

# Thermal stabilization of chemical reactors. I

## The mathematical description of the Endex reactor

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Here we describe the Endex reactor, a novel scheme for thermal control of potentially runaway reactions. The reactor is a composite of individual reactors, each of which houses either an exothermal or an endothermal reaction mixture. In this paper, which is Part I, we introduce the concept of an endothermally stabilized chemical reactor as an enthalpy-coupled thermokinetic system, and give it precise mathematical expression in the form of a four-dimensional dynamical system, for the special case of a continuous stirred tank reactor. The principle of enthalpy conservation is applied in the adiabatic case, which together with the consequence of taking the limit of a system parameter, collapses the structure of the state space to two dimensions. Criteria are defined for which the system is free of all kinds of thermal misbehaviour. This important dynamical result defines bounds for a large region of the parameter space within which this reactor may be operated safely.

**Keywords:** Endex; thermal runaway; thermal stabilization; thermokinetic systems; reactive thermal coupling; adiabatic reactor

### 1. Introduction

Incidents involving the thermal runaway of chemical reactions occur frequently and disastrously in the chemical industry; sometimes with tragic loss of human lives, and injuries to present and unborn generations, and always with considerable damage to property and other economic losses. To appreciate the need for strategic research in this area, one has only to be reminded of the tragedy that occurred at Bhopal, India, in 1984, where many thousands of people lost their lives in horrific circumstances after a thermal runaway reaction occurred in a storage tank at the Union Carbide plant. Although the magnitude of the effect of the Bhopal incident has no antecedent, the frequency of qualitatively similar incidents is such that the causes and consequences of thermal runaway are of great concern to the chemical industry and the wider community. In the UK, for example, about 30 chemical thermal runaway incidents occur each year (Barton & Nolan 1991), while in the USA between 1982 and 1988 there occurred an annual average of 70 severe accidental chemical releases that involved fatalities (Ashford 1993).

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The chemical industry is also an energy-intensive industry. The large amount of heat generated by heat-producing, or exothermal, reactions—such as the partial oxidations, hydrolyses and polymerizations that produce many common and important chemicals—is usually dissipated wholly or partially into the environment. Only in very large and sophisticated chemical plants is this heat recovered efficiently by steam generation. Conversely, reactions such as the steam-reforming production of synthesis gas are heat-absorbing, or endothermal. The required energy is provided by the burning of fossil or nuclear fuels, which must be paid for, and—in a milieu of increasing environmental awareness—industry must also be held accountable for the concomitant emissions of greenhouse gases and other pollutants.

Mathematically, thermal runaway can be due to a saddle-node (fold) bifurcation, a Hopf bifurcation (Guckenheimer & Holmes 1983), or the change of a stable nodal attractor to a stable focus, the transient approach to which may involve a significant temperature excursion that exceeds the design limits of the reactor. The physico-chemical mechanism for these phenomena is the highly nonlinear temperature dependence of chemical reaction rates coupled with heat release by exothermal reactions that results in accelerated self-heating.

This is the background against which the endothermally stabilized exothermal reactor (Endex) idea is proposed. It introduces a radical development in chemical reactor and storage technology, and embodies two concepts that appear to be relatively new in the chemical industry. These were expounded in Ashford's comprehensive study of chemical accidents in the USA, and can be described succinctly as *inherent safety* and *primary thermal stabilization by design*. The foundation of the Endex project is the novel but simple idea that direct thermal coupling between exothermal and endothermal chemical reactions may be able to eliminate instabilities in an adiabatic (insulated) reactor of suitable configuration. In the ideal case, one can envisage choosing a matched pair of reactions so that the propensity of the exothermal reaction to heat is exactly counterpoised by the propensity of the endothermal reaction to cool. It is easy to see intuitively (and it will be proved mathematically later in this work) that, provided there is good thermal exchange between the reactions, both reactions can proceed safely and efficiently to products, without lapsing into the uncontrollable exponential self-heating mode that is typical of exothermal reactions on their own.

The philosophy behind the Endex concept is to preclude thermal runaway by rational design procedures, rather than the more usual palliation methods of dousing, quenching, dumping or containment. It will be shown in this work that Endex reaction systems have the potential to provide built-in thermal safety and control and reduce emissions of pollutants, while at the same time producing saleable commodities using energy that otherwise would be wasted. The Endex reactor can be thought of as an alternative heat exchange and recovery system that is potentially more efficient than the more conventional steam generation that is currently used in industry, given that many chemical reaction enthalpies are greater than the heat of water vaporization.

## 2. The concept of thermal coupling

The thermokinetic behaviour of a single reaction in a continuous stirred tank reactor (CSTR) has been investigated in some detail in the literature (see Ball & Gray

1995; Ball this issue and references therein). Chemical reactions, however, rarely occur in isolation from each other. Thermokinetic coupling takes place when two or more reactions share a common mechanism for heat exchange. It is natural and proper to proceed circumspectly in the exposition of any such system: one has every right to expect dynamical behaviour of formidable complexity from even the simplest array of coupled nonlinear systems. However, this is not an inevitable consequence of thermal coupling. In the living world for example, thermokinetic coupling of chemical reactions is so endemic as to be a self-evident fact, to be noted in any exercise in bioenergetic bookkeeping, but otherwise unremarkable. The living cell may be viewed as a container (chemical reactor) into which reactants (glucose, acetyl CoA, oxygen) flow then undergo several energy-producing reactions, with such exquisite physical and thermokinetic control of energy recovery (mostly in the form of ATP) and loss that the entire process is usually isothermal.

Purposeful thermokinetic coupling of chemical reactions in the technological world is rare, although incidental coupling appears to be widespread in the chemical industry. The latter is usually regarded as having nuisance value, and can be quite dangerous. For example, the catalytic cracking of paraffins proceeds endothermally overall, but it is believed that in some circumstances exothermal condensation reactions can become dominant. There has been some interest recently in the deliberate coupling of reactions that produce synthesis gas, a mixture with a hydrogen-carbon monoxide molar ratio of around 2. An experimental production of syngas by the coupled exothermal partial oxidation and endothermal steam and CO<sub>2</sub> reforming of methane was carried out by Choudhary *et al.* (1994), although no modelling of this process was reported.

There are a few mathematical models for coupled chemical reactors in the literature. In the context of thermal explosion theory, simultaneous parallel reactions have been studied by Gray (1969) and Boddington *et al.* (1984). A study of mass-coupled isothermal CSTRs by Kumar *et al.* (1983) charted the effect of the mass exchange coefficient on the steady-state stability. In that work, exponential rate-acceleration was provided by feedback of an intermediate, while in another work by Bar-Eli (1985) the stability of mass-coupled Brusselators, another isothermal autocatalytic system, was discussed. Tabiś & Essekkat (1993) modelled a system that consisted of two coupled fluidized bed reactors at a steady state, in which an endothermal catalytic cracking process in one reactor was coupled by mass transfer to the exothermal regeneration of the catalyst in the other reactor. A mathematical model for two mass- or heat-coupled exothermal CSTRs was studied by Mankin & Hudson (1986). Within the limitations of the Frank-Kamenetskii approximation, this system was found to exhibit period-doubling, quasi-periodic and chaotic behaviour as the strength of the coupling was varied, although steady-state multiplicity was not investigated. A very interesting model for a thermokinetically coupled tubular reactor was presented by van der Vaart & van der Vaart (1991). As part of research motivated by the cold-start difficulties of methanol-fuelled motor vehicles, they proposed a scheme for an on-board reactor in which the reactions  $2\text{CH}_3\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3\text{OCH}_3$  (exothermal) and  $\text{CH}_3\text{OH} \rightleftharpoons \text{CO} + 2\text{H}_2$  (endothermal) were run over their respective catalysts, packed in the same tube. A sensitivity analysis of trajectories in the phase plane showed that, although stabilization of thermal excursions could be achieved, different sensitivity criteria gave equivocal results. It is a very revealing example of how difficult it is to make global pronouncements about dynamics, rather than steady states.

Some progress has been made in the bifurcation analysis of CSTR models in which an exothermal and an endothermal reaction occur in the same reactor. This problem has usually been treated as an extension of the more general problem of analysing consecutive or parallel reaction systems, of which there has been a large number of studies. A few representative papers which address specifically endothermal/exothermal reaction schemes, each emphasizing a different aspect of the problem, are

Hlaváček *et al.* (1972): original exposition, stability of steady states;

Halbe & Poore (1981): numerical search for regions of multiplicity and bifurcation of periodic orbits, jump phenomena;

Kahlert *et al.* (1981): complex oscillatory behaviour found in the consecutive, but not parallel, endothermal/exothermal scheme;

Jorgensen & Aris (1983): bifurcation of limit cycles to chaotic behaviour;

Moiola (1995): bifurcation curves of oscillatory instabilities.

Some attention has been paid to the question of maximum multiplicity, more as an exercise in elementary catastrophe theory than investigation of the physical basis of multiplicity. An early study of Pikios & Luss (1975) found a maximum multiplicity of three for a consecutive or parallel endothermal/exothermal system, while Chicone & Retzloff (1982) confirmed this result, and also established bounds for regions of attraction in the phase plane.

The mathematical studies cited above have provided essential foundation material for the Endex scheme that is introduced in this paper. However, any concrete proposal to incorporate reactive thermal coupling into a chemical reactor requires a conceptual appreciation of the purposes of an Endex reactor. The concept of the Endex reactor as a versatile thermal stabilization device was proposed by Gray & Jones (1981), who discussed the possible effectiveness of using an endothermally reacting bath to stabilize an exothermal core reaction. They applied thermal explosion theory to analyse the coupled energy equations for a gradientless batch system, using the Semenov approximation of negligible reactant consumption, and found that stabilization was highly sensitive to the relative rates of the two reactions.

For the Endex concept it is important to appreciate the potential for *adiabatic* operation. Since the design and implementation of adequate cooling systems is one of the major preoccupations of chemical engineering practice, the notion of adiabatic operation requires a radical shift in attitude. An ordinary chemical reactor is almost never run adiabatically (unless it is a bomb calorimeter), because for most common industrial reactions the adiabatic temperature rise for full conversion is dangerously high. (For example, the hydration of 2,3-epoxy-1-propanol, discussed by Ball & Gray (1995), has an adiabatic temperature rise of hazardous magnitude:  $\Delta T_{\text{ad}} = (-\Delta H)c_f/\bar{C} = 270$  K.) The concept of an *ideal adiabatic* Endex reactor suggests the interesting and very appealing possibility that the enthalpy released by an exothermal reaction could be recovered fully in the chemical bonds of the endothermal reaction product<sup>†</sup>. This energy would then be fixed in a stable, transportable, durable and saleable form.

<sup>†</sup> Let us note at this point that the necessary decrease in free energy of the system is provided by the increased total entropy of the products.

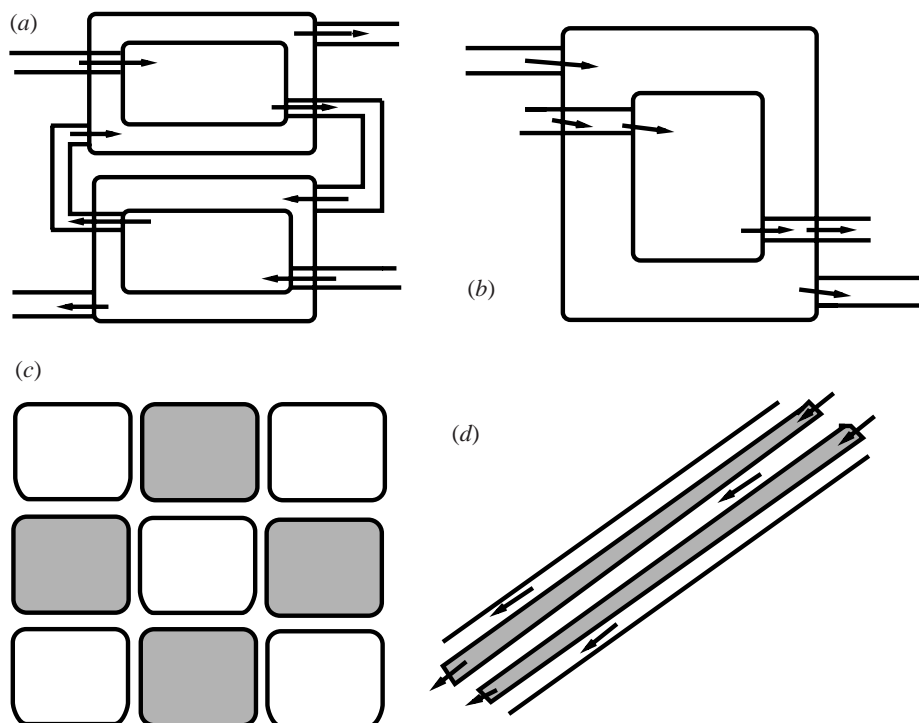


Figure 1. Some possible configurations for an Endex reactor.

The problem of cooling a conventional reactor is closely linked to the question of scale. According to chemical engineering dogma, the absolute volume of a reactor is limited by the practicable surface area available for cooling. While it is a trivial matter to scale-up the volume of a laboratory reactor by a factor of (say) 1000 for production, it is no simple task to scale the cooling surface area by the same factor. The ideal, adiabatic Endex reactor may be independent of scale, in the same way that surface-to-volume ratios are irrelevant in the single adiabatic reactor. The possibility that scaling problems may be eliminated is thus raised.

A few simple configurations for an Endex reactor have been drawn schematically in figure 1.

In the reciprocating arrangement of figure 1*a*, the effluent from one reactor becomes the coolant (or heating fluid) for the other reactor; in (b) the heat exchange surface directly separates the two chambers, while the reactor in (c) is an array of  $n$  coupled cells. The tubular reactor in figure 1*d* will be discussed in a future work. Physical segregation of the endothermal and exothermal reactions by the heat exchange surface is a common feature of all of these reactor configurations. Although this is not essential to the Endex concept, it is likely to have several practical advantages in relation to overall process design. A costly separation step is avoided, and there are many more possibilities for 'mix and match' reaction choices, especially where reactants are incompatible or catalysts highly specific.

Before proceeding with definitions, quantitation and rigorous analysis, let us allow a few impressions to imprint. Let us discuss, in general terms, the kind of thermal behaviour that might be expected to occur in a two-reaction Endex scheme. The

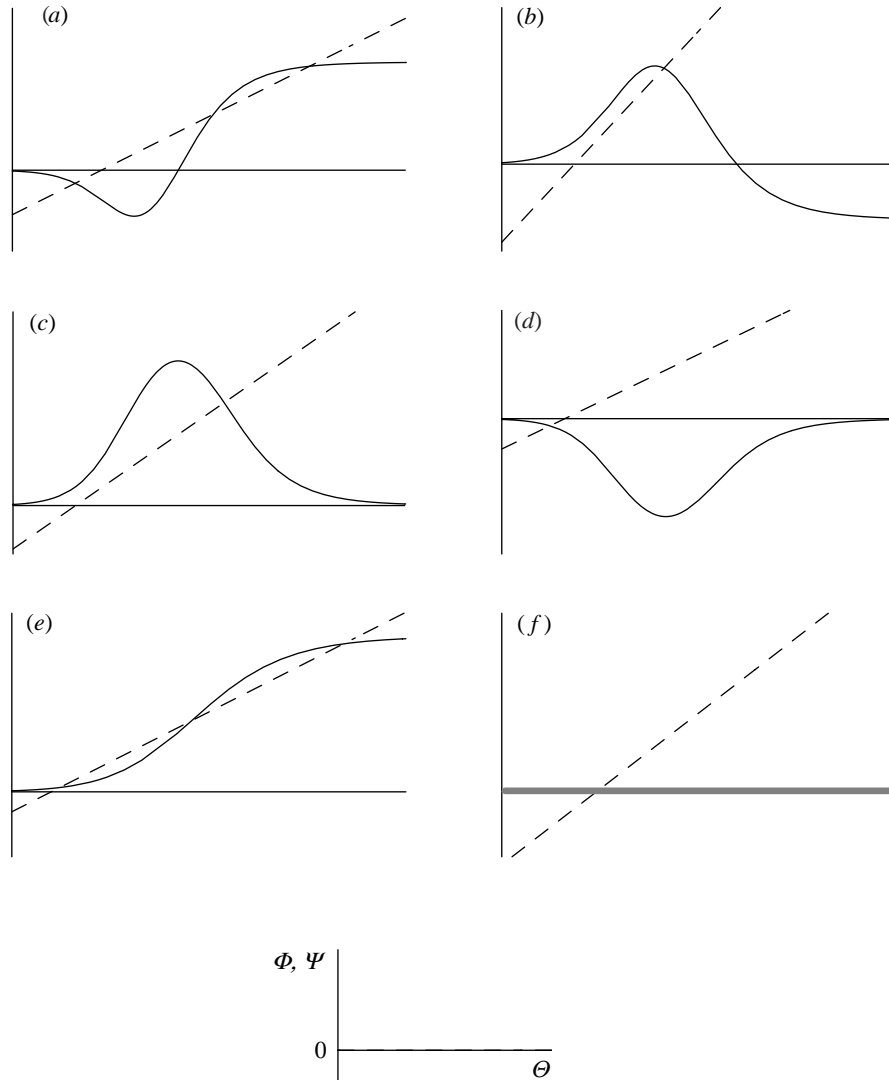


Figure 2. Various possibilities for the dynamic thermal balance in a reactor of Endex configuration.

exothermal reaction will tend to heat the reactor and the endothermal reaction will tend to cool the reactor. The *overall rate* of reactive heating will depend on the relative reaction rates, while the *net thermal effect* will be governed by the relative magnitudes of the reaction enthalpies, which are of opposite sign. Non-reactive cooling occurs at a rate that may depend on such factors as the amount of flow through the system and heat dissipation through the walls or via a cooling system.

To illustrate these ideas, we shall borrow the motif of the thermal balance diagram, familiar from classical thermokinetic theory as a plot of rates of reactive heat generation and linear cooling against system temperature, and exploit its qualitative aspects. Figure 2 comprises a gallery of thermal balance sketches.

In each part of the figure, the overall rate of heating due to reaction,  $\Phi$ , and the net non-reactive cooling rate,  $\Psi$ , are sketched as functions of a system temperature variable,  $\Theta$ . (Note that it is neither necessary, nor desirable, to define these variables precisely. In fact, it is better that they are not defined, for to do so would lead us into a mire of obfuscating detail at this stage. Should this lack of definition cause any discomfort, then let the variable  $\Theta$  represent an averaged temperature of the system. For the rates  $\Phi$  and  $\Psi$ , it is sufficient to assume Arrhenius form for the reaction rates and linear heat loss.) In figure 2*a*, the rate of the endothermal reaction exceeds that of the exothermal reaction so the overall heating rate,  $\Phi$ , is negative at first, although the temperature rises because the net rate is the sum of the endothermal and exothermal rates. Even though kinetic factors favour the endothermal reaction at first, the exothermal reaction is still proceeding at a non-zero rate, heating the mixture and eventually 'taking over'. (This, by the way, is also how unwanted exothermal side reactions can take over a reacting system and lead to thermal runaway.) The rate  $\Phi$  becomes more negative until the exothermal reaction begins to cut in; then it climbs through zero before levelling off because the magnitude of the thermal effect of the exothermal reaction is greater than that of the endothermal reaction. In figure 2*b*, this situation is reversed. In figure 2*c, d* the thermal effects of both reactions are equal (and opposite), but the exothermal rate exceeds the endothermal rate in (*c*), while the reverse is true for (*d*). In figure 2*e*, the rates are equal but the exothermal reaction has the dominating thermal effect. The sketch in figure 2*f* is rather uninteresting but it could represent the 'ideal' situation alluded to above. Both rates and both thermal effects are equal in magnitude and the net rate of heating is zero for all  $\Theta$ . The linear rates of non-reactive cooling,  $\Psi$ , superimposed on the sketches, indicate the propensity for steady-state multiplicity in various situations. Clearly, it is only in figure 2*f* that there is no potential for multiplicity.

### 3. Mass and enthalpy conservation equations

In this section, the descriptive concept of an Endex scheme is given precise mathematical expression.

Consider the CSTR in figure 1*b*. The reaction  $X_1 \rightarrow P_1$  in the inner compartment occurs exothermally and the mixture at any instant is at temperature  $T_1$ . The rate of the reaction is temperature dependent:

$$r_1 = c_1^n k_1(T_1). \quad (3.1)$$

Heat released by this reaction is exchanged with the mixture in the outer compartment, in which the endothermal reaction  $X_2 \rightarrow P_2$  occurs. The instantaneous temperature here is  $T_2$  and the reaction rate is

$$r_2 = c_2^m k_2(T_2). \quad (3.2)$$

At the inner wall, the temperature gradient between the compartments is linear with a combined constant coefficient  $L_{\text{ex}}$ . Loss of heat from the system to the surroundings, maintained at a constant ambient temperature  $T_a$ , may occur through the outer wall; the rate of dissipation is also linear, with the combined constant coefficient  $L_d$ . (More generally, heat may also be exchanged between the outside surroundings and the exothermal reaction, which we have indicated by using the coefficient  $L'_d$ .) This

dynamical system is described by a set of four coupled mass and enthalpy balances:

$$V_1 \frac{dc_1}{dt} = -V_1 c_1^n A_1 e^{-E_1/RT_1} + F_1(c_{1,f} - c_1), \quad (3.3)$$

$$V_1 \bar{C}_1 \frac{dT_1}{dt} = V_1(-\Delta H_1)c_1^n A_1 e^{-E_1/RT_1} + F_1 \bar{C}_1(T_f - T_1) - L_{\text{ex}}(T_1 - T_2) + L'_d(T_a - T_2), \quad (3.4)$$

$$V_2 \frac{dc_2}{dt} = -V_2 c_2^m A_2 e^{-E_2/RT_2} + F_2(c_{2,f} - c_2), \quad (3.5)$$

$$V_2 \bar{C}_2 \frac{dT_2}{dt} = V_2(-\Delta H_2)c_2^m A_2 e^{-E_2/RT_2} + F_2 \bar{C}_2(T_f - T_2) + L_{\text{ex}}(T_1 - T_2) + L_d(T_a - T_2). \quad (3.6)$$

It may seem strange at first that in this formulation of the Endex problem the reactor compartments have separate feedstreams with the tunable flowrates  $F_1$  and  $F_2$ , but there is only a single tunable feed temperature,  $T_f$ . It will be shown in this work, and in forthcoming work on bifurcations in the Endex problem, that separate flowrates (or, more accurately, residence times) profoundly affect the mathematical structure of the model, while separate feed temperatures are more of an algebraic (and, no doubt, practical) nuisance. In Ball (this issue), it was found that it was not the presence of two temperature parameters as such that affected the bifurcation structure of the CSTR, but rather, the existence of finite or zero coupling between the two. The general question of which parameters influence bifurcation behaviour and which do not is a profound and interesting theoretical one, which also has important practical implications. This study of the Endex CSTR provides an opportunity for this question to be addressed in the context of thermokinetic systems.

The symbols and quantities are defined in § 7 at the end of the paper.

#### (a) Dimensionless formulation

A break with tradition in the use of new dimensionless groups, was rationalized by Ball (this issue). The case for consistent use of physically distinct and independently variable dimensionless quantities was also made in Ball & Gray (1995), where the use of such quantities in rational design and operation protocols was emphasized. The definitions of dimensionless variables and parameters are given in § 7 at the end of the paper.

It can be seen from the definitions that there may be some parameter constraints imposed in the process of undimensioning the equations, in the sense that it may be necessary to restrict the quantity that is actually being varied in a group. For example, the parameter  $\alpha$  may be regarded as a variable operating parameter through  $c_{2,f}$ , but only if this reaction is of first order. The specific enthalpy of reaction one,  $(-\Delta H_1)c_{1,f}$ , cannot be regarded as an independently variable parameter (because this quantity also appears in  $\varepsilon_1$ ,  $\varepsilon_2$ ,  $l_{\text{ex}}$ ,  $l_d$ , and  $f_1$ ,  $f_2$  for  $n, m \neq 1$ ), although one can obtain indirect information about the effect of this quantity by regarding  $\Delta H_2 c_{2,f}$  as the variable parameter in  $\alpha$ . Using the defined dimensionless groups, the mass and

enthalpy balances, equations (3.3)–(3.6), are written as follows:

$$\frac{dx_1}{d\tau} = -x_1^n e^{-1/u_1} + f_1(1 - x_1), \quad (3.7)$$

$$\varepsilon_1 \frac{du_1}{d\tau} = x_1^n e^{-1/u_1} + f_1 \varepsilon_1 (u_f - u_1) - l_{\text{ex}}(u_1 - u_2) + l'_d(u_a - u_1), \quad (3.8)$$

$$\frac{dx_2}{d\tau} = -x_2^m \nu e^{-\mu/u_2} + f_2(1 - x_2), \quad (3.9)$$

$$\gamma \varepsilon_2 \frac{du_2}{d\tau} = -\gamma \alpha x_2^m \nu e^{-\mu/u_2} + \gamma f_2 \varepsilon_2 (u_f - u_2) + l_{\text{ex}}(u_1 - u_2) + l_d(u_a - u_2). \quad (3.10)$$

#### 4. The adiabatic case

The adiabatic possibilities of the Endex system have been alluded to in §2. By analogy with the single-reaction exothermal CSTR, it is reasonable to expect that an adiabatic condition will also simplify this system. The two effects of an adiabatic condition in the exothermal CSTR are: (1) to reduce the effective number of state variables; and (2) to exclude oscillatory behaviour. Both of these are desirable outcomes for the Endex CSTR, since we are interested in thermal stabilization. In later work, we shall see that, in general, the second effect cannot be guaranteed, and in this paper we shall pursue the first effect of adiabaticity.

The conservation condition that is intimated by adiabaticity may be extracted by setting the heat loss parameters  $l_d$  and  $l'_d$  equal to zero and summing equations (3.7)–(3.10), giving

$$\begin{aligned} \frac{d}{d\tau} [x_1 + \varepsilon_1 u_1 - \gamma \alpha x_2 + \gamma \varepsilon_2 u_2] &= -f_1 [x_1 + \varepsilon_1 u_1] \\ &\quad - f_2 [-\gamma \alpha x_2 + \gamma \varepsilon_2 u_2] + f_1 [1 + \varepsilon_1 u_f] + f_2 [-\gamma \alpha + \gamma \varepsilon_2 u_f]. \end{aligned} \quad (4.1)$$

One might expect this to have the integrable conservative form

$$\frac{d\phi}{d\tau} = -f(\phi - \phi_f), \quad (4.2)$$

but it can be seen that an additional condition, which is not necessary for the single adiabatic CSTR, must be imposed if equation (4.1) is to have the form of equation (4.2): that of conservation of enthalpy flux. Accordingly, the inverse residence times,  $f_1$  and  $f_2$ , are declared to be the single tunable parameter,  $f$ , and the required form is obtained as

$$\begin{aligned} \frac{d}{d\tau} [x_1 + \varepsilon_1 u_1 - \gamma \alpha x_2 + \gamma \varepsilon_2 u_2] \\ = -f([x_1 + \varepsilon_1 u_1 - \gamma \alpha x_2 + \gamma \varepsilon_2 u_2] - [1 + \varepsilon_1 u_f - \gamma \alpha + \gamma \varepsilon_2 u_f]). \end{aligned} \quad (4.3)$$

Although chemical reactors frequently have more than one feed stream, the conservation of flux condition does not appear to have been applied previously to a thermochemical system; perhaps because the associated adiabatic condition is not usually imposed.

Equation (4.3) has a first integral that yields an expression for one state variable, chosen as  $x_2$ , in terms of the other three and the independent variable:

$$\begin{aligned} \gamma \alpha x_2 &= \gamma \alpha - (1 - x_1) - \varepsilon_1 (u_f - u_1) - \gamma \varepsilon_2 (u_f - u_2) \\ &\quad - [\gamma \alpha (1 - x_{2,0}) - (1 - x_{1,0}) - \varepsilon_1 (u_f - u_{1,0}) - \gamma \varepsilon_2 (u_f - u_{2,0})] e^{-f\tau}. \end{aligned} \quad (4.4)$$

The three-variable reduced system can now be described by adapting equations (3.7), (3.8) and (3.10) with  $x_2$  given by equation (4.4):

$$\frac{dx_1}{d\tau} = -x_1^n e^{-1/u_1} + f(1 - x_1), \quad (4.5)$$

$$\varepsilon_1 \frac{du_1}{d\tau} = x_1^n e^{-1/u_1} + f\varepsilon_1(u_f - u_1) - l_{\text{ex}}(u_1 - u_2), \quad (4.6)$$

$$\gamma\varepsilon_2 \frac{du_2}{d\tau} = -\gamma\alpha x_2^m \nu e^{-\mu/u_2} + \gamma f\varepsilon_2(u_f - u_2) + l_{\text{ex}}(u_1 - u_2). \quad (4.7)$$

Theorems, lemmas and analytic procedures for dealing with systems of more than two degrees of freedom are really scarce. Of course, numerical results are more or less (mostly less) easily obtained, but one aims, as far as possible, to achieve global understanding of a system. By contrast, there are many well-established techniques for elucidating the behaviour of systems with two degrees of freedom. If there exists a physically credible reduction of the Endex system to two state dimensions, then the power tools of planar analysis can be used. Fortunately, there is such a reduction.

Consider an adiabatic Endex CSTR in which heat is exchanged freely between the compartments. In terms of the model represented by equations (4.4)–(4.7), this idealized physical situation corresponds to an infinitely large exchange coefficient,  $l_{\text{ex}}$ . The temperatures in the compartments are now identically equal at all times. This result can be obtained formally as follows. Let  $y = \varepsilon_1 u_1 + \gamma\varepsilon_2 u_2$  and add equations (4.6) and (4.7):

$$\frac{dy}{d\tau} = x_1^n \exp\left(-\frac{1}{u_1}\right) - \gamma\alpha x_2^m \nu \exp\left(-\frac{\mu\gamma\varepsilon_2}{y - \varepsilon_1 u_1}\right) + f(u_f(\varepsilon_1 + \gamma\varepsilon_2) - y). \quad (4.8)$$

The system consists now of equations (4.5), (4.6) and (4.8) ( $x_2$  is still given by (4.4)). Equation (4.6) is multiplied through by  $\delta = 1/l_{\text{ex}}$ :

$$\delta\varepsilon_1 \frac{du_1}{d\tau} = \delta x_1^n e^{-1/u_1} + \delta f\varepsilon_1(u_f - u_1) - (u_1(\varepsilon_1 + \gamma\varepsilon_2) - y)/\gamma\varepsilon_2.$$

In the limit as  $\delta \rightarrow 0$  it is found that

$$u_1 = u_2 \equiv u. \quad (4.9)$$

Finally, the system thus reduced is rewritten in terms of only two state variables:

$$\frac{dx_1}{d\tau} = -x_1^n e^{-1/u} + f(1 - x_1), \quad (4.10)$$

$$(\varepsilon_1 + \gamma\varepsilon_2) \frac{du}{d\tau} = x_1^n e^{-1/u} - \gamma\alpha x_2^m \nu e^{-\mu/u} + f(\varepsilon_1 + \gamma\varepsilon_2)(u_f - u), \quad (4.11)$$

$$\gamma\alpha x_2 = \gamma\alpha - (1 - x_1) - (\varepsilon_1 + \gamma\varepsilon_2)(u_f - u), \quad (4.12)$$

$$u(0) = u_f, \quad x_1(0) = 1, \quad x_2(0) = 1. \quad (4.13)$$

The prescribed initial conditions of equation (4.13) eliminate the transient term that otherwise would be present in equation (4.12) (see equation (4.4)), but even if such rigour is relaxed,  $x_2$  is still given by equation (4.12) after sufficient time, and the initial values of  $u$ ,  $x_1$  and  $x_2$  may be arbitrary†. (For completeness, it should be

† There may be other ways of eliminating the transient implied by equation (4.4), too. For example, let  $x_1(0) = x_2(0)$ ,  $\gamma\alpha = 1$  and  $u(0) = u_f$ .

pointed out, explicitly, that there is no formal adiabatic constraint on the assumption of free heat exchange. That is, the assumption may be applied to the full four-variable Endex system where there may be finite heat losses, to obtain a three-variable scheme.)

If we pause to inspect equations (4.10)–(4.13) and the definitions of the dimensionless groups, we may now verify the remarkable claim made in §2 that the Endex concept can eliminate engineering problems associated with reactor scale-up. Quite simply, there are no surface-to-volume ratios, either explicit or hidden, in these equations.

(a) *The perfect matching solution: an upper bound*

So far, we have reduced the state space of the Endex CSTR in steps until we have obtained a two-variable scheme that is both physically realistic and amenable to techniques of analysis in the phase plane. Our primary interest at this stage, however, is the achievement of thermokinetic stabilization. For arbitrary parameter values, equations (4.10)–(4.13) hold no promise of either global dynamic or steady-state stability. In this section, we will define the concept of the *ideal* Endex reactor precisely, and use it to determine a range of conditions for which the dynamics are free of thermal excursions.

It is obvious that in a viable Endex scheme, any two reactions chosen for thermal exchange would proceed at similar overall rates and have specific reaction enthalpies of comparable magnitude. We shall define the *perfect matching* case as a system for which

$$\alpha\gamma = \nu = \mu = 1, \quad (4.14)$$

and discuss the consequences of such kinetic and thermal matching.

For  $m, n = 1$ , the matched system can be written as

$$\frac{dx_1}{d\tau} = -x_1 e^{-1/u} + f(1 - x_1), \quad (4.15)$$

$$\frac{du}{d\tau} = (e^{-1/u} + f)(u_f - u), \quad (4.16)$$

$$u(0) = u_f, \quad x_1(0) = 1, \quad x_2 = x_1. \quad (4.17)$$

Note that equation (4.16) is uncoupled (independent of  $x$ ), and that the parameters  $\varepsilon_1$  and  $\varepsilon_2$  have dropped out (intrinsic thermal properties are irrelevant for perfect matching conditions). Since the first term on the right-hand side of equation (4.16) is positive, and there is no other  $u$  for which  $du/d\tau$  is zero, we can conclude that this is an integrable system with the solution

$$u = u_f, \quad x_1 = e^{-z\tau} + (f/z)(1 - e^{-z\tau}), \quad (4.18)$$

where  $z = e^{-1/u_f} + f$ . This represents higher conversion for higher  $u_f$ , and for selected  $u_f$  the conversion can be controlled by manipulating the residence time only. A demonstration of this is given in figure 3.

This result and the results that follow are widely applicable because it is usually possible, and often desirable, in both experimental and industrial situations, to run reactions under first-order conditions.

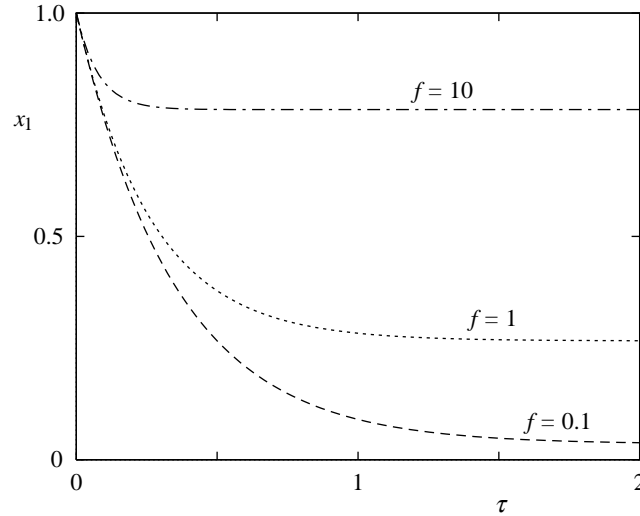


Figure 3. In the perfectly matched Endex CSTR, the conversion can be controlled simply by manipulating the residence time. This example is for a feed temperature,  $u_f$ , of 0.035 and a scaling factor,  $\theta$ , of 0.0338.

Our interest in the perfectly matched system is primarily as a bound on the temperature for systems that are not perfectly matched. Indeed, we can show that equation (4.18) defines the upper bound for  $u$  in solutions to equations (4.10)–(4.13) for a wide range of thermokinetically mismatched reactions (where we assume the reaction exponents  $n$  and  $m$  to be 1). For this purpose, we rewrite equation (4.11) in the form

$$(\varepsilon_1 + \gamma\varepsilon_2) \frac{du}{d\tau} = (\varepsilon_1 + \gamma\varepsilon_2)(f + e^{-\mu/u})(u_f - u) + x_1 e^{-1/u}(1 - e^{(1-\mu)/u}) - e^{-\mu/u}[(\gamma\alpha - 1) + (\gamma\alpha - 1)(\nu - 1) + x_2 + (\varepsilon_1 + \gamma\varepsilon_2)(\nu - 1)u_f]. \quad (4.19)$$

If  $v \equiv u_f$  and the temperature solution of the perfect matching case is substituted into equation (4.19), of which  $v$  is not a solution, we obtain a differential inequality of the form

$$(\varepsilon_1 + \gamma\varepsilon_2) \frac{dv}{d\tau} > (\text{right-hand side}), \quad (4.20)$$

provided  $\gamma\alpha \geq 1$ ,  $\nu \geq 1$ ,  $\mu \leq 1$ . By using a well-known comparison theorem (McNabb 1986),  $v \equiv u_f$  is an upper bound for the solution of equation (4.19). This important result may be summarized thus:

$$u(\tau) \leq u_f, \quad \text{for all } \gamma\alpha \geq 1, \nu \geq 1, \mu \leq 1. \quad (4.21)$$

It is a rare dynamical result of considerable generality in the area of thermokinetic systems analysis. It states unequivocally that there is a broad defined range of thermokinetic parameter values over which the Endex CSTR remains free of thermal excursions.

To what extent can the criteria in (4.21) be realized in practice? If we inspect the definitions of the thermokinetic parameters in (4.21)

$$\begin{aligned} \gamma &= V_2/V_1, & \alpha &= \Delta H_2 c_{2,f} / (-\Delta H_1) c_{1,f} \\ \mu &= E_2/E_1, & \nu &= A_2 c_{2,f}^{m-1} / A_1 c_{1,f}^{n-1}, \end{aligned}$$

we can see that there is room for some manipulation of the reaction parameters. The thermal effect group,  $\gamma\alpha$ , can be controlled by reactor design and operational criteria, as well as by reaction selection. To a large extent, the kinetic parameters are fixed by selection of the reaction pair. However, for catalysed reactions there is the potential for some manipulation of the rate constant through the amount and type of catalyst. The scope for kinetic manipulation should be assessed experimentally after tentative selection of an Endex reaction pair.

In any case, perfect thermokinetic matching is not necessary to achieve safe thermal stabilization. We can easily define some upper limits on thermal excursions shown by solutions to equations (4.10)–(4.13). The isoclinic curve in the  $u, x$  space given by  $du/d\tau = 0$  is of course crucial here, and in general it will have up to three branches (when the system has three steady states). The third (upper) branch of this curve will act as an upper bound for thermal excursions. The third (upper) singularity will be on this curve and its temperature value will be a single measure of the likely extent of thermal excursions. Figure 4*a–c* shows how this measure can be lowered readily by use of an endothermal reaction.

Figure 4*a* is a typical normalized thermal balance diagram for an adiabatic CSTR running an exothermal reaction. The third steady state represents the aftermath of runaway and is highly undesirable. The lower steady state represents negligible conversion and the middle one is unstable. Coupling of this system to an endothermal reaction can lower the temperature as shown in figure 4*b*, where the upper steady state now occurs at a dimensionless temperature,  $u \approx 0.45$ , corresponding to a conversion of over 40% (figure 4*c*). We have produced a situation in which runaway from the lower steady state, where conversion is negligible, to the upper steady state is highly desirable. The upper branch of the isoclinic temperature curve will be in the region of this steady state for  $0 \leq x_1 \leq 1$ , and can be calculated for specific parameter values without difficulty.

## 5. A specific example

Much of the analysis of the Endex problem so far is rather abstract. In the first place, the system described by equations (3.3)–(3.6) is once-removed from reality by recasting in dimensionless form. Inevitably, there will be some doubt as to whether the values given to the dimensionless parameters correspond to physically meaningful, or at least practicable, quantities. Of course, dimensional quantities are always recoverable from the definitions of dimensionless groups, but some are still combined quantities or ratios so that re-dimensioning may not always yield unequivocal information about a single quantity. What is needed is some form of reassurance that throughout the analysis we are working in a realistic region of parameter space. Secondly, singularity theory methods, which will be used in forthcoming work on bifurcations in the Endex system, add progressively many more degrees of abstraction. One may rightly inquire whether the moments of higher-order singularities that may be encountered in the model are experimentally observable.

It is best to allay these concerns by constructing a model Endex reactor ‘in virtual reality’ using real reactions. This simulation provides a connection to the real world, as well as a practical proposition for an Endex scheme. The hydration of 2,3-epoxy-1-propanol in a CSTR that was studied experimentally by Vermeulen & Fortuin (1986) and theoretically by Ball & Gray (1995) would seem to be a good candi-

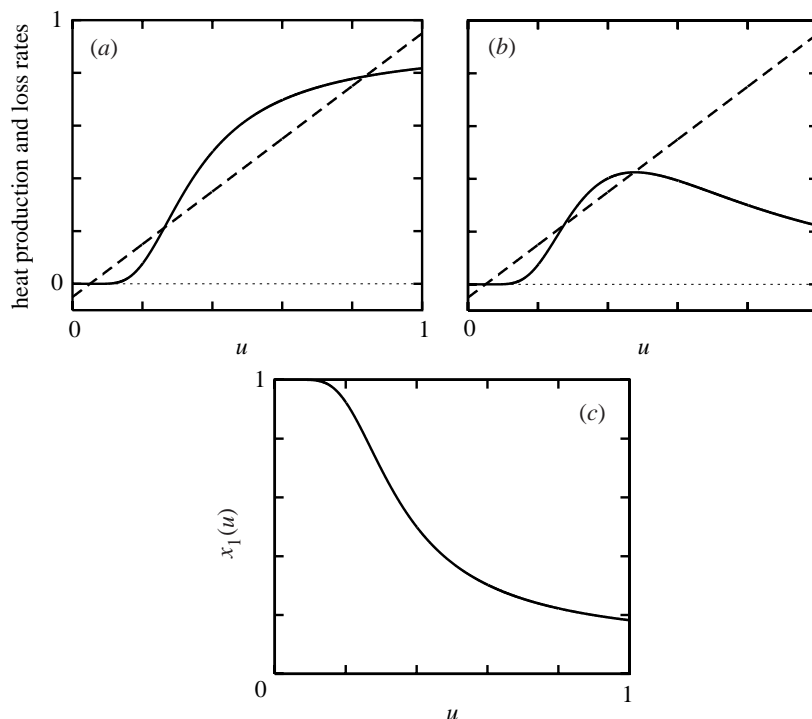


Figure 4. The effect of thermokinetic coupling on the upper steady state. (a) In the single adiabatic CSTR an excursion to the upper steady state means certain thermal runaway. (b) and (c) show that the effect of thermokinetic coupling is to bring the upper steady state to a region where the temperature is safe and the conversion is high.

date for endothermal stabilization. Thermal runaway and oscillations were observed in this reaction, and the bifurcation analysis indicated that pathological thermal behaviour was endemic to the system. A good endothermal partner would have at least a comparable rate within the same temperature range. From the literature, we have chosen the endothermal conversion of 2,3-dichloro-1-propanol to epichlorohydrin to partner the hydration reaction (Carrà *et al.* 1979). (Note that both of the reactions chosen for this simulation involve the highly reactive epoxide functional group  $-\text{CH}(\text{O})\text{CH}-$ . Over the past 20 or so years, epoxides have acquired major economic importance as precursors for, or intermediates in the synthesis of, a very wide range of fine and bulk organic chemicals. Epoxide chemistry is a very active area of research and development.) With these two reactions, an Endex CSTR is simulated that has the specifications and parameters listed in table 5. For comparative purposes, the dimensions and physical dimensions and properties of the simulated reactor follow closely those of the reactor studied in Ball & Gray (1995), although a solid mass capacitance parameter or a mechanical work term has not been included.

What might be the character of the thermal states of this system? To begin with, let us return to dimensional quantities and restore to the thermal balance diagram the quantitative aspects that earlier were temporarily shelved. From equations (3.4) and (3.6), the total rate of heat production by reaction is

$$\mathcal{P} = V_1(-\Delta H_1)c_1A_1e^{-E_1/RT_1} + V_2(-\Delta H_2)c_2A_2e^{-E_2/RT_2}, \quad (5.1)$$

Table 1. Parameters and reaction quantities used to plot the heating and cooling rates in figure 6

('1' refers to the exothermal reaction  $\text{CH}_2(\text{OH})\text{CHOCH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ; and '2' refers to the endothermal reaction  $\text{CH}_2\text{ClCHClCH}_2\text{OH} \rightleftharpoons \text{CH}_2\text{ClCHOCH}_2 + \text{HCl}$ . The value of the loss coefficient,  $L_d$ , for the Endex CSTR has been chosen to account for the flow of the endothermal feed mixture, i.e. the slope of the heat removal line is the same in both sections of the reactor.)

	1	2
$A$ ( $\text{s}^{-1}$ )	$1.35 \times 10^{10}$	$6.4 \times 10^8$
$E$ ( $\text{kJ mol}^{-1}$ )	73.4	71.06
$\Delta H$ ( $\text{kJ mol}^{-1}$ )	-87.7	66.1 <sup>a</sup>
$\bar{C}$ ( $\text{J l}^{-1} \text{K}^{-1}$ )	2920	2920 <sup>b</sup>
$c_f$ ( $\text{mol l}^{-1}$ )	10.0	10.0 <sup>b</sup>
$V$ (l)		0.257
$F$ ( $\text{l s}^{-1}$ )		$4.6 \times 10^{-3c}$
$T_f$ (K)		286 <sup>c</sup>
$T_a$ (K)		286 <sup>c</sup>
	single CSTR	Endex CSTR
$L_d$ ( $\text{J s}^{-1} \text{K}^{-1}$ )	32.7 <sup>c</sup>	19.3 <sup>c</sup>

<sup>a</sup>From tabulated standard enthalpies of formation.

<sup>b</sup>Nominal value.

<sup>c</sup>Variable quantity.

and the total heat flux and loss rate is

$$\mathcal{R} = F_1 \bar{C}_1 (T_f - T_1) + F_2 \bar{C}_2 (T_f - T_2) + L_d (T_a - T_2). \quad (5.2)$$

It is assumed here, that the reactant concentrations can be approximated adequately by their steady-state values:

$$c_1 = c_{1,s} = \frac{F_1 c_{1,f}}{V_1 A_1 e^{-E_1/RT_1} + F_1}, \quad c_2 = c_{2,s} = \frac{F_2 c_{2,f}}{V_2 A_2 e^{-E_2/RT_2} + F_2}. \quad (5.3)$$

The rates  $\mathcal{P}$  and  $\mathcal{R}$  are functions of the two state variables  $T_1$  and  $T_2$ , so there is no simple planar construction for a thermal balance diagram. Figure 5 shows the surface that is formed when  $\mathcal{P}$  is plotted as a function of both  $T_1$  and  $T_2$ .

It tells us that the stabilizing effect of the endothermal reaction becomes less significant as the difference between  $T_1$  and  $T_2$  becomes greater. Thus, figure 5 contains implicit information about the effect of the heat exchange coefficient,  $L_{\text{ex}}$ , which was eliminated in forming the *total* heat flux and loss rate  $\mathcal{R}$  in equation (5.2). In the ideal reactor, we wish to maximize heat exchange and minimize the difference  $T_1 - T_2$ . From equation (4.9), in the limit of perfect heat exchange (infinite  $L_{\text{ex}}$ ), we may write  $T_1 = T_2 = T$  in equations (5.1)–(5.3), which allows us to construct the more familiar planar thermal balance diagram shown in figure 6*b*. Compare this with figure 6*a*, a thermal balance diagram for the exothermal reaction on its own (i.e.  $V_2 = 0$ , which implies also  $F_2 = 0$ .)

The Endex configuration appears to be stabilizing insofar as the high conversion (upper) steady state occurs now at a more manageable temperature. However, the

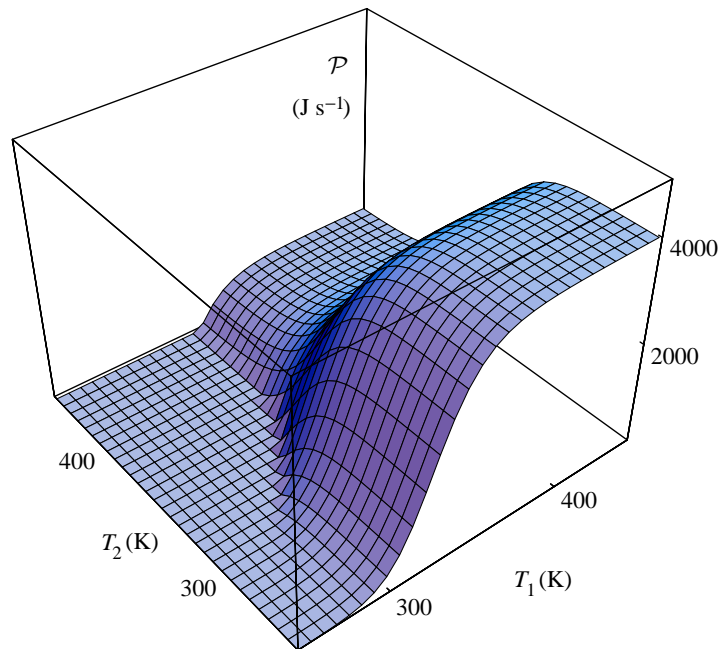


Figure 5. Three-dimensional representation of total reaction heating rate of the example reactions as a function of  $T_1$  and  $T_2$ .

following points should be noted: (1) all information about the possible effects of the exchange coefficient,  $L_{\text{ex}}$ , on multiplicity has been sacrificed; and (2) thermal balance diagrams contain no information about oscillatory or other dynamical instabilities. If we require more information about the behaviour of an Endex system than that which may be extracted from a thermal balance diagram, we must use phase-plane analysis, for the dynamics, or bifurcation analysis, for the steady states.

A phase-plane portrait of the simulated system is shown in figure 7*a*. It should be compared with figure 7*b*, a comparable phase portrait of states in the single exothermal reactor of Ball & Gray (1995).

(We have switched now to scaled dimensionless groups. For practical reasons, the dimensionless equations must be scaled by the factor  $e^{1/\theta}$ . Using this and the dimensionless parameter definitions and the assignments in table 5, the values of the dimensionless parameters used to compute figure 7 are as given in the figure caption.) Stabilization at these parameter values is unequivocal: the transient in figure 7*b* is considerably damped in (*a*), while the limit cycle in (*b*) is eliminated in (*a*) through a switch in stability of the steady state. With the above formalization of the assumption of free heat exchange, the thermal balance diagram of figure 6*b* that indicated stabilization of the exothermal reaction with respect to steady-state multiplicity can be interpreted now with more confidence because there are no 'hidden' complications that may be associated with imperfect heat exchange between the compartments.

There is also potential for improvement in the matching qualities of this example Endex pair. The exothermal and endothermal reactions are homogeneously acid and

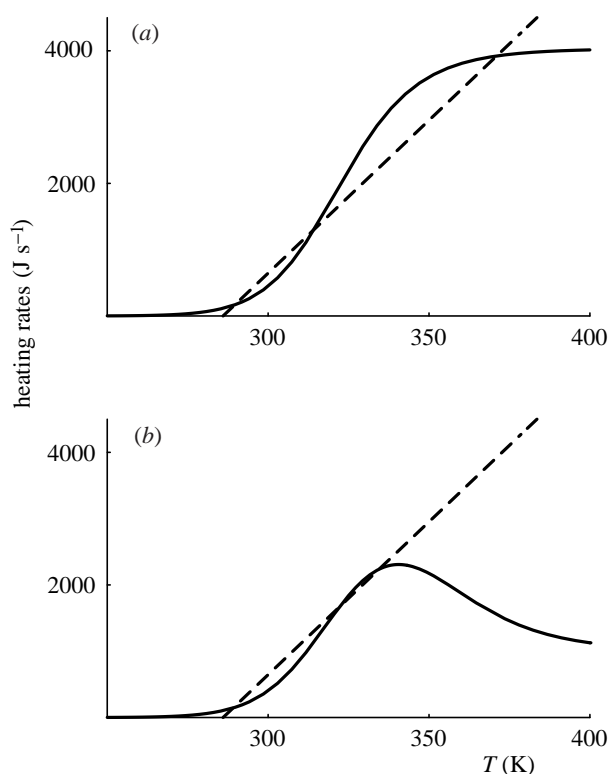


Figure 6. Rates of heat generation by reaction (solid curves) and heat removal by flow and loss (dashed lines) as functions of reactor temperature. (a) Reaction 2,3-epoxy-1-propanol  $\rightarrow$  glycerol on its own in a cooled CSTR; (b) reaction pair 2,3-epoxy-1-propanol  $\rightarrow$  glycerol and 2,3-dichloro-1-propanol  $\rightarrow$  epichlorohydrin in an idealized Endex CSTR. Parameter values are given in table 5.

base catalysed, respectively. It has long been established that the activation energies for such aqueous hydration/dehydration reactions are dependent on the amount of acid or base present, although data for these particular reactions are not available. It is reasonable to expect that it may be possible, after appropriate experimentation, to tune the kinetic parameters so that the criteria in (4.21) are more closely approximated.

## 6. Conclusion

The main result of this paper is that stabilization of a rogue or runaway exothermal reaction is both possible and feasible in the Endex reactor. We have derived the useful dynamical result that there exists a large region of parameter space over which thermal excursions in the Endex reactor are forbidden. A specific example system in which an exothermal hydration reaction and an endothermal dehydration reaction were paired was discussed.

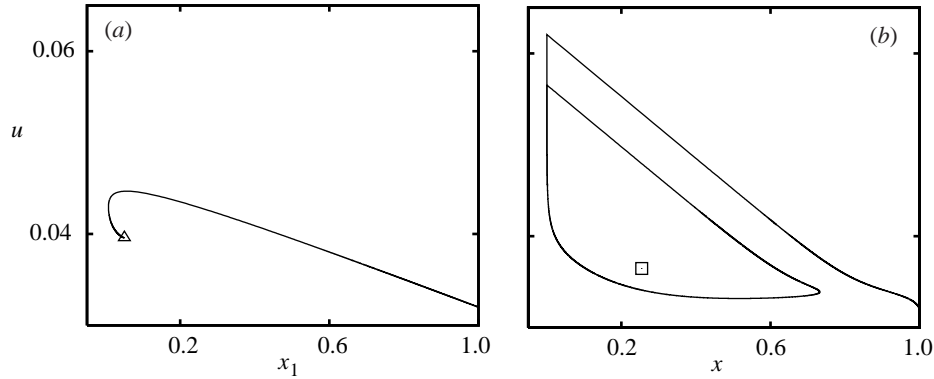


Figure 7. Comparative phase-plane portraits of single and Endex CSTR dynamics. (a) Two-dimensional Endex model with the example pair of reactions,  $\alpha = 0.754$ ,  $\mu = 0.968$ ,  $\nu = 0.047$ . (b) Single CSTR model with the exothermal reaction of the example pair only, in which a non-reactive loss term with coefficient  $l_d e^{1/\theta} = 500$  is included to simulate comparable conditions. In both (a) and (b),  $u_f = 0.031$ ,  $f e^{1/\theta} = 2.04$ ,  $\varepsilon_1 = \gamma \varepsilon_2 = 29.5$  and  $\theta = 0.0338$ .

## 7. Notation and definitions

### (a) Dimensional quantities

$A$	first-order frequency factor ( $s^{-1}$ )
$c$	concentration of reactant ( $\text{mol l}^{-1}$ )
$\bar{C}$	weighted volumetric specific heat capacity of feed mixture ( $\text{J l}^{-1} \text{K}^{-1}$ )
$E$	activation energy ( $\text{J mol}^{-1}$ )
$F$	feed flowrate ( $\text{l s}^{-1}$ )
$\Delta H$	reaction enthalpy ( $\text{J mol}^{-1}$ )
$k$	reaction rate constant
$L$	combined heat transfer coefficient ( $\text{J s}^{-1} \text{K}^{-1}$ )
$m, n$	reaction rate exponents
$r$	reaction rate
$R$	gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ )
$t$	time (s)
$T$	temperature (K)
$V$	reaction mixture volume (l)
$X$	reactant

### (b) Dimensionless groups and parameters

$$\begin{aligned}
 f_1 &= F_1/V_1 A_1 c_{1,f}^{n-1}, & f_2 &= F_2/V_2 A_1 c_{1,f}^{n-1}, \\
 l_{\text{ex}} &= L_{\text{ex}} E_1/V_1 A_1 c_{1,f}^n (-\Delta H_1) R, & u &= RT/E_1, \\
 x &= c/c_f, & \alpha &= \Delta H_2 c_{2,f}/(-\Delta H_1) c_{1,f}, \\
 \gamma &= V_2/V_1, & \varepsilon &= \bar{C} E_1/c_{1,f} (-\Delta H_1) R, \\
 \mu &= E_2/E_1, & \nu &= A_2 c_{2,f}^{m-1}/A_1 c_{1,f}^{n-1}, \\
 \tau &= t A_1 c_{1,f}^{n-1}.
 \end{aligned}$$

## (c) Other symbols

$\mathcal{P}$ = rate of heating due to reaction,	$\mathcal{R}$ = rate of non-reactive cooling,
$y = \varepsilon_1 u_1 + \gamma \varepsilon_2 u_2$ ,	$z = e^{-1/u_i} + f$ ,
$\phi$ = an eigenfunction,	$\delta = 1/l_{\text{ex}}$ ,
$\theta$ = dimensionless scaling factor (0.0338).	

## (d) Subscripts

0	of an initial state or condition
1	of the exothermal reaction, of the reactor compartment housing the exothermal reaction
2	of the endothermal reaction, of the reactor compartment housing the endothermal reaction
a	ambient, of the surroundings
d	dissipative, of heat transfer to the surroundings
ex	exchange, of heat transfer between reactions
f	of the feed
s	of the steady state

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