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The temperature scanning reactor
II: Theory of operation

N.M. Rice [a], B.W. Wojciechowski [b,*]

[a] *Department of Mathematics and Statistics, Queen's University, Kingston, Ont., Canada*
[b] *Department of Chemical Engineering, Queen's University, Kingston, Ont., Canada*

Abstract

The theoretical development of the defining equations for the Temperature Scanning methodology and for operation of Temperature Scanning Reactors is presented. Batch Reactors, Stream Swept Reactors, Continuous Stirred Tank Reactors and Plug Flow Reactors are considered in detail. For all these reactor types, we show that rates of reaction, with their associated temperatures and levels of conversion, can be measured quickly and accurately. This can be done under non-isothermal conditions, without invoking any approximations and unhindered by the complexity of the unknown kinetics of the reaction under study. The TS methodology is robust and it reduces errors normally encountered in one-off experiments. It can reveal the presence of collateral effects such as catalyst decay and diffusion limitations. The equations for dealing with these effects, although not presented here, follow directly from the considerations presented. The kinetic data-gathering capabilities of the TSR are limited only by the availability of analytical methods for continuous (or at least frequent) monitoring of the composition of the reactor output stream. As long as a satisfactory analytical method is available for the system under study, there is no need to use traditional, isothermal, steady-state methods; TS methods will yield better data, faster and over a broader range of conditions, at no cost in veracity.

Keywords: Theory; Temperature scanning; Reactor design; Transient kinetics

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1. Introduction

As detailed in the previous article [1], laboratory studies of reaction kinetics and associated selectivity phenomena have always been hampered by the tediousness of experimental data-gathering procedures, and by the difficulty of maintaining isothermal conditions during a run. The consequences of these problems are apparent in the sketchy kinetic data normally produced in laboratory studies. The Temperature Scanning Reactor systems described in Ref. [1] overcome these difficulties by increasing data generation rates by some orders of magnitude, while removing all concerns connected with maintaining isothermal conditions during a run.

Below we present the mathematical foundations for four types of Temperature Scanning Reactors (TSRs), in the order of their increasing complexity: the batch reactor (TS-BR), the stream-swept reactor (TS-SSR), the continuous stirred tank reactor (TS-CSTR) and the plug-flow reactor (TS-PFR).

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[*] Corresponding author.

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For each reactor type, we consider the simple reaction A → B (this does not imply that simple kinetics are required, in order for the methods outlined to be applicable). For each type, a temperature scanning run consists of starting the reactor in some condition, and letting it run for some time, during which time the operating temperature is ramped in some way, more or less carefully depending on the particular variety of reactor being used. A temperature scanning experiment consists of one or more runs, depending on the type of reactor used. Conversion and temperature are monitored during each run, and reaction rates are calculated from this data. The reaction rates so obtained correspond to points spread throughout a region on the X–T (''reaction phase'') plane, and by appropriate interpolation one can obtain collections of isothermal or isokinetic rates. One can then perform the usual data fitting to proposed rate expressions.

We will use the following notation:

t = (clock) time into a run
V = volume of fluid in reactor (l)
N = number of moles of A in reactor (mol)
X = percentage conversion
C_A = concentration of reactant
C_{A0} = initial concentration of reactant
T = temperature of reactant
T_R = temperature of reactor body
T_C = temperature of catalyst
T_E = temperature external to reactor body
W = weight of catalyst in reactor (g)
ϕ = W/V = catalyst load (g/l)
$r(X,T)$ = reaction rate $(1/W)\mathrm{d}N/\mathrm{d}t$ (mol/s/g)

2. The defining equations for the TS Batch Reactor (TS-BR)

Consider a constant volume batch reactor for which the temperature of the reactant can be ramped (either by internal heaters; or by heating the reactor body with external heaters; or simply by using the heat of reaction). We assume that stirring in the reactor is vigorous and thorough enough so that conditions are always uniform throughout the reactor. Using appropriate probes, C_A and T are monitored continuously (or at least at short time intervals). Then X, T, T_R, T_C obey the following rate equation:

$$r_A = \frac{1}{W}\mathrm{d}(C_A V)/\mathrm{d}t = -\frac{C_{A0}}{\phi}\frac{\mathrm{d}X}{\mathrm{d}t}, \tag{1}$$

together with the heat transfer equations:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -k_1 r(X,T) - k_2(T - T_R) - k_3(T - T_C), \tag{2}$$

$$\frac{\mathrm{d}T_R}{\mathrm{d}t} = k_4(T - T_R) - k_5(T_R - T_E), \tag{3}$$

$$\frac{\mathrm{d}T_C}{\mathrm{d}t} = k_6(T - T_C), \tag{4}$$

where $k_1, \ldots, k_6$ are well defined combinations of "constants" involving the heat of reaction, heat capacities, surface areas, heat transfer coefficients, and the density of the reacting mixture.

The above is a simplified model, of course. A more complete model would have separate terms for the various components of feed, reactor and catalyst. Also, some of the "constants" may in fact vary with temperature and conversion. The main point still applies: however the equations evolve, Eq. (1) holds at every instant, and hence may be used to measure rates of reaction simply by numerically differentiating the observed concentration C_A over time t.

Obtaining reaction rates for a batch reactor is, therefore, extremely simple in principle. There is considerable freedom as to how the temperature may be ramped; in fact, the operator should use very different ramping rates in the various runs of any one experiment, so as to move the reaction over as large a region in the X–T plane as possible. Once reaction rates have been calculated along the X–T trajectories of the separate runs and have yielded the X–r–T triplets for each run, one may proceed to "sieve" the full data set from the experiment for any constant temperature T, and, hence, get isothermal rates. These can then be fitted as usual to proposed rate expressions at isothermal conditions. More generally, the data set from the whole experiment can be fitted to rate expressions, with the rate parameters expressed as functions of temperature. Even if isothermal fittings are undertaken, the sieving procedures can be done using many different temperatures so that one may examine the temperature dependence of the rate constants in great detail.

3. The defining equations of the TS Stream Swept Reactor (TS-SSR)

For a Stream-Swept Reactor we consider an experiment with some material A in a reactor being swept by a fluid, and either reacting, or adsorbing, or desorbing to produce some product B. Denote by N_0 the total amount of A present in the solid at the beginning of a run, and by $N(t)$ the amount of A left at time t (in convenient units — moles, grams, etc). Consider the rate of reaction (using slightly different units than for the other reactors):

$$r(t) = -\frac{1}{N_0}\int_0^\infty \frac{\mathrm{d}N}{\mathrm{d}t}\,\mathrm{d}t. \tag{5}$$

Supposing all of A eventually reacts or desorbs so $N(\infty) = 0$, and we have:

$$N_0 = -\int_0^\infty \frac{\mathrm{d}N}{\mathrm{d}t}\,\mathrm{d}t. \tag{6}$$

Then Eq. (5) becomes

$$r = \frac{\mathrm{d}N/\mathrm{d}t}{\displaystyle\int_0^\infty \frac{\mathrm{d}N}{\mathrm{d}t}\,\mathrm{d}t}. \tag{7}$$

Now consider two cases:

1. where the material in the reactor can be measured directly (e.g., by weighing), and
2. where the product B can be measured as it exits the reactor.

In either of these cases it is easy to calculate reaction rates, as follows.

In case (i), let W be the amount of inert material in the reactor, and $M(t)$ the total amount of reactive sample in the reactor, so:

$$M(t) = W + N(t). \tag{8}$$

If $M(t)$ is measured and recorded continuously then at the end of the run one may calculate:

$$N_0 = M(0) - M(\infty), \tag{9}$$

and

$$N(t) = M(t) - M(\infty). \tag{10}$$

It may be that $N(t)$ can be measured and recorded directly, in which case the above two steps are unnecessary. In any case, $N(t)$ or $M(t)$ may be numerically differentiated to calculate $\mathrm{d}N/\mathrm{d}t = \mathrm{d}M/\mathrm{d}t$. From this, Eq. (5) may be used to calculate r_A.

In case (ii), let $P(t)$ measure the rate at which the product B exits the reactor at time t. $P(t)$ might for instance be the concentration of B in the exit stream. $P(t)$ is proportional to $\mathrm{d}N/\mathrm{d}t$; the proportionality constant will depend on the stoichiometry of the reaction, on the rate of flow of the fluid through the reactor, and on the units of measurement used for A, B and $P(t)$, but there will be some constant ρ such that

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\rho P(t). \tag{11}$$

Then from Eq. (3) we have

$$N_0 = \int_0^\infty \rho P(t)\mathrm{d}t, \tag{12}$$

and, hence, from Eq. (7) it follows that:

$$r = \frac{\rho P(t)}{\int_0^\infty \rho P(t)\mathrm{d}t} = \frac{P(t)}{\int_0^\infty P(t)\mathrm{d}t.} \tag{13}$$

Note that neither case (i) nor case (ii) requires any calibration of measuring instruments, or knowledge of the stoichiometry of the reaction, or even knowledge of the flow rate; all such factors cancel out in Eqs. (5) and (13), yielding quantitative rates from relative measurements.

The physical set-up for a Stream-Swept Reactor experiment is the same as for a Temperature-Programmed Desorption (TPD) experiment, and in both cases the temperature of the sweeping fluid and of the sample is ramped. However, for a Stream-Swept Reactor experiment, it is essential to record the temperature (T) and conversion ($N(t)$) as functions of time (t). The stream can be temperature-ramped in any convenient way; the specifics do not affect Eqs. (5) or (13). At any time t the fraction of A converted is (for case (i) and case (ii) respectively):

$$X = \frac{\int_0^t \frac{\mathrm{d}N}{\mathrm{d}\tau}\mathrm{d}\tau}{\int_0^\infty \frac{\mathrm{d}N}{\mathrm{d}\tau}\mathrm{d}\tau} = \frac{\int_0^t P(\tau)\mathrm{d}\tau}{\int_0^\infty P(\tau)\mathrm{d}\tau}. \tag{14}$$

Thus, for each time t we have some temperature T, conversion X, and the corresponding rate r_A given by Eq. (5) Eq. (13), i.e., we have the X–r–T triplets. Each single run thus produces rates along some curve in the X–T plane. As in the batch reactor discussed above, several of these curves, for different ramping rates of the reactor, can be combined to yield sets of isothermal rates. And again as in the TS-BR described above, from this one can obtain isothermal rate constants and their temperature dependence.

A word of caution is required. If the interaction of the gas phase with the solid is reversible and near equilibrium at reaction conditions, this procedure will yield net rates of the reaction. In order to assure that only the forward reaction rate is being observed, one must sweep the solid sample at a rate fast enough to reduce the reverse reaction to insignificance. The required sweeping rate is the rate at which the measured rate of reaction ceases to change with further increases in sweeping rate.

4. The defining equations for the Ts-Continuously Stirred Reactor (CSTR)

The situation for a CSTR is somewhat more complicated than for a batch reactor because of the fluid flowing continuously into and out of the reactor, and because of volume expansion due to heating and reaction.

Consider a CSTR for which the temperature of the feed and the temperature external to the reactor can be ramped in some controlled way. We assume that the stirring in the reactor is vigorous and thorough enough so that the fluid can be considered to be a microfluid. This means that, although different molecules will have different residence times and histories, they will lose their identity and will have no determinable past history. It also means that the concentration measured at the outlet gives the current concentration inside the reactor. The variables C_A, X, T, T_R, T_C, T_E, V, W, ϕ, $r(X,T)$ will have the same meaning as for the batch reactor. In addition we denote:

T_I = inlet temperature of feed
F_0 = inlet feed rate of reactant A (mol/s)
f_0, f = inlet and outlet volumetric flow rates (l/s)
C_{A0}, C_A = inlet and outlet concentration of A (mol/l)
$1/\tau$ = space velocity f_0/W (l/s/g)
δ = volume dilation factor due to heating and reaction (expanded volume)/(original volume)

In order to get an expression for the reaction rate, we will need the net rate of accumulation of reactant A in the reactor. For this, we must consider flow rates in and out of the reactor. In any short time dt, the volume of feed entering the reactor is $f_0 \mathrm{d}t$ and a corresponding expanded volume $\delta f_0 \mathrm{d}t$ leaves. In addition, during this time the dilation factor δ changes by some amount $\mathrm{d}\delta$, and the proportional change $\mathrm{d}\delta/\delta$ forces out of the reactor a corresponding portion of the total amount of fluid inside, namely $(\mathrm{d}\delta/\delta)V$. Thus, the total volume exiting in time dt is $\delta f_0 \mathrm{d}t + (\mathrm{d}\delta/\delta)V$. Consequently, the outlet volumetric flow rate is

$$f = \delta f_0 + \frac{V}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}t}. \tag{15}$$

Since, for a dilation factor δ, the relation between conversion and concentration is given by

$$C = \frac{C_0}{\delta}(1 - X), \tag{16}$$

it follows that the outlet rate for reactant A is

$$r = Cf = C\delta f_0 + C\frac{V}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}t},$$

$$r = F_0(1 - X) + CV\frac{1}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}t}. \tag{17}$$

From the definition of r we see that the rate of disappearance of reactant A due to reaction is $-rW$. Also, the choice of units for space velocity means that $F_0 = C_{A0} f_0 = C_{A0} W/\tau$. Consequently the net rate of accumulation of moles of A in the reactor is:

$$\begin{aligned}\frac{dN}{dt} &= \text{input rate} - \text{output rate} - \text{loss via reaction},\\ &= F_0 - F_0(1-X) - CV\frac{1}{\delta}\frac{d\delta}{dt} + rW,\\ &= \frac{C_{A0}W}{\tau}X - CV\frac{1}{\delta}\frac{d\delta}{dt} + rW. \end{aligned} \tag{18}$$

At steady state, when $dN/dt = 0$ (and, hence, $d\delta/dt = 0$), this reduces to the usual design equation for a steady state CSTR:

$$-r = C_{A0}X/\tau.$$

In the general non-steady-state case we may still solve Eq. (18) for r. Noting that $N = VC_A$ so that $dN/dt = V\,dC_A/dt$, and that, from Eq. (16), $d(\delta C_A) = -C_{A0}\,dX/dt$, Eq. (18) yields:

$$\begin{aligned}-r &= \frac{C_{A0}}{\tau}X - C_A\frac{V}{W}\frac{1}{\delta}\frac{d\delta}{dt} - \frac{V}{W}\frac{dC_A}{dt},\\ &= \frac{C_{A0}}{\tau}X - \frac{1}{\phi\delta}\left(C_A\frac{d\delta}{dt} + \delta d\frac{C_A}{dt}\right),\\ &= \frac{C_{A0}}{\tau}X - \frac{1}{\phi\delta}\frac{d}{dt}(C_A\delta),\\ &= \frac{C_{A0}}{\tau}X + \frac{C_{A0}}{\phi\delta}\frac{dX}{dt}. \end{aligned} \tag{19}$$

The second term is crucial; it takes account of the accumulation of product occurring during the non-steady-state mode of operation. Indeed, just as the first term corresponds to steady-state operation, the second term corresponds essentially to a batch operation: if there were zero flow, so that $\tau = \infty$, and there were no volume expansion, so $\delta = 1$, then Eq. (19) becomes the batch Eq. (1).

The development of Eq. (19) given above is based on the assumption of perfect mixing, so that local conditions always equal average conditions. Individual molecules, however, will either react or not react while in the reactor, and will have different residence times in the reactor in which to react. In Appendix A an alternate derivation of Eq. (19) is given, based on the time distribution of individual molecules within the reactor.

It is perhaps disconcerting to have both clock time t and space time τ appear in Eqs. (18) and (19) since they are very different measures of time. A check of units verifies, however, that each term in Eq. (19) has units of mol/s/g, which are the units chosen for r.

The CSTR system, therefore, obeys the following reaction equation:

$$\frac{dX}{dt} = -\frac{\phi\delta}{C_{A0}}r(X,T) - \frac{\phi\delta}{\tau}X, \tag{20}$$

and the heat transfer equations:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -k_1\delta r(X,T) - \frac{\phi\delta}{\tau}(T - T_1) - k_2(T - T_R) - k_3(T - T_C), \tag{21}$$

$$\frac{\mathrm{d}T_R}{\mathrm{d}t} = k_4(T - T_R) - k_5(T_R - T_E), \tag{22}$$

$$\frac{\mathrm{d}T_C}{\mathrm{d}t} = k_6(T - T_C), \tag{23}$$

where $k_1, \ldots, k_6$ as before are "constants" in various equations involving the heat of reaction, heat capacities, surface areas, heat transfer coefficients, or the density of the reacting mixture. These heat transfer equations are essentially the same as Eqs. (2)–(4) for the batch reactor, with the addition in Eq. (21) of the term $\phi\delta/\tau(T - T_I)$ to account for cool inlet feed mixing with hot reactant. The factor ϕ/τ (which equals f_0/V) accounts for the mixing of inlet fluid into the reactor, and the factor δ accounts for the difference in density between inlet fluid and fluid in the reactor.

As with the batch reactor, the above is a simplified model. But even with elaborate models the main point still applies: no matter how the equations evolve, Eq. (20) holds and, hence, Eq. (19) may be used to calculate rates of reaction. The experimental procedure, therefore, is to vary input temperature T_I continuously, (and/or the external temperature T_E, and/or the space velocity) to drive the reaction into various X, T regions. Continuous monitoring of the output concentration C and temperature T, along with some way of measuring or calculating δ, allows one to calculate X and $\mathrm{d}X/\mathrm{d}t$, and, hence, $r(X, T)$ from Eq. (19) and gives the X–r–T triplets.

There is a practical difficulty associated with the measurement of the volumetric exit flow rate and hence of δ. Two possibilities for calculating δ suggest themselves:

1. given enough information about the chemical reaction, one may calculate directly $\delta = (1 + \epsilon X)T/T_I$ using a known expansion factor ϵ; or
2. one may use measured inlet and outlet flow rates.

In this latter case, when δ is changing it will not exactly equal f/f_0; however, as detailed in Appendix B, its value can be tracked continuously via the differential equation obtained from Eq. (15):

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = \frac{\delta}{V}(f - \delta f_0). \tag{24}$$

Note that an interesting opportunity presents itself, in that the operation of a TS-CSTR can roam at will throughout the parameter space defined by the various temperatures and flow conditions of the reactor. Since Eq. (19) gives the reaction rate as a function of instantaneous conditions in the reactor, independent of any history of how those conditions were reached, the reactor operator may freely vary inlet flow temperature, inlet flow rate, external temperature, and internal heating. As described in detail in Ref. [1], this offers a grand opportunity for ingenious schemes of data gathering designed to acquire data at preferred conditions of output temperature and conversion.

There is one source of concern, and it echoes a similar concern in traditional steady-state CSTR experiments. What temperature represents the *real* reaction temperature in a catalytic CSTR? In simulations we have used the reactor outlet temperature; however, the temperature of the bed itself may better represent the reaction temperature for catalytic reactions carried out in CSTRs. In that case the bed temperature would have to be measured and data sets assembled with this parameter included for the purpose of determining activation energies and other temperature dependencies.

5. The defining equations for the TS Plug Flow Reactor (TS-PFR)

Obtaining reaction rates from a TS-PFR is considerably more complicated than from any of the previously considered reactors. As we will see, it is not possible to obtain rates from a single run; rather, one must assemble data from several runs in a particular way. As a result, the operating conditions (temperature ramping, space velocity, etc.) must be controlled much more carefully. Consider an experiment consisting of several runs with a temperature scanning plug flow reactor. In order for the analysis below to be valid, the following operating requirements must be met:

1. The reactor must be of uniform effectiveness along its length (e.g., uniform diameter and uniformly packed with catalyst).
2. The reactor must have the same catalyst load $\phi = W/V$ for each run.
3. Each run must start with the reactor in the same steady-state condition (not necessarily isothermal).
4. During each run the temperature of the input feed is ramped. The ramping may be linear or non-linear, and may go up or down or both, but it must be exactly the same for each run.
5. The external temperature surrounding the reactor may also be ramped, again in the same way for each run, but not necessarily the same as the inlet feed.

In the first instance we assume that the feed rate (and, hence, space time for the reactor) is kept constant during each run (a different constant for each run). It is by comparing corresponding data from different runs with different space times that we will be able to calculate rates.

The variables X, T, T_R, T_C have the same meaning as before, except than now they are functions of both time-into-run (clock time, t), and position along the reactor (since we will generally not have uniform conditions along the reactor). $T_I(t)$ and $T_E(t)$ also have the same meaning as before, and in fact the temperature ramping restrictions mentioned above require that each of $T_I(t)$ and $T_E(t)$ must be the same function of clock time t for each run.

For a plug travelling through the reactor there are three different time measurements that must be considered:

t = time into run at the moment of input of a plug (''clock time'')
τ = space time (= 1/space velocity defined on input conditions)
s = length of time a plug has been in the reactor (''contact time'').

Space time τ is a convenient but imprecise measure of the time a plug of feed takes to flow through a reactor. A plug at any given position in a long reactor is associated with a space time corresponding to that for a reactor of that total length. Thus, a plug travelling through a long reactor has an increasing space time associated with it. We need to establish the relation between this space time τ, defined on the input conditions, and the ''real'' contact time s. If the linear velocity through the reactor were constant, then τ would be proportional to s: namely $\tau = \phi s$, where ϕ, as before, is the catalyst load W/V. However, volume expansion due to reaction and heating results in the linear velocity varying along the reactor due to dilation by a factor δ, and this fact complicates the relation between τ and s. Nevertheless, for any short increment along the reactor the dilation factor will be nearly constant, so the velocity will be nearly constant at $\delta \cdot$ (inlet velocity). Consequently, for that short increment $d\tau = \delta \cdot \phi \cdot ds$. This is the relationship we will need below.

A small increment of feed (plug) with inlet volume V_{p0}, inlet temperature T_0, and with N_0 initial moles of reactant A will expand on reaction and heating to volume $V_p = \delta V_{p0}$ with some N moles of A. The amount of catalyst covered by this increment is $W_p = (W/V)V_p = \phi V_p$. Also, since $X = 1 - N/N_0$ we have $\mathrm{d}N/\mathrm{d}s = -N_0 \mathrm{d}X/\mathrm{d}s$. Consequently, the rate of reaction is:

$$-r = -\frac{1}{W_p}\frac{\mathrm{d}N}{\mathrm{d}s} = -\frac{1}{\phi V_p}\frac{\mathrm{d}N}{\mathrm{d}s} = -\frac{1}{\delta\phi V_0}N_0\left(-\frac{\mathrm{d}X}{\mathrm{d}s}\right),$$
$$= \frac{C_A0}{\phi\delta}\frac{\mathrm{d}X}{\mathrm{d}s}. \tag{25}$$

The condition of a plug will depend, of course, on both how long (s) it has been in the reactor and at what time (t) into a run it entered the reactor. X, T, T_R, T_C are, therefore, determined by the following rate and heat equations:

$$\frac{\partial X(s,t)}{\partial s} = \frac{-r(X,T)\delta(X,T)\phi}{C_0}, \tag{26}$$

$$\frac{\partial T(s,t)}{\partial s} = -k_1\delta r(X,T) \quad -k_2\delta[T(s,t) - T_R(s,t)] \\ \qquad -k_3\delta[T(s,t) - T_C(s,t)], \tag{27}$$

$$\frac{\partial T_R(s,t)}{\partial t} = k_4[T(s,t) - T_R(s,t)] - k_5[T_R(s,t) - T_E(t+s)], \tag{28}$$

$$\frac{\partial T_C(s,t)}{\partial t} = k_6[T(s,t) - T_C(s,t)]. \tag{29}$$

Using the relationship $\phi\delta \cdot \mathrm{d}s = \mathrm{d}\tau$ established above, Eqs. (26) and (27) can be more conveniently expressed in terms of space time τ rather than contact time s as:

$$\frac{\partial X(\tau,t)}{\partial \tau} = \frac{-r(X,T)}{C_{A0}}, \tag{30}$$

$$\frac{\partial T(\tau,t)}{\partial \tau} = -\frac{k_1}{\phi}r(X,T) \quad -\frac{k_2}{\phi}[T(\tau,t) - T_R(\tau,t)] \\ \qquad -\frac{k_3}{\phi}[T(\tau,t) - T_C(\tau,t)]. \tag{31}$$

Indeed, the dilation factor δ disappears from the equations. Of course, even though δ does not appear explicitly in Eqs. (28)–(31), it will be necessary, as in the case of the TS-CSTR, to measure or calculate δ, since that will be needed to convert measured outlet concentrations C_A to conversions X via the relation $X = 1 - \delta C_A/C_{A0}$.

The operating requirement noted above, that each run must begin with the reactor in the same steady-state condition, guarantees that each of the initial functions $X(\tau, 0)$, $T(\tau, 0)$, $T_R(\tau, 0)$, $T_C(\tau, 0)$ is the same for each run. We have already noted that each of $T_I(t)$ and $T_E(t)$ is the same for each run.These, together with the additional boundary conditions:

$$X(0,t) = 0, \tag{32}$$

$$T(0,t) = T_I(t) \tag{33}$$

completely determine the evolution of the differential Eqs. (28)–(31). It follows that these equations will evolve identically for each run. This is the crucial point that will allow us to assemble data from different runs in order to calculate kinetic rates.

As noted before, some of the "constants" $k_1, \ldots, k_6$ (involving the heat of reaction, heat capacities, surface areas, heat transfer coefficients, and density of feed) may in fact vary with temperature and conversion. This does not affect the main point: even though some k_i are functions of X and T rather than constants, Eqs. (28)–(31) are driven solely by the values of X and T and related temperatures, and evolve independently of everything except the boundary conditions; thus they evolve identically for each run. We do need to assume that the k_i have no significant dependence on the linear velocity of the feed, since that will change from run to run.

The following procedure may thus be used to calculate kinetic rates:

1. Choose a ramping schedule for the feed temperature (and for external temperatures if desired) and choose some number, n, of feed rates. Denote by $\tau_1, \ldots, \tau_n$ the space time corresponding to each of these feed rates.
2. Measure conversion and temperature at the reactor outlet during each run to obtain $X(\tau_i, t)$ and $T(\tau_i, t)$ for each t and τ_i.
3. For any fixed clock time (time-into-run) $t = t_0$, fit a curve to the N points $X(\tau_i, t_0)$ for $i = 1, 2, \ldots, n$ to get a fitted curve $X(\tau, t_0)$. Similarly, fit a curve to the N temperature points $T(\tau_i, t_0)$.
4. Find slopes along the $X(\tau, t_0)$ curve.
5. From Eq. (30), conclude that for any τ the derivative $-C_{A0} \cdot \mathrm{d}X(\tau, t_0)/\mathrm{d}\tau$ gives the rate $r(X, T)$ at conversion $X = X(\tau, t_0)$ and temperature $T = T(\tau, t_0)$.

In Ref. [1] a detailed description is given of how one may view data assembled from different runs as equivalent to data that would be observed at different positions along a single long reactor. In brief, Eqs. (28)–(31) show that an increment of feed entering the reactor at some given clock time t_0 will experience exactly the same conversion and temperature profile as it travels through the reactor, no matter which run is being considered. The only difference is that in runs with a longer space time the increment will spend longer in the reactor and hence will traverse farther along the profile. Thus the various outlet conditions measured for different runs (for the given clock time t_0) correspond exactly to the conditions that a hypothetical single increment would experience at various points along its conversion and temperature profile, i.e., at various points as it moves through a hypothetical long reactor.

The calculation procedure described above is, therefore, equivalent to somehow observing an increment of feed as it moves through a reactor, measuring $X(\tau)$ along the way, and calculating the rate as $r(X, T) = -C_{A0} \cdot \mathrm{d}X(\tau)/\mathrm{d}\tau$.

Just as with the other temperature-scanning reactor configurations, once one has a wealth of rates $r(X, T)$ for some region in the X–T plane one may extract isothermal rates by suitable interpolation, and then proceed to fit proposed rate expressions. It is possible, and easy, using a TS-PFR to obtain all the rate data that a plug flow reactor can yield in a given system. This is done by performing a series of runs in which the run with the highest space velocity (shortest space time) is limited by the maximum pressure drop one can tolerate across the catalyst bed, while the other limit is set by a space velocity barely high enough to yield turbulent flow in the reactor. A suitable number of runs between these two limits will yield every rate measurable in that system in a PFR.

One should take note that it is tempting, but invalid, to try to obtain isothermal rates more directly from the raw data by assembling, from different runs, outlet conversions at some given fixed outlet temperature T_0. As can be readily seen, increments exiting at some given temperature T_0 in different runs (with different space times) must have entered the reactor at different temperatures, that is, at different clock times. These increments do not experience the same conversion and temperature profiles as they arrive at the outlet of the reactor and so there is no reason to expect their conversion values X to be comparable. Numerical simulations have shown that such an assembly of isothermal outlet data will not give correct rates. It is essential to assemble data corresponding to a fixed inlet temperature (that is: at the same clock time), not at a fixed outlet temperature.

6. Up-and-down temperature ramping in the TS-PFR

The productivity of a TS-PFR can be substantially enhanced by implementing more elaborate methods of temperature ramping. As described above, the simplest procedure for data gathering begins each run with the reactor and catalyst at a uniform starting temperature. At the end of the run there will be some temperature profile along the reactor, and before the next run can start, the reactor and catalyst are cooled back down to the same starting conditions. One could ramp the inlet temperature up and then down, collecting data all the time, but unfortunately, although one does get new data on the down-ramp side of the run, the down-ramp normally covers almost the same X, T region as the up-ramp.

More fruitfully, we can carry out two independent but interwoven sets of runs: a set of up-ramps using some set of space velocities, and a set of down-ramps with a different set of space velocities. This makes it possible to drive the reaction into a significantly different X, T region during the down-ramp set of runs. The only wasted time now is a pause at the top and the bottom of each run to bring the reactor to steady-state at each initial condition.

The two sets of runs, the up-set and the down-set, are treated as separate experiments for the purposes of data interpretation but the X–r–T triplets extracted from the two experiments belong to the same "reaction phase" (X–T) diagram. The two experiments can therefore serve to confirm the appropriateness of the procedures used or to reveal any collateral problems such as diffusion limitations or catalyst decay.

7. Ramping the space velocity in the TS-PFR

So far we have been supposing that space velocity is held constant during each run. We will now show that it is possible to change flow rates during a run, but this must be done with some care. The difficulty is that increments entering the reactor at the same clock time in two different runs must encounter exactly the same conditions at equal contact times along their journey. This includes, for instance, the temperature profile of the reactor itself. Changing flow rates carelessly in different runs could result in corresponding increments encountering various reactor temperatures at different times, thus destroying the equivalence that is necessary to successfully assemble data from different runs.

The appropriate way to change space velocities is developed in an informal argument below. A more formal mathematical version of essentially the same argument is given in Appendix C. Consider running three hypothetical reactors simultaneously. They will be identical except that reactor 2 is twice as long as 1 and 3. Consider feed flowing into the first reactor during the run, with some flow rate f_1, and, hence, some particular space time τ_1. For reactors 2 and 3 we can achieve twice the space time, $2\tau_1$, simply by taking the second inlet flow rate to be $f_2 = f_1$ and the third as $f_3 = f_1/2$. The "uniform effectiveness" of the reactors, as spelled out in Eqs. (28)–(31) along with the operating requirements and boundary conditions, guarantees that reactors 2 and 3 are completely equivalent; reactor 3 at all times has the same conversion and temperature profiles as reactor 2, just uniformly compressed into half the length.

Now suppose the flow rate into reactor 1 varies with clock time as $f_1(t)$. To match this, the flow rate into reactor 2 should also vary as $f_2(t) = f_1(t)$; this will result in reactor 2 having the same profiles as reactor 1, only extending further. To match reactor 2, reactor 3 should have the varying flow rate $f_3(t) = f_1(t)/2$. By the same ''uniform effectiveness'' argument, reactor 3 will still be completely equivalent to reactor 2, i.e., it will have exactly the same profiles as reactor 2, but again uniformly compressed into half the length. Feed increments entering reactors 1, 2, 3, at some given clock time t, will encounter identical conditions at equal contact times along their way; the only difference is that the increments in reactors 2 and 3 will spend longer in the reactor, and will emerge with twice the space time.

Similarly we could consider running simultaneously a number of identical reactors (all the same length) using flow rates that are various fixed fractions of the first flow rate $f_1(t)$. Increments entering these reactors at the same clock time t would traverse the same conversion and temperature profiles, getting more or less far along these profiles, and exiting with different space times. One could then plot the exit (X, τ) values and differentiate to get rates $-C_{A0} \cdot dX/d\tau$.

The operating procedure which can actually be used is effectively the same as this, only instead of simultaneously running several identical reactors one uses the same reactor over and over again in one run after another, with different space velocities. For the first run, ramp the inlet temperature as usual, and in addition ramp the inlet flow rate $f_1(t)$ in any convenient way (linearly or non-linearly). For each subsequent run use the same temperature ramp, as usual, but ramp the inlet flow rates as follows: for each of the runs 2, 3, ..., n choose any convenient constant γ_i, and use the flow rate function $f_i(t) = f_1(t)/\gamma_i$.

Rates are then calculated in essentially the same way as before. The only difference is that one needs to calculate appropriate space times. But for any given clock time t_0 the corresponding space time for the ith run is $\tau_i(t_0) = W/f_i(t_0) = W\gamma_i/f_1(t_0)$. Thus, we need only collect corresponding exit conversions $X_i(t_0)$ and temperatures $T_i(t_0)$, fit a curve to the points $(X_i(t_0), \tau_i(t_0))$ for $k = 1, \ldots, n$, and differentiate this curve to get rates $-C_{A0} \cdot dX/d\tau$ for various values of τ (and hence X). For each of these rates the corresponding T value is obtained by fitting a curve to the points $(X_i(t_0), \tau_i(t_0))$ and interpolating to the appropriate value of τ.

8. Conclusions

The equations defining the modes of operation in temperature scanning reactors are derived without any approximations. The assumptions made are minimal and confined to the ''boundary conditions'' which are most numerous for the PFR. In all other reactor types only the condition requiring uniformity persists. The rate data obtained from a TSR is therefore valid under all but the most unusual circumstances, normally ones which an operator can and should avoid. This is not to say that TSR rate data is proof against misinterpretation.

A TSR provides the correct global (i.e., overall) rates regardless of the complexity of the underlying process. It will, for example, report the correct overall rate including the effects of diffusion. The use of such rates in mechanistic rate expressions will obviously lead to problems. Other effects such as catalyst decay or failure to achieve adsorption–desorption equilibrium will also distort the observed rates of reaction. Fortunately, routinely available TSR methods reveal such problems quite readily. If the extracted rates of reaction or, more directly, the X versus T plots obtained at different ramping rates do not coincide at each space velocity, a collateral effect is distorting the data. To find this out one needs only do two runs, at two different ramping rates, for a selected constant flow rate and plot the results on the X–T plane. It may well be that in the face of such a simple test for collateral effects more care will be taken to eliminate them.

9. Nomenclature

C_0, C = initial and subsequent concentration of A,
F_0 = inlet rate of A,
$k_1, \ldots, k_6$ = constants for heat transfer equations,
L = length of PFR,
N_0, N = initial and subsequent number of moles of A in reacting volume,
N_R = number of moles of A in reacting fluid in CSTR,
N_T = total number of moles of A in CSTR,
$r(X, T)$ = rate of reaction,
s = length of time plug has been in PFR (''contact time''),
t = time into run at input of plug into PFR (''clock time''),
T = $T(s, t)$ = temperature of reactant,
T_C = $T_C(s, t)$ = temperature of catalyst,
$T_E(t)$ = external temperature,
$T_I(t)$ = temperature of input feed,
T_R = $T_R(s, t)$ = temperature of reactor,
v = $v(s)$ = linear velocity of a plug in PFR at contact time s,
v_0 = linear velocity of inlet feed to PFR,
V_0, V = initial and subsequent volume of feed increment in PFR,
V_R = volume of reacting fluid in CSTR,
V_T = total volume of fluid in CSTR,
X = $X(s, t)$ = fractional conversion of reactant,

9.1. Greek symbols

α = space velocity increase factor in up-and-down temperature ramping,
β = ratio of residence time to space time in PFR with no volume expansion,
$\delta(X, T)$ = ''dilation'' factor = expanded volume/original volume,
ε = fractional volume change constant due to reaction,
φ = ratio V_R/V_T,
τ = space time (= 1/space velocity)

Appendix A. Time-distribution derivation of TS-CSTR reaction Eq. (19)

Let $H(t, z)$ be the expected residence time distribution of a molecule that enters the reactor at clock time t, i.e., the probability that such a molecule will still be in the reactor z time units later at time $t + z$. Similarly, let $G(t, z)$ be the reaction time distribution, i.e., the probability that a molecule of reactant entering the reactor at time t will still be unreacted at time $t + z$. Denote by H_1 and H_2 the partial derivatives of H with respect to the first and second variables, and similarly for G.

Note that $H(t-z,\ z)\cdot G(t-z,\ z)$ gives the probability that a molecule entering at time $t-z$ is still in the reactor and unreacted by time t. Assuming a constant inlet feed rate F_0, so that $F_0 \mathrm{d}z$ gives the number of moles of A that enter the reactor over any short time period $\mathrm{d}z$, we see that at time t the total number of mole of A in the reactor is

$$M(t)=F_0\int_0^{\infty} H(t-z,\ z)G(t-z,\ z)\mathrm{d}z. \tag{34}$$

For a short time interval $\mathrm{d}z$, $[H(t,\ z)-H(t,\ z+\mathrm{d}z)]/H(t,\ z)$ is the probability that a molecule in the reactor at time $t+z$ will leave within the time period $\mathrm{d}z$. This probability is given by

$$\begin{aligned} p(t+z)\mathrm{d}z &= \frac{1}{V}f(t+z)\mathrm{d}z \\ &= \frac{1}{V}\left(\delta f_0+V\frac{1}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}z}\right)\mathrm{d}z. \end{aligned} \tag{35}$$

Hence

$$p(t)=\frac{\phi\delta(t)}{\tau}+\frac{1}{\delta(t)}\frac{\mathrm{d}\delta(t)}{\mathrm{d}t}. \tag{36}$$

In the limit as $\mathrm{d}z \to 0$, the above yields

$$-H_2(t,\ z)=p(t+z)H(t,\ z). \tag{37}$$

Now, by the chain rule,

$$\frac{\partial}{\partial z}H(t-z,\ z)=-H_1(t-z,\ z)+H_2(t-z,\ z), \tag{38}$$

so

$$H_1(t-z,\ z)=-\frac{\partial}{\partial z}H(t-z,\ z)-p(t)H(t-z,\ z). \tag{39}$$

Similarly, $[G(t,\ z)-G(t,\ z+\mathrm{d}z)]/G(t,\ z)$ measures the probability that an unreacted molecule of A at time $t+z$ will react within a time period $\mathrm{d}z$. Since $W\cdot r(t+z)\mathrm{d}z$ measures the number of moles of A reacting in time $\mathrm{d}z$, while $C_\mathrm{A}V$ is the total number of moles of A in the reactor, the probability of a molecule reacting in time $\mathrm{d}z$ is given by

$$\hat{r}(t+z)\mathrm{d}z=-\frac{Wr(t+z)}{C_\mathrm{A}V}, \tag{40}$$

so

$$\hat{r}(t)=-\frac{\phi}{C_\mathrm{A}}r(t). \tag{41}$$

Thus, again letting $\mathrm{d}z \to 0$, we have

$$-G_2(t,\ z)=\hat{r}(t+z)G(t,\ z). \tag{42}$$

Again, by the chain rule we have:

$$\frac{\partial}{\partial z}G(t-z,\ z)=-G_1(t-z,\ z)+G_2(t-z,\ z), \tag{43}$$

and so

$$G_1(t-z,\ z)=-\frac{\partial}{\partial z}G(t-z,\ z)-\hat{r}(t)G(t-z,\ z). \tag{44}$$

Now, since the total number of moles of A in the reactor equals $C_A V$, and $F_0/V = C_A\phi/\tau$, we see from Eq. (34) that

$$C_A(t) = \frac{C_{A0}\phi}{\tau}\int_0^\infty H(t-z,\, z)G(t-z,\, z)\mathrm{d}z. \tag{45}$$

Consequently, since $H(t, \infty)\cdot G(t, \infty) - H(t, 0)\cdot G(t, 0) = 0 - 1 = -1$, we get

$$\begin{aligned}
\frac{\mathrm{d}C_A}{\mathrm{d}t} &= \frac{C_{A0}\phi}{\tau}\int_0^\infty \frac{\mathrm{d}}{\mathrm{d}t}[H(t-z,\, z)G(t-z,\, z)]\mathrm{d}z \\
&= \frac{C_{A0}\phi}{\tau}\int_0^\infty H_1(t-z,\, z)G(t-z,\, z) + H(t-z,\, z)G_1(t-z,\, z)\mathrm{d}z \\
&= \frac{C_{A0}\phi}{\tau}\int_0^\infty -\left[\frac{\partial}{\partial z}H(t-z,\, z)\right]G(t-z,\, z) - H(t-z,\, z)\frac{\partial}{\partial z}G(t-z,\, z)dz - \frac{C_{A0}\phi}{\tau}[p(t) + \hat{r}(\\
&= -\frac{C_{A0}\phi}{\tau}\int_0^\infty \frac{\partial}{\partial z}[H(t-z,\, z)G(t-z,\, z)]dz - [p(t) + \hat{r}(t)]C_A(t) \\
&= -\frac{C_{A0}\phi}{\tau}[H(t-z,\, z)G(t-z,\, z)]|_0^\infty - \left[\frac{\phi\delta}{\tau} + \frac{1}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}t} - \frac{\phi}{C_A}r\right]C_A(t) \\
&= \frac{C_{A0}\phi}{\tau} - \frac{\phi\delta C_A}{\tau} - \frac{C_A}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}t} + \phi r,
\end{aligned} \tag{46}$$

Therefore,

$$\begin{aligned}
-r &= -\frac{C_{A0}}{\tau}\left[1 - \frac{\delta C_A}{C_{A0}}\right] - \frac{1}{\delta\phi}\left[C_A\frac{\mathrm{d}\delta}{\mathrm{d}t} + \delta\frac{\mathrm{d}C_A}{\mathrm{d}t}\right] \\
&= \frac{C_{A0}}{\tau}X - \frac{1}{\delta\phi}\frac{\mathrm{d}}{\mathrm{d}t}[C_A\delta] \\
&= \frac{C_{A0}X}{\tau} + \frac{C_{A0}}{\delta\phi}\frac{\mathrm{d}X}{\mathrm{d}t},
\end{aligned} \tag{47}$$

which is Eq. (19) as required.

Appendix B. Calculating the volume dilation factor $\delta(t)$ for the TS-CSTR

In cases where the stoichiometry is well known, one can calculate the dilation factor $\delta = (1 + \epsilon X)T/T_0$. More generally, however, it may be necessary to determine δ from measured flow rates at the inlet and outlet of the reactor. From Eq. (24) we know that $\delta(t)$ satisfies the differential equation:

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = \frac{\delta}{V}(f - \delta f_0), \tag{48}$$

with some initial condition $\delta(0) = \delta_0$.

In practice it will be sufficient to update $\delta(t)$ directly from this equation. That is, over a short time interval $\mathrm{d}t$ one may update the current value of δ by calculating

$$\mathrm{d}\delta = \frac{\delta}{V}(f - \delta f_0)\mathrm{d}t. \tag{49}$$

This simple differencing scheme is quite stable for this equation, and has the advantage of being self-correcting; that is, any measurement errors do not accumulate but have less and less effect over time.

Alternatively, in the case where f_0 is held constant during a run, it turns out that Eq. (48) has an analytic solution, where

$$h(t) = \exp\left[\frac{1}{V}\int f(t)\mathrm{d}t\right]. \tag{50}$$

$$\delta(t) = \frac{\delta_0 h(t)}{\dfrac{\delta_0 f_0}{V}\int h(t)\mathrm{d}t + 1}, \tag{51}$$

To use this formula to calculate δ in real time during a run one must continually monitor $f(t)$, update $h(t)$ via Eq. (37), and then update $\delta(t)$ via Eq. (36).

Appendix C. Ramping space velocity in the TS-PFR

Consider the first run, where the inlet flow varies with clock time as $f_1(t)$. In the PFR system Eqs. (28)–(31), $T(\tau, t)$ denotes the temperature of a feed increment that entered the reactor at clock time t and has been in the reactor for a contact time s that corresponds to a space time τ. $T_R(\tau, t)$ denotes the temperature of the reactor body at the position of that increment. Strictly speaking, however, to keep proper track of the reactor temperature we should be considering a slightly different function, namely the temperature $\bar{T}_R(\ell, t)$ at that position ℓ along the reactor. Now, $\tau = W_\ell/f_1(t)$, where W_ℓ = weight of catalyst up to position ℓ, and $\ell = V_\ell/A$, where V_ℓ = reactor volume up to position ℓ and A = cross-section area of reactor. Thus $\ell = 1/(\phi A)\cdot f_1(t)\cdot\tau$, where ϕ is the catalyst load W_ℓ/V_ℓ. Consequently, the relation between T_R and $\bar{T}_R$ is:

$$T_R(\tau, t) = \bar{T}_R(l, t) = \bar{T}_R\left(\frac{f_1(t)}{\phi A}\tau, t\right). \tag{52}$$

It is the function $\bar{T}_R(f_1(t)\tau/(\phi A), t)$ which should really appear in Eqs. (28)–(31), and similarly for the catalyst $\bar{T}_C(f_1(t)\tau/(\phi A), t)$. The evolution of these equations clearly depends on $f_1(t)$, and using different flow rate functions in different runs could result in incomparable results. However, taking flow rate functions to be multiples of one another results in the profiles being corresponding compressions or expansions of one another, as follows.

For the ith run, with flow rate $f_i(t) = f_1(t)/\gamma$, measure lengths scaled by γ_i. With this scale, and with flow $f_i(t)$, the scaled reactor temperature profile is:

$$\begin{aligned}\hat{T}_R(l, t) &= \bar{T}_R(\gamma_i l, t) = \bar{T}_R\left(\gamma_i \frac{f_i(t)}{\phi A}\tau, t\right)\\ &= \bar{T}_R\left(\frac{f_1(t)}{\phi A}\tau, t\right).\end{aligned} \tag{53}$$

This is the same function as for the first run, (and similarly for a scaled catalyst temperature profile), so Eqs. (28)–(31) will evolve exactly the same for each run. The only difference is that the profiles occur as scaled versions of each other. This is the situation described informally above, and is the basis for the kinetic rate calculations outlined there.

References

[1] B.W. Wojciechowski, Catal. Today, 36 (1997) 167.