problem is non-existent if the operating lines of the reactor-reaction combination form a set of parallel lines within the range of conditions scanned in an experiment. Failing that, the space velocities used in the individual runs of the TS-PFR experiment must be so spaced on the X versus T plane that the splining function used between points in Fig. 16 affords a good interpolation and therefore produces valid rates from the raw data. This is a matter to be dealt with on the basis of experience or solved by the simple expedient of doing a few more runs per experiment; for example, by replacing an experimental program of ten up rampings by one of ten up ramps with each followed by a down ramp, over the same range of space velocities. When the data density is adequate and the splining function operates efficiently, no extent of heat transfer will distort the data. The choice of the splining function is, therefore, important and, in extended programs investigating a series of homologous systems, splining functions which are particularly applicable to the system at hand can be developed.

Some catalysts require time to come to chemical equilibrium with the feed: Fischer–Tropsch catalysts are a good example of this type of behaviour. Systems of this kind may never be amenable to TSR studies. On the other hand, it may be possible to study slowly-evolving systems of this sort by examining their catalytic properties rapidly, over a wide range of reaction conditions, at selected stages of their transformation.

Catalysts which exhibit a rapid decay of activity will also be suitable for TSR studies, although the requisite theory is only now becoming understood. Cracking catalysts in particular present a major challenge. Other less-rapidly-decaying catalysts, such as reforming catalysts, may be studied at various stages of deactivation. Such studies would clearly delineate not only the progression of activity changes but also the changes in selectivity. In fact, it may be possible to examine such catalysts periodically, at various stages of deactivation, while they are on-stream in an industrial reactor. This information should indicate the optimum changes in ''severity'' which are required to move the process along a path of optimum performance. A TSR used in this way becomes an instrument for monitoring plant performance.

There may be opportunities among these constraints. For example, diffusion limitations are hard to spot in catalysts tested under steady state conditions. This has added to confusion as to the specific activity and selectivity of catalysts tested in the absence of information regarding the extent of diffusion limitation. The dangers of this lack of information are made the more real when we remember that catalysts are routinely tested at ''standard conditions'', while the objective may be to increase activity. There is reason to expect that certain operating modes of the standard TS-PFR will readily identify the presence of diffusion limitations on a given catalyst.

4. Conclusions

We have presented new and broadly applicable methods of data acquisition in the study of chemical reactions. These hold promise of substantially altering the research environment in the study of chemical kinetics, reaction mechanisms, and in catalyst development. TSR operation yields valid results, over a broad range of conversion and temperature, at realistic reaction pressure, temperature and feed composition, producing vast amounts of kinetic data, in a very short time, in an apparatus no more expensive and easier to operate than the currently available laboratory reactor systems and their associated off-line analytical facilities. Appropriate temperature scanning methods have been described above for all of the basic reactor types, as well as for the SSR configuration. This latter configuration makes kinetic data readily available from a new type of reactor, much like the present TA instruments which are not yet designed for this purpose. Their application to the study of solid phase transformations offers interesting and untapped possibilities for the study of kinetics in the solid phase.

In this work we have discussed the applications of temperature scanning with reference to chemical reactions only. It seems clear that heat and mass transfer as well as other physical properties may be studied in this way. Measurement of the rates of phase changes or of rates of changes in electrical or optical properties may well be speeded up by equivalent procedures. In fact, it is probably fair to say that TS methods can be applied to all systems which are temperature and time dependent.

Beyond this generalization of the applicability of temperature scanning to physical properties, one can foresee the application of this methodology to other systems, even further removed from chemical reaction-rate studies: systems whose triplets of data show conceptual and formal parallels to the kinetic triplets treated in this work. In the case of chemical kinetics, the application of temperature scanning is made possible by abandoning the paradigm of isothermal steady-state operation in favour of temperature scanning and data collection ''on-the-fly''. In other fields other paradigms may have to be questioned before transient operations can be implemented.

Finally, the development of sophisticated ''kinetics instruments'' based on TS technology holds out a promise of improving the effectiveness of studies in reaction kinetics, and thereby bringing about rapid progress in the affected research areas. The ideal ''kinetics instrument'', like every other new technology, will have its limitations, along with unexpected opportunities for further evolution. Where this will lead is hard to foresee, but one thing seems clear: after temperature scanning is made available in commercial laboratory reactors, few researchers will wish to continue with the present tedious methods of data gathering.

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