Interpreting chemical kinetics from complex reaction—advection—diffusion systems: Modeling of flow reactors and related experiments

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A B S T R A C T

The present discourse is directed toward the community that wishes to generate or use flow reactor data from complex chemical reactions as kinetic model development and validation targets. Various methods for comparing experimental data and computational predictions are in evidence in the literature, along with limited insights into uncertainties associated with each approach. Plug flow is most often assumed in such works as a simple, chemically insightful physical reactor model; however, only brief qualitative justifications for such an interpretation are typically offered. Modern tools permit the researcher to quantitatively confirm the validity of this assumption. In a single complex reaction system, chemical time scales can change dramatically with extent of reaction of the original reactants and with transitions across boundaries separating low temperature, intermediate temperature, and chain branched (high temperature) kinetic regimes. Such transitions can violate the underlying assumptions for plug flow interpretation. Further, uncertainties in reaction initialization may confound interpretation of experiments for which the plug flow assumption may be appropriate. Finally, various methods of acquiring experimental data can also significantly influence experimental interpretations. The following discussions provide important background for those interested in critically approaching the relatively vast literature on the application of flow reactors for generating kinetic validation data. The less frequently discussed influences of reactor simulation assumptions on modeling predictions are addressed through examples for which the kinetic behavior of specific reactant combinations may cause experimental observations to depart locally from plug flow behavior.

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1. Introduction

Flow reactors are used extensively in the chemical process industry, and their configuration and integration with other types of reactors are discussed widely in introductory chemical reaction engineering texts, see for example [1–3]. Such tutorials consider fundamental principles, and discussions typically proceed in the context of industrial design, application, and optimization for chemical processing. These discussions generally assume simplified chemical kinetics using first or second order reactions, or perhaps empirical chemistry composed of a small number of reaction steps. An idealized plug flow reactor analysis is introduced, and using the above chemistries, sources of departure from ideal behavior are examined toward offering “corrections” to the predictions of ideal performance. Such treatment with engineering examples is useful, but not particularly informative for those in the combustion chemistry community interested in elucidating chemical kinetics by generating or modeling flow reactor data. Instead, exploitation of flow reactor data depends upon an appreciation of the coupling among the chemical species, momentum, and energy fields that comprise the chemically reacting flow, and how this coupling may be affected by the specific detailed reaction system of interest. In the present work, we tailor the standard departure-from-ideality discussion to focus directly on several such issues that bear on scientific interpretation of flow reactor experiments for complex reaction systems. Though our discussion focuses primarily on flow reactors, generalizations also extend to other experimental reacting flow configurations such as shock tubes, laminar flames, rapid compression machines, etc., as suggested in this paper and elsewhere (e.g., [4–12]).

Historically, a large body of literature (see for example [13–21]) has been generated on the use of tubular flow reactors in the “direct” characterization of reaction parameters either for a single reaction or a system of a few elementary reactions. Many of these works implement experimental design considerations to approximate plug flow conditions, discuss the possible departures from ideality, and present interpretive, quantitative methods to correct for the non-idealities. We encourage the specialist interested in flow reactor design and interpretation to become familiar with this material. However, for those interested in using flow reactor data, especially for development and validation of detailed chemical kinetic models, a more general appreciation of flow reactor assumptions, experimental characteristics, and operational modes is of additional value. We offer several literature-based examples illustrating common, representative situations where chemistry—facility interactions may drive experimentally observable behavior to depart from otherwise ideal assumptions of reactor physics. This in turn may lead to significant interpretive uncertainties for experiments and modeling. These examples have not been singled out to intentionally criticize particular research, but to demonstrate in concrete terms the significance of a particular aspect to kinetic interpretations of results.

Our discussion cannot comprehensively consider the vast physical and chemical parameter space accessible to the experimental facilities considered here, nor do we intend on providing explicit criteria and parameters for reactor design and operation. Nevertheless, the present discussions should provide a basis from which to assess these more general topics. We begin by considering an ideal plug flow reactor, represented conceptually and mathematically in Fig. 1. Using this canonical basis for comparison, we illustrate the effects of varying (A) initial conditions and (B) boundary/interior conditions on the ideality of the flow reactor response. Techniques for interpreting measurements of downstream reactor conditions at specific residence times or spatial locations are discussed throughout. Finally, we close with an illustration of the coupling among these non-idealities, which is more representative of real flow reactor experiments.

2. The ideal plug flow reactor

Fig. 1 schematically shows the reaction of a species $i$ in an isobaric plug flow reactor (PFR) as a function of the axial reactor coordinate $z$. Initial conditions $Y_{i0}$ and $T_0$ (species fraction and temperature, respectively) are addressed in the following section, but for now are assumed to be easily attained and well-characterized, as are the final conditions $Y_f$ and $T_f$. The species fraction $Y_i$ may be mass- or molar-based without loss of generality in the following discussions.

Under steady-state conditions, the associated conservation equations are written for a simple global chemical reaction that describes the rate of overall reactant conversion $\dot{w}$ and an

![Fig. 1. Species and energy conservation equations and boundary conditions for a simple exothermic chemical reaction in a one-dimensional adiabatic, steady flow.](image-url)
associated heat release rate, $wQ$, which manifests as a sensible enthalpy change measured by the temperature $T$. Homogeneous gas phase chemistry under idealized thermal conditions (i.e., either adiabatic or isothermal) is assumed, although this formalism can be generalized to accommodate reactions and heat transfer at the reactor wall. Notably, for prescribed temperature profiles (isothermal or otherwise), the energy equation is no longer con- straining. The continuity equation satisfies $u = U_p(T(\tau), Y(\tau))$, where $U_p$ is the plug flow velocity, which is influenced by both temperature and mole number change as a function of $\tau$ under the ideal gas assumption applied at constant pressure. This canonical PFR model assumes that, despite axial gradients in $Y_i$, the axial diffusion terms are negligibly small in comparison to the advection and reaction terms in each of the species and energy equations. Then, under the simple coordinate transformation $\xi = \frac{z}{U_p}$, temporal profiles of $Y_i$ and $T$ can be constructed from the spatial profiles. The resulting mathematical formulation is a simple initial value problem (IVP) commonly used to represent an ideal plug flow reactor. With slight modification in base assumptions, this formulation also describes ideal single pulse and reflected shock tube experiments. The value of both of these plug-flow-type reactor models is that temporal profiles of $Y_i$ and $T$ yield direct insights on the chemical kinetic model, provided that all of the ideal reactor assumptions are satisfied. In other words, plug flow reactor and shock tube are phenomological equivalent, as are their generalized departures from ideality. We will refer to this duality between shock tubes and flow reactors in our later discussion.

In a flow reactor, the “thickness” of the reaction zone is defined by the relative equality of chemical and advective time (length) scales. The ratio of these scales defines $Da$, the Damköhler number for characteristic species $i$. To achieve optimal temporal (spatial) resolution, flow reactor experiments tend toward $Da = O(1)$ to maximize the reaction zone thickness with respect to the reactor length. This desired mode of operation is also implicit for more closely attaining the presumption of negligible axial diffusion.

Relaxation of the axial diffusion constraint leads to an interesting result, however. The relative magnitude of the axial diffusion term in comparison to both the advective and chemical source terms in the model equations dictates whether their solution approximates a plug flow reactor or a laminar premixed flame problem. In the latter problem, the characteristic advective, diffusive, and chemical terms are all of similar magnitude, and solution of the laminar flame model equations exists for only one plug flow mass flux eigenvalue. This eigenvalue is associated with the one-dimensional laminar burning velocity and a unique reaction zone (flame, or wave) thickness [22]. Though not as formally exact as the analogy between flow reactors and shock tubes, the similarity established between flow reactors and laminar premixed flames will be useful in our subsequent discussions.

It should be apparent from the layers of idealization that developing experiments to emulate the simple ideal PFR condition is an extremely complicated problem. Likewise, determining whether plug flow reactor modeling is a sufficient representation of a particular experimental configuration involves deconvolution and evaluation of coupling among physical model idealizations, expected non-idealities, uncharacterized uncertainties, and the particular chemical kinetic system intended to be probed by experiment. These observations implicitly extend to other reactor configurations, as well.

Since the mid 1970s [23] and the introduction of stiff equation solvers [24], both computational speeds and understanding of the intricacies of detailed kinetic models have improved. Multi-dimensional modeling of flow reactor experiments has been pursued recently, though the challenge of doing so for detailed kinetic studies remains significant [25]. Modern numerical tools of varying complexity (e.g., CHEMKIN-PRO [26], ANSYS [27], CFD-ACE+ [28], OpenFOAM [29], and Cantera [30]) permit investigation of departures from the idealized reactor model; however, detailed kinetic models frequently must be reduced to accommodate multi-dimensional predictions [31]. Further, advanced modeling still depends on flow-field approximations and descriptions of initial/boundary conditions. Propagated uncertainties from these input parameters may not reduce model prediction uncertainties relative to predictions of simpler tools. In contrast, zero- or one-dimensional computations are possible today for very high degrees of kinetic complexity. Thus, for most chemical kinetic research existing in the literature, and even presently, it is common to analyze flow reactor results using a plug flow model coupled with a fully detailed chemistry model.

In short, no panacea technique exists for developing, interpreting, or modeling a flow reactor (or related) experiment. We offer examples and techniques to deconvolve and evaluate the experiments, but it is ultimately incumbent upon the modeler to evaluate (and the experimentalist to demonstrate) thoroughness in the consideration of both the physical experiments and their subsequent interpretation. We find that the most important issues in both plug flow and non-plug flow tubular reactor experiments and their modeling comparisons are 1) establishment of suitable inlet conditions to the reaction zone to be analyzed; 2) treatment of axial and radial gradients over the reaction region, including the role of surface interactions; 3) methods of collecting chemical species and temperature information in the reaction zone; and 4) the uncertainties associated with the chemical and thermal character- ization diagnostics themselves. Each of these points further depends on the chemistry under study, which adds an additional layer of interpretive complication. We will deal principally with items 1) and 2), as diagnostic methods 3) and their uncertainties 4) are discussed at length elsewhere (e.g., [32–34]).

Frequently, predictions of an assumed coupled chemical and physical model are compared to experimental results toward development or “validation” of the chemical kinetic part of an assumed model. However, a less frequently considered perspective expands the problem — comparison of experimental observations with model predictions may be used to develop or validate the joint physical and chemical model assumptions for particular reaction conditions. The substance of our discussion comes from this latter perspective, from which we aim to derive insight into the interactions among facility, chemistry, and interpretation by comparing idealized model predictions to “surrogate” non-ideal experimental data.

## 3. Reaction initialization

Because of the initial value problem nature of flow reactor experiments, careful characterization and reporting of initial conditions (boundary conditions under spatial transform) immediately upstream of the diagnostic section is of utmost importance to producing flow reactor data that can be properly interpreted. Likewise, the initial conditions assumed as model inputs are equally important for chemical kinetic development and validation.

For the case of a PFR governed by the ideal reactor IVP, we previously assumed that initial conditions $Y_{i0}$ and $T_0$ are easily attained and well-characterized. To preclude any uncharacterized reaction before time $t = 0$, this idealization essentially requires a non-reacting system to pass through infinite gradients in $Y_i$ and/or $T$ at time $t = 0$ in order to become reactive at initial conditions $Y_{i0}$ and $T_0$. This perfect, instantaneous change in temperature and/or instantaneous mixing of reactants at a well-defined “time $t = 0$” is clearly physically unrealizable. Even shock wave experiments, as we discuss below, may have confounding non-idealities in the definition of initial conditions.

In this section, we provide examples illustrating the effect of relaxing the idealization assumed for $Y_{i,0}$ and $T_0$ on interpretation of otherwise ideal plug flow IVP problems. We consider two approaches for treating the initialization of reaction conditions in flow reactors, as evident in the experimental literature and supported by more limited computational studies:

1. Individually preheating the reactants to $T_0$, followed by fast finite-rate mixing to achieve $Y_{i,0}$ at the entrance to the reactor, for example [24,35–45]. This method has been applied in both laminar and turbulent flow reactor studies.

2. Premixing reactants and diluents to composition $Y_{i,0}$ at some low temperature where reaction rates are negligibly slow, followed by fast finite-rate heating to achieve $T_0$ at the entrance to the reactor, for example [46–49]. This approach is common to many laminar flow reactor studies and also generalizes to shock wave experiments.

Later, we discuss several interpretive computational techniques [39,50–52] that remove the need to explicitly treat these initialization methods through avoiding the application of the absolute experimental reaction time scale.

### 3.1 Reactant mixing effects on initialization

In the first initialization approach, the reactor is designed to rapidly mix preheated reactants that are at or near the reaction temperature $T_0$. Degradation of individual reactants during preheating is assumed to be negligible, and the reactant mixing location is assumed to represent the onset of reaction (initial condition) in the experimental frame. It is frequently assumed that mixing times to establish homogeneity are negligibly small and, for purposes of interpretation and computation, can be ignored relative to the overall reaction times within the reactor itself [38,41,42,44,53,54]. This is also a fundamental assumption applied in interpreting jet-stirred reactor experiments [55].

The validity of this fast-mixing assumption depends significantly on reaction conditions and experimental objectives, but surprisingly, is seldom scrutinized for the specific reaction system under study. Fig. 2 provides an example where the assumption causes significant departures from ideality. This illustration is based on modeling work of Gokulakrishnan et al. [56] (later reported in the Supplement to Zhao et al. [52]), which considers methane oxidation experiments originally reported in Bendtsen et al. [40]. We focus presently on the phenomenology of mixing initialization. For the sake of clarity and for the remainder of the examples provided herein, we generally avoid comparison among kinetic models and literature experimental measurements to instead focus on interpretative aspects of facility–chemistry interactions.

We use an isothermally perfectly stirred reactor (PSR) model to represent characteristic mixing time effects at chemically reacting conditions ($T_0$) for various PSR residence times, $t_{psr}$. This model is itself a vast simplification of a complex reactant mixing process (cf., [43,57]), but the uncertain $t_{psr}$ parameter is here presumed to illustrate the finite time scale of the fast mixing assumption [58]. Output species composition from the PSR calculations initializes ($t = 0$) a downstream ideal isothermal PFR model, for which the governing IVP is integrated to $t = t_{pfr}$. The sum of $t_{psr}$ and $t_{pfr}$ is set equal to the overall experimental reactor residence time for the experiment [40]. This coupling between PSR and PFR models is relatively simple to implement in commercial codes such as CHEMKIN-PRO [26].

Fig. 2a displays the predicted CO mole fraction at the PFR exit as a function of the PSR residence time. This presentation is most directly insightful for the type of flow reactor configuration that uses a fixed sampling point at the end of the reactor. Such a configuration affords no direct spatial (temporal) resolution of the reacting flow over the length of the reactor section, and so uncertainties in initial conditions due to the uncharacterized mixing process translate with high sensitivity into uncertainties in the measurements. It is clear from the figure that small changes in mixing time scales upstream of the ideal PFR may have a dramatic impact on the CO mole fraction measurable at the PFR exit. For example, a PSR residence time of ~15 ms (~7% of the overall reaction time) results in over an order of magnitude increase in CO exit plane mole fraction relative to the instantaneous mixing case (i.e., $t_{psr} = 0$).

![Fig. 2. PSR–PFR numerical simulations of mixing initialization effects on CO profiles in the PFR reaction section, using initial reaction conditions of [40] for “Experiment A” at 1140 K (2276 ppm CH₄, 3.69% O₂ and 4% H₂O in N₂, 219 ms overall residence time): a) PFR exit CO mole fraction as a function of PSR residence time, $t_{psr}$; b) Absolute reaction time-referenced CO mole fraction profiles in interior of the PFR at various values of $t_{pfr}$; c) Relative reaction time-referenced CO mole fraction profiles shown in b) shifted by their corresponding $t_{psr}$](image-url)
For this type of reactor configuration, an often employed experimental strategy to yield temporal resolution is variation of the overall mass flow rate, and hence the overall residence time \( \tau_{\text{psr}} + \tau_{\text{fl}} \). However, this strategy is subject to the same kind of uncertainty described for the fixed mass flow rate case. Moreover, such a strategy may serve to increase overall uncertainty since mixing rate is a function of mass flow rate, leading to variation in mixing processes when the mass flow rate is changed.

Through the artifice afforded by kinetic modeling, we remove the experimental configuration-imposed constraint considered above and, in Fig. 2b, we compare experimentally inaccessible CO time histories in the PFR interior for several values of \( \tau_{\text{psr}} \). The CO mole fractions computed at 219 ms correspond to the simulated experimentally observable data shown in Fig. 2a, but the time history provides additional insight on the effect of imperfect mixing initialization. The curves of CO vs. overall reaction time are remarkably similar in shape and magnitude, but appear displaced relative to each other in terms of time. In foreshadow of later discussion, Fig. 2c demonstrates that the curves essentially collapse on top of each other when simply shifted by their relative \( \tau_{\text{psr}} \) mixing times. Hence, the reaction gradient \( \text{d}Y_{\text{i}}/\text{d}t \), which directly couples to the chemical kinetic source term, appears unperturbed as a result of non-ideal mixing initialization, even if this non-ideality does affect reckoning of species histories with respect to absolute reaction time.

Mixing time scale effects on observations are related to the detailed kinetic system under study. For example, we have published similar mixing perturbation analyses for dimethyl ether (DME) \([52]\) and n-decane \([59]\) oxidation studied in our own Variable Pressure Flow Reactor. For the DME experiments, calculated species profiles for even very large \( \tau_{\text{psr}} \) mixing times were only marginally different than for \( \tau_{\text{psr}} = 0 \) for most of the reaction temperatures we considered \([52]\). That is, for the specific experimental conditions probed, DME observations were relatively insensitive to mixing perturbations. We return to DME in the following sections and show that this apparent insensitivity is highly condition-dependent, which is a caveat that generalizes beyond the kinetics of this particular exemplar fuel. On the other hand, for the n-decane data we reported in Ref. \([59]\), significant sensitivity to the mixing perturbation was confirmed experimentally by comparing reactor exit measurements with time-resolved species history data to characterize a temperature-dependent relative residence time shift similar to the one applied in Fig. 2c.

As evidenced by these examples and several to follow, experimental and computational sensitivities to initialization perturbations depend substantially on reaction conditions, and as a corollary, the particular kinetic model used for analysis. The important insight from the previous examples is that both the interpretation of experimental data as well as the comparison of data to model predictions requires careful assessment of the potential impact of uncertain upstream mixing effects on the overall disparities with computational predictions. This is particularly important when using absolute time scales referenced to the point of mixing.

The present finding extends to other mixing initialization non-idealities, such as perturbations in gas-phase chemistry caused by impurities in the reactants or due to heterogeneous surface reactions in the mixing region. We address reactant impurities below. Readers interested in perturbations caused by surface reactions in the initialization region are encouraged to consult references \([60–62]\).

### 3.2. Reactant thermalization effects on initialization

A second common flow reactor initialization approach premixes reactants \( Y_{i,0} \) at temperatures that preclude significant reaction extent, and then rapidly heats the premixture to the reaction temperature \( T_0 \) to initiate reaction \([37–48,53,63–67]\). The “thermalization” process, which generally requires a high surface area to volume ratio to achieve rapid heat transfer, poses a significant potential for surface reactions to perturb the gas phase kinetics, though we do not elaborate on this point further here.

A variety of models can be used to interpret the reactant thermalization process and its perturbations on initial ideal reactor species composition \( Y_{i,0} \). We illustrate here potential interpretive consequences of a fast finite-rate heating assumption comparable to the fast species mixing assumption discussed in the preceding section. Ideally, thermalization establishes temperature homogeneity of reactants \( Y_{i,0} \) on a negligibly small time scale, and this process can then be ignored relative to the overall reaction time for purposes of interpretation and computation. Our analysis further extends to thermalization processes actually found in flow reactors with appreciable spatial (temporal) temperature ramps between the initial premixture temperature and the desired reaction temperature \( T_0 \). For these temperature ramping cases, the thermalization process can be characterized by an assumed coupled heat transfer and reacting flow model. However, subsequent interpretation of the reaction system will depend on the resolution and phase fidelity of the applied thermalization model.

As with species mixing, the validity of the fast thermalization assumption depends significantly on reaction conditions and experimental objectives. Fig. 3 provides an example where the assumption of negligible thermalization perturbation may cause important departures from ideology for some reaction conditions, but also appears to be a good approximation for others. Here we refer to axial length coordinates rather than time scale, though this should be no cause for confusion following the preceding discussion on distance-time equivalence in ideal plug flow reactors.

Our illustrative model uses two PFRs in series meant to represent a single PFR of overall length \( L \). The first series reactor, termed here the “thermalization PFR”, has a prescribed spatially linear axial temperature profile within reactor length \( (300 \text{ K}) \) and the reaction temperature \( T_0 \), but is otherwise an ideal plug flow reactor. It is intended to represent characteristic thermalization effects at chemically reacting conditions \( (Y_{i,0}) \) for various thermalization processes as presently embodied by a length scale \( L_{th} \). This thermalization length (time history) is the uncertain parameter of present interest.

The thermalization PFR feeds an ideal isothermal PFR of length \( L - L_{th} \). As with reactors such as those described in Refs. \([48,49,65–70]\), the present simulations hold initial reactant composition, mass flow rate, pressure, and sampling point location constant. Example reaction conditions are loosely based on those described by Herrmann et al. \([69,70]\) for fuel rich DME oxidation. Note that in the PFR—PFR simulation results presented in Fig. 3, we do not account for the small change in total mole number that may occur during reaction. This in no way impacts the general trends observed from the simulation results.

Figs. 3a and b display predicted DME conversion at the exit of the thermalization PFR and overall PFR, respectively, as a function of the uncertain parameter \( L_{th} \) and the nominal isothermal reaction temperature \( T_0 \). In particular, Fig. 3a highlights the sensitivity of the mixture composition entering into the isothermal PFR to the thermalization history embodied in \( L_{th} \). Fuel conversion is clearly temperature dependent, but with non-monotonic complexity derived from the well-known two stage chemistry exhibited by DME (and hence our frequent emphasis on attention to condition-dependence). Further, Fig. 3b demonstrates that above \( T_0 \sim 925 \text{ K} \), no fuel remains to be detected at \( L = 900 \text{ mm} \). At higher temperatures, the desirable \( Da = O(1) \) condition for flow reactors no longer holds for the indicated reaction conditions.

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\( \text{23} \)
Fig. 3. Numerical simulations of thermalization effects on PFR fuel conversion using initial reaction conditions of Herrmann et al. [69] (8567 ppm DME, 2.14% O2 in Ar at 1 atm): a) and b) are operational condition maps showing fuel conversion as a function of thermalization length, Lth, and nominal reaction temperature T0 at a) the exit of the thermalization PFR and b) at an overall length L of 900 mm, which includes L0. c) Absolute reactor length-referenced fuel conversion profiles in the PFR interior at various values of L0 and 900 K — the inset shows the relative reactor length-referenced profiles by shifting each profile accordingly to match that for L0 = 0 mm; d) Relative reactor length-referenced fuel conversion profiles in interior of PFR at various values of L0 and 700 K. For L0 = 180 mm, no amount of axial shift within the 900 mm reactor length will collapse the profile on top of the others, so this profile is displayed with no shift.

Fig. 3a and b may be interpreted together as an operational map in L0 and T0 for this specific reactant composition, pressure, and reactor geometry. This map suggests conditions that may be best suited for study of the complex chemistry of DME oxidation. Two temperature bands between ~540 and 650 K and ~885–915 K are indicated in which substantial DME consumption occurs in the ideal PFR reactor section. Moreover, at these conditions, little DME consumption occurs in the non-ideal thermalization section for any value of 0 ≤ Lth ≤ 200 mm. Such maps are clearly generalizable to other reactor configurations and chemical systems, and can be applied to consider additional experimental non-idealities and kinetic model dependencies.

We now turn our focus to consider the response of the system to initialization at fixed temperatures of 900 K and 700 K. As indicated in Fig. 3c for the comparatively unreactive conditions at 900 K, small changes or uncertainties in thermalization length (time) scales upstream of the ideal isothermal PFR section influence the apparent DME conversion measurable at the overall reactor exit L. This is additionally evident in the operational map. More generally, in considering the parameter Lth as indicative of an uncharacterized thermalization process, it is clear that the systematic uncertainty implicit in choice of any specific thermalization model can contribute significantly to uncertainty in species fractions measured at point L.

Fig. 3c shows that at these conditions, the apparent DME mole fraction varies with Lth in the fixed axial coordinate reference frame; however, the spatial profiles of DME collapse on top of each other upon relative axial displacement (figure inset). This result is analogous to the discussion provided above regarding mixing initialization. However, the reactor response to thermalization can differ significantly depending on reaction conditions. Fig. 3d indicates the PFR–PFR system response upon heating to an isothermal temperature of 700 K. In this case, little reaction occurs in the isothermal PFR section following the thermalization PFR. However, the thermalization PFR accesses lower temperatures with higher reactivity, permitting non-negligible extent of reaction during flow preheating. This indicates that 700 K is in the negative temperature coefficient (NTC) kinetic regime at these conditions. Depending on T0 and Lth, relatively more reaction may occur in the thermalization section (Fig. 3a) for conditions when the flow thermalization time scale is sufficiently long to permit low temperature reactions of DME. Given enough reaction time at conditions favoring low temperature chemistry during the non-ideal thermalization process, simple axial profile shifting may not allow reaction gradient collapse, which is a point we return to in the following section.

In contrast to the 700 K case, comparatively little reaction occurs in the thermalization section at 900 K regardless of the value of Lth. Instead, reaction principally occurs in the isothermal PFR section (Fig. 3c). Reaction profiles at other temperatures permit reaction in both the non-ideal thermalization PFR and the ideal isothermal PFR. In any case, it is clear that the rich, condition-dependent phenomenology generalizing the simulation results of Fig. 3 is diagnostically inaccessible to reactor configurations that sample from a fixed point L.

In summary, the thermalization and mixing perturbations to IVP initialization considered here and above, as well as the reactant impurity perturbations discussed below, may often be generalized...
introduction of a non-specific, lumped initialization perturbation which negligibly affects the principal reaction gradient under relative temporal (spatial) shift. This reaction gradient contains substantial information about the chemical kinetic system of interest, aside from induction chemistry reactions like RH + O2 → HO2 + R to which the shape and magnitude of the gradient may not be sensitive. Reaction features referenced to absolute flow times (locations), such as ignition delay times [71–73] or measurements at fixed sampling points [42, 63, 65–70], may suffer from significant interpretive ambiguity.

4. Avoiding the need to characterize reaction initialization

The preceding examples describe the often non-linear responses of otherwise ideal plug flow reactors to uncertainties in prescribed initial conditions. These examples have not been contrived to elicit pathological behaviors. Instead, simulated conditions illustrate literature experiments which have been conducted with the intent of characterizing complex reaction systems. In this section, we continue to use literature-based examples to illustrate interpretative techniques that avoid the need to explicitly characterize reaction initialization processes.

Where inherent difficulties with such characterization, particularly for systems referencing absolute length/time coordinates, have led us [24, 50, 51, 60] and others (e.g., [73–76]) to pursue methods that require only accurate relative coordinates spanning the domain of significant chemical reaction gradient. Examples of some of these methods are illustrated for oxidation of carbon monoxide, methane, and DME in the Supplemental Materials published by Zhao et al. [52], and are expanded upon below. Our focus here is on interpretive techniques that enable comparison of complex kinetic model predictions with both (a) the predictions of other kinetic models and (b) experimental data. Experiment-to-experiment comparisons may also be accommodated by some of these tools, but these cases are not elaborated upon here.

The methods described below are most directly applicable to reactor histories (T(2 ← t) and/or Yi(2 ← t)) generated from fixed initial conditions. Profile-shifting tools can also be adapted to “reactivity” experiments (Yi(1/0), Yi(T), Yi(P)) measured at fixed reaction coordinate) akin to those discussed earlier with reference to Figs. 2 and 3, as demonstrated by, for example, Jahangirian et al. [59]. Such interpretations are subject to higher uncertainty since the pertinent spatial or temporal reaction gradient cannot be resolved for fixed initial conditions. Beyond the PSR—PFR and PFR—PFR methods previously discussed, we consider below three additional approaches to treat uncertain reaction initialization processes for IVP-type reactors and reactor simulations:

1. Intentional perturbative doping of the initial composition Yi,0 with radicals or other reactive species [75–79]. If instead, the perturbations are considered to be unintentional and stochastic [7] the same phenomenology is equivalent to non-ideality in initialization due to reactant impurities. Below, we explore the duality between intentional doping and inadvertent impurity.

2. Temporal or spatial coordinate-shifting of experimental or simulation results based on nominal initial conditions (e.g., [24, 50–52, 74, 80–83]), which is perhaps the most easy-to-implement technique presently discussed. Coordinate-shifting often returns results equivalent to those found by perturbative doping, PSR—PFR, and PFR—PFR techniques, but without additional computational complexity.

3. Computational re-initialization of simulations informed by experimental species measurements at a new initialization coordinate 0, such as described in Refs. [52, 60, 75]. This permits estimation of new initial conditions when non-ideal initialization perturbations are so large that previously mentioned techniques may fail to characterize the pool of reactive intermediates generated from non-ideal processes.

In keeping with the IVP nature of ideal PFR and shock wave experiments, each of these techniques remains essentially zero-dimensional under appropriate coordinate transform, and can be applied anywhere within the reactor domain for which plug flow assumptions are justified. Additional literature is available describing approaches that attempt to model the mixing region upstream of the IVP region in more detail (e.g., [43, 57]); however, this implementation overshadows both the computational attractiveness of and the implicit chemical insight from the idealized downstream IVP. Though we find that the zero-dimensional techniques 1–3 are often useful for interpretation of IVP-type reactors, each has a range of validity. Due consideration is warranted for every set of reaction conditions and each kinetic system.

4.1. Perturbative doping of initial conditions

One approach to aligning uncertain absolute experimental coordinates with corresponding computational coordinates is to intentionally perturb the simulated initial mixture Yi,0 with small concentrations of reactive intermediates. This technique can also be used for comparing reaction gradient predictions among models with disparate initiation chemistry since perturbative doping often tends to reduce the computed reaction initiation length/time scale, as in the studies of [75–79].

This grouping of exemplar studies includes interpretations of both flow reactors and reflected shock reactors, and follows from the similarity of the two systems derived from shared IVP-type reactor flow physics. Under common assumptions of ideality, adiabaticity (or isothermality), and the same initial reaction conditions, the ignition delay time and reaction gradient phenomena in PFRs are the isobaric IVP analogues to isochoric processes measured by traditional reflected shock techniques. Accordingly, initialization perturbation effects — intentional or not — are generally similar for both types of reactors.

Without loss of generality for PFR cases, we provide a reflected shock reactor example to describe the method of intentional perturbative doping to align regions of major reaction gradients. The
present approach and illustrative conditions come from the study of Hong et al. [79], which measured H$_2$O time histories from reflected shock wave oxidation of dilute H$_2$/O$_2$ mixtures in Ar. The effectively isobaric reaction conditions examined by Hong et al. were intentionally designed through modeling predictions to achieve nearly exclusive sensitivity of the H$_2$O profile behavior to the elementary rate coefficient for H + O$_2$ → OH + O.

Fig. 4 displays simulated H$_2$O histories at varying levels of initial H atom doping/impurity [H]$_0$, which serves to modify the initial Y$_{i,0}$ condition. Despite orders of magnitude changes in [H]$_0$ the results clearly demonstrate an essential invariance of the major H$_2$O gradient region with relative time coordinate. The absolute characteristic time for the reacting system responds roughly logarithmically to the doping parameter [H]$_0$, which is in intuitive accord with the exponential time dependence of radical pool growth predicted by simple ignition theory. This has significant implications for measurement and model prediction of absolute-time referenced ignition delays, both in shock tubes and flow reactors; see e.g., [4,5,7,72,84,85] for further discussion.

The reaction gradient manifesting in the H$_2$O profile primarily carries the rate coefficient information for H + O$_2$ → OH + O, so non-ideal perturbative initialization negligibly affects the rate coefficient measurement objective sought in Ref. [79]. Indeed, intentional perturbative doping was required in the interpretation of these experiments to counteract the effects of presumed experimental impurities and align kinetic model predictions with experimentally measured H$_2$O profiles. Uncertainties in the reported rate coefficient data would have been considerably larger had doping not been considered to align the reaction gradients in predictions and experiments. This has been discussed in similar context in Refs. [86,87] and comments associated with Ref. [85].

Fig. 5 clearly demonstrates the duality between actual experimental impurity and modeled doping effects invoked by the Hong et al. study. For illustrative purposes, we treat the original Hong et al. modeling prediction as surrogate experimental data subject to, in this case, a known 1.2 ppb [H]$_0$ “impurity” as assumed in Ref. [79]. We follow the [H]$_0$ doping procedure of [79] to determine the [H]$_0$ required for each of several literature kinetic models to replicate the surrogate experimental result. Initial conditions for simulation of the surrogate experiment with four kinetic models are intentionally seeded with a to-be-determined [H]$_0$ to align individual model-predicted and surrogate experimental H$_2$O profiles. Depending on the trial kinetic model used, the required H atom doping ranges from 0.0 to 1.1 ppb, though it is not unlikely that kinetic models exist for which unphysically “negative” amount of H atom doping would be necessary to align reaction gradients.

The perturbative effects explored above are not limited to H atom, which has only a tentative chemical basis as impurity within the context of the actual experiments themselves [7]. In addition to H atom, the same relative reaction gradient results can be achieved by doping of other very reactive species such as OH, as also shown in Yetter et al. [51] and below. Moreover, this kind of reaction gradient-invariant doping result generalizes to plug flow reactors, and can be therefore compared to the techniques and non-idealities of IVP initialization discussed both above and below. It is apparent from the present examples that doping/impurity perturbations often fall under the same lumped initialization perturbation discussed in the preceding section for non-ideal mixing and thermalization processes.

4.2. Profile-shifting

From the preceding discussions, it should be apparent that the responses of otherwise ideal IVP-type reactors to Y$_{i,0}$ and/or T$_0$ perturbations due to isolated effects of species mixing, thermalization, or impurities can often be lumped together. Moreover, these

Fig. 5. Duality between physical experimental impurity and modeled doping perturbation demonstrated in formation of H$_2$O for conditions noted in Fig. 4. Model results of Hong et al. [79], which employed [H]$_0$ = 1.2 ppb doping, are considered here as surrogate “impure” experimental data and shown as symbols. The simulation results of four different literature kinetic models are compared against these surrogate experimental data both unperturbed and with the appropriate level of “doped” [H]$_0$ to match the observed experimental trend. Model 1 [78]; Model 2 [125]; Model 3 [126]; Model 4 [127].
perturbations preserve the spatial or temporal reaction gradient—
in other words, they simply shift the species and/or temperature
profile along the reference coordinate of the ideal reactor (Figs. 2b,
2c, 3c, 3d, 4, 5). In the following discussion, we refer to “profile-
shifting” as the general phenomenon resulting from these types of
initialization perturbations and we refer to “coordinate-shifting” as
a particular method to achieve profile-shifting. The need for
distinction is apparent since, for many conditions, the profile-
shifting result unifies responses found from using the PSR–PFR
(mixing), PFR–PFR (thermalization), and doping methods previ-
ously discussed with the coordinate-shifting method under present
consideration.

Of these methods, coordinate-shifting precisely avoids the need
to characterize and interpret anomalies resulting from reaction
initialization. It makes no particular assumption about the cause of
initialization perturbation, only that there may be a lumped, non-
specific perturbation to initial conditions for the reactor IVP.
Coordinate-shifting is also the most facile to implement of the
methods heretofore discussed. Unlike the non-linear response of
perturbative doping to the assumed doping input (Fig. 4), coordinate-shifting aligns major reaction gradients through a
fundamentally linear displacement in the temporal (spatial) reactor
reference coordinate. Furthermore, it does not require coupling of
two separate chemistry-dependent models like the PSR–PFR or
PFR–PFR approaches.

Our discussion in the present section accomplishes three ob-
jectives. First, we describe the coordinate-shifting method in more
detail. Then we provide an additional literature-based example to
complement an explanation of the chemical basis that unifies all
four methods having characteristic profile-shifting results. Finally,
and importantly, reference to this chemical basis will permit an
understanding both of the remarkable unification of profile-
shifting phenomenology, as well as the limits where the equiva-
Iency among these various approaches may fail. In the following,
we use time to designate the reference coordinate system of the
ideal IVP-type reactor, though results also hold for axial position
through \( t \leftarrow z \) transform.

### 4.2.1. Coordinate-shifting

The coordinate-shifting method compares model predictions
with other model predictions or experimental results by removing
reference to the absolute reactor time scales. Modeled initialization
is subject to coupled uncertainties of the physical and chemical
models employed (which are often the subjects of investigation),
while uncertainties in experimental initialization (one subject of
the present discussion) may arise from any contributions to the
aforementioned non-specific initial condition perturbation. By
invoking the translation-invariance property of the ideal reactor
IVP, simulated and experimental time coordinates may shift by an
arbitrary additive constant relative to a specified reaction time scale.
In practice, and without loss of generality, it is convenient to fix one
time scale based on either the nominal simulated initialization time
or the given experimental time scale. Coordinate-shifting then
determines the particular additive constant \( \tau_{\text{shift}} \) that aligns the
reaction gradients at a sensitive reaction feature (or set of features),
for example, the 50% consumption point of a major reactant or the
peak mole fraction of a major intermediate. The time-shift constant
\( \tau_{\text{shift}} \) accounts for the initialization uncertainties in both models and
experiments, and so contains little direct kinetic insight on the
particular non-ideal initialization processes and/or reaction initia-
tion chemistry that manifest in the shift. This coordinate-shifting
approach has been applied numerically and experimentally as
described frequently in the literature [39, 50, 80—83, 86—89].

As with all of the methods discussed above, the coordinate-
shifting technique should not be applied without computational
testing for each condition-specific, coupled chemical and physical
model seeking to characterize experimental observations. Exam-
pies of such computational testing are presented below. Once
verified, the methodology is both straightforward and easily
adopted for both local and global sensitivity analyses as well as
model optimization approaches [86, 87, 89]. For example, Scire et al.
[87] utilized coordinate-shifting to match experimental and
computed data for multiple species measurements over the reac-
tion time history as a means of optimizing the coordinate-shift, as
well as defining derived rate coefficient uncertainties attributable
to coordinate-shifting.

### 4.2.2. Chemical basis for profile-shifting phenomena

Yetter et al. [51] show that predicted reaction profiles for
oxidation of CO in the presence of moisture agree well with
experimental data when the computed profile is coordinate-shifted
to match the point of 50% consumption of the initial CO mole
fraction. In related computations, Yetter et al. also show that per-
turbative radical (fast time-constant species) doping produces only
local effects on the predicted radical pool development during reac-
tion initiation. In other words, at the conditions considered,
perturbations to initialization do not lead to memory effects on the
subsequent reaction gradients in the principal region of reactant
destruction downstream. Instead, the perturbed radical pool
returns rapidly to that supported by the local, slow time-constant
species (e.g., fuel and \( \text{O}_2 \)). This behavior is also evident in the
shock tube example above (Figs. 4 and 5).

As a further example toward generalization of the Yetter et al.
observations to lumped initialization perturbation, Fig. 6 presents
computational demonstration of profile-shifting results for essen-
tially adiabatic, isobaric \( \text{H}_2 \) oxidation in a flow reactor [90]. Simu-
lations show that for the specific reaction conditions tested, the
chemical induction (ignition delay) time is affected to varying de-
Lgrees by the following:

1. Perturbative doping of \( Y_{1,0} \) with varying mole fractions of \( \text{OH} \)
   (Figure 6a).
2. Non-ideal mixing (Figure 6b) using the PSR–PFR model dis-
cussed above.
3. Finite rate thermalization (Figure 6c) using the PFR–PFR model
discussed above.
4. Combined perturbations 1–3 (Figure 6d), which can be
   considered to represent the effects of thermalization and
   convective mixing with additional radical back-mixing due to
   axial diffusion/dispersion processes.

Further, none of these initialization perturbations affect the
downstream species gradients, which are easily recovered by co-
ordinate shifting. Identical conclusions exist for isothermal and/or
isochoric reaction assumptions and, with caveats not elaborated on
here, extend as well to systems with heat loss (e.g., rapid
compression machines [9]).

Fig. 6 is suggestive of the chemical principle underpinning the
profile-shifting phenomenology. Relative to the ideally initialized
case, an initialization perturbation leads to premature or delayed
formation of reactive species (here \( \text{OH} \)) associated with a small,
only negligible conversion of initial reactants \( Y_{1,0} \). This observation
essentially generalizes the limitations on the premise of perturba-
tive doping and unifies this profile-shifting result with those due to
mixing and thermalization. Parallels with extent of reaction metrics
are also evident, though not further explored here.

The fast reaction time scales of the non-ideally introduced
reactive species require these species to adjust to the local kinetics
defined by slow time constant species (i.e., the rate-limiting ki-
etics to be studied in the IVP reactor). Moreover, the relatively low
**Initialization perturbation effects on the consumption of H₂ (left panels) and generation of OH (right panels) for the flow reactor conditions of Mueller et al. [90] (1.0% H₂, 1.5% O₂ in balance N₂ at 2.55 atm and 943 K initial temperature). Unperturbed simulation results are shown as solid lines; dashed and dash-dot lines are model results for the perturbed conditions. Symbols show the perturbed results coordinate-shifted (by the noted times in the figures) to match the unperturbed results. Legends and shifts shown on left panels apply to right panels as well.**

**a) Reactive Radical Doping**

**b) Non-ideal Mixing**

**c) Finite-rate Thermalization**

**d) Combined Perturbations**

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Fig. 6. Initialization perturbation effects on the consumption of H₂ (left panels) and generation of OH (right panels) for the flow reactor conditions of Mueller et al. [90] (1.0% H₂, 1.5% O₂ in balance N₂ at 2.55 atm and 943 K initial temperature). Unperturbed simulation results are shown as solid lines; dashed and dash-dot lines are model results for the perturbed conditions. Symbols show the perturbed results coordinate-shifted (by the noted times in the figures) to match the unperturbed results. Legends and shifts shown on left panels apply to right panels as well. **a)** Effects of OH radical addition (1 and 10 ppm) to the initial reactant concentrations; **b)** effects of non-ideal mixing, modeled by the PSR–PFR approach described in the text, for PSR residence times of 0.05 and 0.1 s; these times are shown by the shaded regions in the figures; **c)** thermalization effects, modeled by the PFR–PFR approach described in the text, for linear axial temperature gradients (from 300 K to 943 K) resulting in residence times of 0.1 and 0.2 s in the thermalization PFR; **d)** effects of a combination of perturbations a)–c) by considering 1 PFR thermalization (300–943 K in 0.1 s) followed by 2 addition of 1 ppm OH ending in 3 0.05 s mixing in a PSR; the PSR portion has been shaded in the figures.
concentrations of the reactive species preclude substantial changes to the concentrations of the slow time constant species pool, despite the ability for fast time constant species to react, even selectively, with slow time constant species. As embodied in Figs. 2–6, the net effect of initialization perturbation is often a relatively local excursion from the ideal reaction trajectory. After a relatively short time encoded by \( t_{\text{shift}} \) or other assumed initialization parameter, this excursion converges to a trajectory that is negligibly different from the ideal trajectory (at the level of most experimentally achievable time/spatial resolutions). In this way, coordinate-shifting accounts for the premature/delayed reactivity induced by non-specific initialization perturbations. It is worth noting that the fast/slow species argument invoked here finds analogy in conventional asymptotic and computational singular perturbation (CSP) formalisms \([91,92]\) and also in application of kinetic model reduction techniques (e.g., \([93]\)). Further, the trajectory convergence for small initialization perturbations is characteristic of Hadamard well-posedness \([94]\) in the mathematical–physical formulation of the ideal IVP reactor.

Profile-shifting methods are especially useful for comparing model predictions and experimental data for systems involving small molecules (e.g., \( \text{H}_2, \text{CO}, \text{CH}_3\text{OH}, \text{CH}_4, \text{C}_2\text{H}_6\text{O} \)) as principal reactants, though shifting is useful for larger molecules as well (e.g., \([59,95–97]\)). Small molecules often exhibit relatively slow reaction initiation compared to their major reaction gradient time scales. This facilitates separation of initiation processes from those in the principal reaction domain, where the definition of slow/fast species may change (e.g., \([98,99]\)). Though these shifting techniques appear useful in many cases, we reiterate that the viability of any profile-shifting is not general, but instead depends on both the experimental design and kinetic system of interest. We expand on limitations of these methods in the following section.

### 4.2.3. Failures of profile-shifting approaches

In Fig. 3d, we provide a clear, if exaggerated, counterexample to the unified profile-shifting results in support of our preceding caveat. For non-ideal thermalization initiation at \( T_b = 700 \, \text{K} \), no amount of coordinate-shifting within physically reasonable reactor length scales can align the ideal (\( L_{th} = 0 \, \text{mm} \)) and perturbed (\( L_{th} = 180 \, \text{mm} \)) reaction gradients. Minimal fuel reactivity at 700 K also implies unphysically long isothermal \( t_{\text{res}} \) residence times are required to achieve DME conversion similar to the \( L_{th} = 180 \, \text{mm} \) thermalization case. Moreover, for this case, required doping levels for modeling would amount to many percent of the initial reactant mole fractions. In short, at \( L_{th} = 180 \, \text{mm} \) the non-ideal initialization perturbation is too large to permit any of the profile-shifting responses.

We note similar difficulties with profile-shifting in interpretation of the flow reactor pyrolysis of \( \text{C}_2\text{H}_5\text{OH} \) \([60,62]\). In these experiments, \( \text{H}_2\text{O} \) elimination from \( \text{C}_2\text{H}_5\text{OH} \) is observed to occur at a rate that is inconsistent with local homogeneous gas phase reactions. Instead, unimolecular \( \text{H}_2\text{O} \) elimination is promoted by higher mole fractions of \( \text{C}_2\text{H}_5\text{OH} \) in the region where fuel vapor mixes with \( \text{N}_2 \) carrier gas, as well as by heterogeneous reaction on the mixer surfaces. As a result, substantial \( \text{C}_2\text{H}_5\text{OH} \) destruction to \( \text{C}_2\text{H}_4 \) and \( \text{H}_2\text{O} \) occurs prior to entering the reactor diagnostic section where plug flow assumptions are valid, and reaction within the PFR test section is therefore characteristic of an initial mixture of \( \text{C}_2\text{H}_5\text{OH}, \text{H}_2\text{O}, \) and \( \text{C}_2\text{H}_4 \) rather than of pure \( \text{C}_2\text{H}_5\text{OH} \). Thus we describe a different method of aligning computational predictions with experimental data to compare detailed reaction profiles and computations \([60]\). This computational re-initialization approach is discussed in the following section.

The unified profile-shifting response can break down for a number of reasons. As described above as well as in a specific example below, cases for which the initial reactants \( Y_{i0} \) are significantly consumed within the domain of non-ideal initialization are symptomatic of such a breakdown. This large perturbation situation violates the assumption of negligible depletion of slow species from their unperturbed \( Y_{i0} \) values, and for non-isothermal cases, the assumed value of \( T_b \). Moreover, a significant pool of reaction history-specific intermediates may blend the fast/slow reaction time scale spectrum, convolving the effects of non-ideal initialization with the chemical processes contained in the principal reaction gradient. As a result, coordinate-shifting cannot align the principal reaction gradient. The complex composition of the reactive intermediate pool induced by large perturbation precludes use of simple perturbative doping techniques, as a single dopant cannot capture the distribution of characteristic reaction selectivities and time scales inherent in the intermediate pool. Likewise, PSR and PFR initialization techniques may generate a pool of reactive intermediates with which to update \( Y_{i0} \), but for large extents of reaction, these can fail in replicating the specific reactivity of the unknown experimental intermediate pool.

### 4.3. Computational re-initialization

For the reasons outlined above, the equivalence of different profile-shifting techniques is not always valid, nor can profile-shifting methods be universally applied to the interpretation of experimental or simulated IVP-type reactor results. Despite this, the preceding discussion points toward a more general, albeit computationally more involved, method for reaction initialization. The recurring objection to using profile-shifting techniques in the preceding paragraphs — especially for conditions of significant initial reactant conversion — is largely due to the unknown selectivity and reactivity characteristics of the significant intermediate pool established during non-ideal reaction initialization. It follows that a technique to closely approximate this intermediate pool at some point (\( z \) or \( t \)) in a domain where ideal IVP reactor assumptions apply could establish an approximately equivalent intermediate pool and permit integration thereafter. We elaborate below on such a method, termed here "computational re-initialization", which provides a kinetic model-based estimate of the initial reactant pool from experimental measurements taken at a new initialization point \( \bar{0} \). The new, model-based initial condition estimate is used to initialize kinetic modeling simulations for comparison to experimental data for coordinates downstream of \( \bar{0} \).

#### 4.3.1. Specific reaction intermediate pool governs reaction trajectory

We more concretely motivate the need for approaches like computational re-initialization by referring back to Fig. 3d. At present, we consider the non-ideal initialization of a surrogate experiment (represented by the \( L_{th} = 180 \, \text{mm} \) result) to be uncharacterized, rather than having resulted from the specific thermalization history previously assumed in reference to Fig. 3. In this case, no physically reasonable profile-shift from any of the previously described methods — even given the most accurate of detailed kinetic models — can be found to align the principal reaction gradients of this surrogate experiment and the \( Y_{i0} \) simulation (represented by the \( L_{th} = 0 \, \text{mm} \) result). If we consider a new initialization point \( z = \bar{0} \) in the surrogate experiment to be located at the beginning or inside of the ideal isothermal PFR section (i.e., \( z \geq 180 \, \text{mm} \) in the coordinates of Fig. 3d), then prescription of \( Y_{i0} \) permits the desired outcome, which is solution of the ideal reactor IVP for all \( z \geq \bar{0} \). It is interesting to compare the initial unperturbed DME/O\(_2\)/Ar \( Y_{i0} \) mixture to the mixture \( Y_{i\bar{0}} \) that might be used to re-initialize model simulations. To be specific, we take \( z = \bar{0} \) to be the...
beginning of the ideal isothermal PFR section in the surrogate experiment (z = 180 mm in Fig. 3d). Upon significant uncharacterized conversion in the non-ideal initialization zone, the initial \( Y_{0} \) (8567/21440 ppm DME/O₂ converts to 7960/20790/996/602/117/21 ppm of DME/O₂/CH₄/O₂/H₂O/CO₂/H₂O₂, among dozens of other species that participate in the overall DME oxidation mechanism. It is the inherently different reactivity of this intermediate pool, relative to any other reactant pool generated by the unperturbed mixture at any location inside the reactor length, which precludes use of coordinate-shifting methods for these conditions.

4.3.2. Description and demonstration of computational re-initialization approach

The preceding illustration provides a basis from which to develop the computational re-initialization technique, though complete quantitative characterization of all species fractions at point \( t \) or \( z \) = 0 is an especially idealizing assumption. This is unlikely even for a single flow coordinate, particularly one immediately upstream of all or part of a nearly ideal IVP-type reactor section. The significant task of computational re-initialization is then to determine the corresponding species fractions for which experimental measurements are not available at point \( 0 \), either for lack of an appropriate diagnostic or because of large uncertainties in their estimation. Importantly, we demonstrate below that using only a specific set of experimentally measured species fractions \( Y_{k0}^{j} \) (where \( k \) is the number of measured species) to initialize kinetic models may significantly alter the apparent simulated system reactivity. Additional specificity and selectivity is provided by the unknown species fractions \( Y_{k0}^{j} \) estimated to exist in the reactant pool at point \( 0 \). Specification of both the unmeasured and measured species gives \( Y_{0}^{j} \) (where \( n \) is the total number of species in the kinetic model) estimated to exist in the unperturbed reactor input. Formally, the reactor IVP can be initialized.

The computational re-initialization method (also referred to in some of our publications as “initialization” or “initial condition matching”) is more complex than coordinate-shifting or other reaction initialization methods based on the unperturbed reactor input discussed above. The undetermined species fractions \( Y_{k0}^{j} \) are estimated from both the experimental species fraction measurements \( Y_{k0}^{j} \) as well as the particular kinetic model used for interpretation or validation. Here we provide an exemplar method for computational re-initialization as demonstrated by Li et al. [60]. In such cases, comparisons of experiment and predictions can be made only downstream of the re-initialization location as the illposed inverse problem yielding upstream comparisons would involve large uncertainties. The Li et al. computational re-initialization approach assumes that an isothermal, isobaric quasi-steady state condition is established among the measured and unmeasured species at point \( 0 \). The available measured species pool \( Y_{k0}^{j} \) constrains the unmeasured species pool. The isobaric assumption, in particular, is maintained in computations of \( Y_{0}^{j} \) by offsetting the generally small mole number change due to production of unmeasured species by a change in mole fraction of the diluent bath gas such as Ar, He, or N₂. High dilution is typically employed to establish the IVP condition for examining complex reaction systems, and thus slight changes in the diluent mole fraction do not pose problems in achieving good closure in experimental atom conservation consistent with the unperturbed reactor input \( Y_{0}^{j} \).

The unmeasured species pool \( Y_{k0}^{j} \) (hence, \( Y_{0}^{j} \)) is estimated in the following way. First, an initial estimate for \( Y_{k0}^{j} \) is constructed from the measured species fractions \( Y_{k0}^{j} \) and the assumption that all unmeasured species fractions \( Y_{k0}^{j} \) = 0; note that here \( k \) = \( m + 1 \), \( m + 2 \), ..., \( n - 1 \) and that the abundant diluent species (for convenience considered to be the last species, \( n \)) \( Y_{k0}^{j} \) is obtained from the balance \( (Y_{n0}^{j} - 1 - \sum_{k=0}^{m} Y_{k0}^{j}) \). Then an ordinary differential equation solver [100] is used along with the kinetic model to reach a quasi-equilibrium condition \( (i.e., d/dz = 0) \) by integrating along a coordinate system \( \xi \) orthogonal to the reactor coordinate \( t \) or \( z \). This process is constrained by forcing \( \sum_{j=0}^{m} Y_{k0}^{j} = 0 = 0 \) and \( \sum_{j=0}^{m} Y_{k0}^{j} \) during integration. Convergence and tolerance criteria, such as the relative change in the diluent species fraction from the initially assumed value, are employed during integration. The solution obtained for \( Y_{n0}^{j} \) (and thus, \( Y_{k0}^{j} \) and \( Y_{0}^{j} \)) after integration is further numerically refined using a non-linear algebraic system solver based on the hybrid method of Powell [101].

Alternative descriptions of this method appear in Refs. [52,60], which also demonstrate its application for initializing kinetic model simulations of small molecule reaction experiments in a flow reactor. Ethanol pyrolysis simulations of Li et al. [60] reveal excellent agreement in both stable and radical species profiles obtained by using different points \( t \) = 0 in the region downstream of reactor non-idealities. Accordingly, computational re-initialization was used to evaluate the kinetic model of Marinov [102] against the flow reactor data of Li et al. [60] and identify thrusts for kinetic model improvement [103–105]. In high pressure DME pyrolysis experiments [52], significant reaction (~20% fuel conversion) was inferred in the reactor mixing region upstream of the first experimental measurement point. To facilitate evaluation of several kinetic models and determine sensitive reactions, computational re-initialization was successfully applied in this study as well.

Fig. 7 presents an additional illustrative example of computational re-initialization applied to the methane oxidation conditions reported by Hunter et al. [75]. In their experiment, species time histories were measured along the reactor axis downstream of an extended mixing region. The extent of this mixing region is such that it leads to initialization conditions for which computational re-initialization may be applicable. Moreover, unlike other thermally idealized cases provided in examples above, we demonstrate here the application of an initialization technique to a case involving a temperature profile \( T(t) \) prescribed by experimental measurements [75].

In this example, we apply varying \( a \) priori assumptions regarding which species \( Y_{k0}^{j} \) are experimentally available to re-initialize simulations. Though the responses to the present assumptions are expectedly condition-dependent, this manner of assumption is completely consistent with the realities of experimental diagnostics asserted above: quantification of all species in a reactive system is unlikely. Sensitive species for one set of conditions may not be sensitive for another (cf., [75,77]); further, \( a \) priori knowledge of which species to measure is, by the nature of research, uncertain.

We take the point of re-initialization \( 0 \) to be 0.1 s as defined by the time scale of the unperturbed Hunter et al. surrogate experimental data. Case 1 (Fig. 7a) assumes that experimental diagnostics permit measurement of only the stable major species CH₄, O₂, H₂O,
CO and CO₂. Comparison of the model-predicted and surrogate experiment CH₄ profiles reveals that modeling using the Li et al. [60] computational re-initialization method described earlier to obtain $Y_{M}^{\beta}$ given $Y_{j_0}^{M}$ much better predicts the experiment than simply using $Y_{j_0}^{M}$ while setting $Y_{k_0}^{U} = 0$, which we term here “direct re-initialization”. The difference between the two predictions is the specific reactivity of the unknown reactant pool $Y_{k_0}^{U}$, which the computational re-initialization technique estimates and which further demonstrates our premise that the specific intermediate pool governs the reaction trajectory. To demonstrate the relative insensitivity of the results to choice of re-initialization point, Fig. 7a also shows the similar simulation results based on $\tilde{t} = 0.2$ s.

In Case 2 (Fig. 7b), we assume that stable species C₂H₆, C₂H₄, CH₃OH, and H₂ are measured in addition to Case 1 species. This results in modest improvement of the computational re-initialization simulation profile, while the direct re-initialization profile hardly improves relative to results obtained for Case 1. Likewise, Case 3 (Fig. 7c) assumes that relatively advanced diagnostics permit measurement of more reactive species HO₂, H₂O₂, and CH₃ in addition to the Case 1 species. Compared to simulations of Case 1, both the computational re-initialization and direct re-initialization profiles improve. Though not shown, simulation profiles similar to those of Fig. 7c result from considering all species of Cases 1–3 in $Y_{j_0}^{M}$.

Thus far, we have not assumed measurement of CH₂O, which is a species Hunter et al. [75] identified to be extremely important for re-initialization after retrospective modeling of their CH₄ oxidation experiments (and was incidentally, unimportant for initialization of similar C₂H₆ oxidation experiments [77]). As demonstrated in Fig. 7d, for Case 4 (CH₂O in addition to Case 1 species are measured), use of this single species for both computational and direct re-initialization approaches provides remarkable improvements in comparison of simulated CH₄ profiles with the surrogate experimental data.

The experimental CH₂O measurement at $t = \tilde{t}$ was available to Hunter et al. for purposes of direct re-initialization as applied in their study, but as Cases 1–3 demonstrate, this was a fortunate coincidence that does not generalize to the realities of making experimental measurements in complex kinetic systems. On the other hand, as evidenced by all of the computational re-initialization results in Fig. 7a–c, the estimated CH₂O (among other species) implicit in the $Y_{k_0}^{U}$ reactant pool provides an improved estimate of simulated reactivity despite the much weaker constraint on a priori knowledge of which species should be experimentally measured.

Despite the favorable results for the above examples and for other small molecule pyrolysis and oxidation systems, the computational re-initialization method applied here is subject to increased uncertainties with chemical systems having larger numbers of unmeasured species and/or too few constraining measured species fractions at $t$ or $z = \tilde{t}$. The method is also dependent on both model and experiment, as are all of the initialization approaches described previously. However, the present results support the observation that, with an appropriate set of species measurements, successful model predictions can...
be made while avoiding the need to characterize initialization non-idealities, regardless of the adiabatic/isothermal/non-isothermal nature of the reactor. Further research on developing more advanced computational re-initialization methods based upon relative sensitivity analysis and recent new insights into computational singular perturbation methods [106] is warranted.

Though we do not elaborate further here, it should be clear that the principles demonstrated in this example suggest similar analyses can be insightful for ranking of experimental species quantification diagnostics as more- or less-constraining for the purposes of both the re-initialization problems considered here as well as model validation and interpretation in general. Often, advanced single-species measurements of very reactive intermediates (e.g., CH₃, HO₂) afford no better mechanistic constraint than a single stable species measured by accurate diagnostic approaches (e.g., CH₂O). The implicit comparative cost-of-constraint advantage when simultaneously measuring multiple constraining stable species through well-established quantitative techniques like FTIR spectrometry or gas chromatography should not be underestimated.

5. Consideration of axial/radial gradients and complex chemical kinetics

The preceding discussions have assumed nearly ideal IVP-type reactors in their illustration of both potential reactor responses and data interpretation methods for non-ideal initialization conditions. The following discussion now considers ideal initialization conditions (e.g., Y₀ and T₀) that are not elaborated upon departures from the simple plug flow interpretation described in Fig. 1. Departures from the ideal plug flow interpretation may arise from:

1. Axial and/or radial gradients among the scalar chemical species, momentum, and/or energy fields. These couple together nonlinearly, both through the steady-state scalar transport operator as well as the chemical kinetic source term, \( w \);
2. Non-idealities imposed by the reactor wall boundaries, such as surface reaction and/or finite-rate heat transfer, which may contribute to the aforementioned axial and radial scalar field gradients; and
3. Ambiguities arising from the applied diagnostic methods (e.g., localized volume vs. line-of-sight optical methods, localized vs. total exit flow extractive sampling; perturbations from invasive probe sampling vs. non-intrusive techniques).

The rich behavior embodied by each of these topics represents the gamut of problems faced in reactive flow analyses, and in-depth discussion of each topic and their associated individual and coupled impacts is beyond the scope of the present article. Our discussions are limited here to several examples of these individual sources of possible departure from IVP assumptions. We conclude with an example that demonstrates the coupling between all of the above classes of departure. As before, the exemplar reaction system analysis is based upon a configuration and experimental result found in the literature [67].

5.1. Some conditions with(out) essentially plug flow interpretations

Expanding on the analysis of Lee and coworkers [107,108], we consider the following non-dimensionalized, steady axisymmetric reaction–advection–diffusion conservation equation for the scalars \( Y_i \) (i = 1, 2, ..., n, and T):

\[
U \frac{\partial Y_i}{\partial Z} - \frac{1}{Re} \left( \frac{\partial}{\partial R} \left( R \frac{\partial Y_i}{\partial R} \right) + \frac{\partial^2 Y_i}{\partial Z^2} \right) = D \frac{\partial \tilde{w}(Y_i)}{\partial t}.
\]

Despite some simplifications not presently discussed, Eq. (1) permits illumination of the particular reacting flow physics applicable to flow reactor configurations found in the literature. Here \( R \) is the radial reactor coordinate scaled by the inner reactor diameter \( d \); \( Z \) is the axial reactor coordinate scaled by the reactor length \( L \); \( \varepsilon \) is the inverse of reactor aspect ratio, \( \varepsilon = d/L \); \( U = u_T(R)/U_m \) is the axial velocity relative to the mean (plug flow) velocity; \( Pe_i \) is the diameter-referenced Péclet number for species \( i \) or \( T \) defined as the product of the flow Reynolds number and species Schmidt number; \( Pe_i = U_{ref}/D_i; D_i \) is the relative diffusivity of species \( i \) or the bulk thermal diffusivity \( \alpha \); \( Da a \) is the Damköhler number for the species \( i \) or temperature in the reacting system, defined by the quotient of the advective time scale \( U_{ref}/L_d \) with the characteristic reaction time for \( i \); and \( \tilde{w}(Y_i) \) is the non-dimensional chemical kinetic source term describing reactions among \( n \) species at the local temperature \( T \).

Eq. (1) assumes purely axial flow (i.e., \( U_{ref}(R, Z) = 0 \)) and permits density variations through the term \( \tilde{w}(Y_i) \). This generalized governing equation is also subject to boundary (inflow/initialization) conditions at \( Z = 0 \), as well as boundary conditions imposed by the wall \( (R = \frac{d}{2}) \). At present, these boundary conditions are assumed to be idealized for species and temperature: \( Y_i(0) \) and \( T(0) \) hold for \( Z = 0 \), and neither heterogeneous reactions nor heat transfer is supported by the wall at \( R = \frac{d}{2} \). Moreover, the flow obeys the no-slip condition at the wall. So far, we have imposed no additional assumptions on the magnitude or form of the individual advection, diffusion, or reaction terms in this governing equation, and so within the present framework, it remains mathematically exact.

Interpretation of reactor experiments and simulation critically depends on the choice of assumptions regarding the interior governing equations and boundary conditions. Clearly, careful justification of applied assumptions is imperative regardless of whether a reaction system satisfies plug flow or a less idealizing flow field. Though our examples are not exhaustive, in the following sections we seek to relax several of the present assumptions toward demonstrating cases where a proposed plug flow interpretation of flow reactor results requires careful reflection.

5.1.1. Essentially plug flow systems

Inspection of Eq. (1) reveals that for the desired flow reactor operating point of \( Da_i = O(1) \), chemical plug flow (Fig. 1) is satisfied for cases when diffusion terms are of substantially different order than the \( O(1) \) advection and reaction terms. This can occur when diffusion is either significantly slower or, perhaps counterintuitively, significantly faster than advection and reaction. This phenomenon will be further discussed as it applies to both turbulent and laminar flow reactors. We also point out here that unlike kinetic systems involving few species and few reactions, applying the \( Da_i = O(1) \) assumption for all species is difficult given the species-specific reactivity spectra typical of complex reaction systems. Moreover, the chemical timescale of an individual species may change dramatically with chemical reaction history, for example, during crossing of an explosion limit condition [109,110]. Nevertheless, the conceptual utility of this assumption serves well for the present discourse.

The case of slow diffusion relative to reaction and advection occurs under conditions of developing turbulent flow (therefore roughly \( 0.02 < \varepsilon < 0.2 \)) [18,35,38,43,111], in which the velocity field in Eq. (1) can be described by a fairly radially uniform potential core of plug flow velocity \( U_{ref}(Z) \). Within the context of the plug flow approximation, a \( Z \) dependence in velocity can be applied to
account for potential core acceleration due to boundary layer growth on the reactor walls, axial non-isothermality, etc. Radial gradients in $Y_i$ are assumed to be negligible in the potential core, and so the governing reactor equation reduces to

$$U_0 \frac{\partial Y_i}{\partial z} + \frac{\varepsilon}{P_{ei}} \frac{\partial^2 Y_i}{\partial z^2} = \hat{w}(Y_i). \quad (2)$$

Glassman and Eberstein [112] provide a more detailed eddy length/time scale argument supporting assumptions for this case. The high advective velocities and modest aspect ratios associated with developing turbulent flow drive the axial diffusion term of $O(\varepsilon/P_e)$ to be very small relative to reaction and advection, thereby recovering the desired plug flow interpretation, provided flow is sampled from the potential core. To cast "very small" more quantitatively, we refer to the analytical results of Levenspiel [3] and Wehner and Wilhelm [113] for Eq. (2) under the assumption of a first order global reaction. Their results indicate that neglecting axial diffusion under the aforementioned conditions leads to a correction in $U_0[\varepsilon]$ on the order of the small parameter $\varepsilon/P_e$ which in most cases will be significantly smaller than other uncertainties in experimental observables. Similar criteria apply to consideration of temperature gradients occurring within the reaction region, whether associated with chemical enthalpy changes from reaction or convective heat transfer to/from walls.

Notably, the enhanced mixing commonly associated with fully developed turbulence (e.g., [114]) does not directly apply for the preceding developing potential core conditions within a tubular reactor. Enhanced "turbulent diffusivity" results from fluid mechanical dispersion, and dispersion depends on the differential advection in shear flows to promote species and thermal gradients for molecular diffusion. When shear rates are small, such as in the contiguous region about the centerline of the axial potential core discussed above, the net effect is that local molecular species and temperature transport are not significantly enhanced by the turbulent flow field as long as chemical reactive gradients are small. Our recent large eddy simulation [115] of turbulent flow reactor methyl formate pyrolysis [61] further supports the validity of this radially decoupled potential core assumption. Moreover, this work also shows that for turbulent developing flow reactors of sufficiently large $\varepsilon$, net radial diffusion times through the laminar sub-layer at the reactor wall can be sufficiently long in comparison to overall axial chemical reaction/advection time scales such that surface reactions do not substantially couple with the potential core.

Under the developing flow conditions discussed above, turbulence is a positive feature toward approximating plug flow behavior, and has no unfavorable characteristics as long as turbulence--chemistry interactions minimally distort turbulence-averaged kinetic rate coefficients reflected in the chemical source term. The work of Seeley et al. [18,116] is particularly illuminating on this matter, given the wide range of fast flow conditions that were studied.

Seeley investigated several small molecule elementary reactions over pressures spanning 2–760 Torr and temperatures near 300 K. At pressures greater than about 50 Torr, the flows examined were of the developing turbulent flow type discussed above, leading to essentially radially uniform (plug) profiles. Lower pressure ($\leq 10$ Torr) experiments were of the fully-developed laminar flow type subsequently discussed as another essentially plug flow operating condition. Notably, the elementary rate coefficients determined by both the turbulent and laminar flow experiments showed excellent agreement with each other as well as with literature values. Moreover, the rate coefficients determined using turbulent flow conditions did not need correction for wall reactions, which is a typical concern for classical low pressure, laminar fast flow experiments. The work of Seeley et al. provides additional substantiation of the utility of developing turbulent flows for the exclusion of wall effects on kinetic interpretation. Further, the results demonstrate that turbulence--chemistry coupling effects for flow reactor experiments meeting plug flow interpretation criteria are negligible relative to other (small) experimental uncertainties.

The differences in the character of flow fields admitting plug interpretation is remarkable. In addition to the relatively slow diffusivity embodied in the developing turbulent flow case described above, an essentially plug flow can also be achieved for relatively fast diffusivity in a fully-developed laminar flow condition such as considered by Seeley et al. [18,116] and many others investigating elementary reaction chemistry in low pressure flow tube experiments (e.g., [13,14,17,37,117]). These laminar fast flow experiments are characterized by radial uniformity in species and temperature depending on both the shear flow implicit in the radial velocity profile $U = 2(1 - (2\varepsilon)^2)$ as well as relatively fast radial molecular diffusion (as a result of the very low pressure and the reactor aspect ratio $1/\varepsilon$). Both of these flow attributes were assumed to be negligible in the case of the developing turbulent flowfield discussed above; however, they may also result in interactions of heterogeneous wall and gas phase reactions.

For the case that $\varepsilon < 1$ and $P_{ei} \sim O(1)$ for fully-developed laminar flow, the radial diffusion term of Eq. (1) dominates all other terms (including axial diffusion), and to leading order $O(1)$, $\nabla[Y]/R = C_{\varepsilon}$ constant. One physical interpretation of this result is that a relatively elongated reactor aspect ratio and high diffusivity permit radial diffusion to establish a quasi-steady state at each axial location $Z$ on time scales much faster than other processes in the reacting flow. The reaction and convection terms balance at $O(1)$, establishing an axial gradient in $Y_i$ characterized by the plug flow velocity, and thereby recover the one-dimensional steady plug flow equation in $Z$. Further, the axial diffusion term of $O(\varepsilon \ll 1)$ can be considered negligible.

5.1.2. Systems requiring multi-dimensional interpretation

Despite the phenomenological insight offered by the developing turbulent flow and fully-developed laminar flow examples with their attendant assumptions, the scaling arguments presented above suffer from ambiguity in definition of characteristic dimensions, particularly $L$ and $D_{a,n}$, and can become complicated by the large spectrum of diffusivities and relative reactivities for the $n$ reacting species. Complications arise when the reacting system crosses a reaction-limiting condition that substantially changes the local source/sink ratio of a controlling species. For a fixed reactor geometry and reactant feed stream, this leads to local violation of the $D_{a,n} = O(1)$ assumption around which the prior plug flow discussion was premised. Regardless of the character of the flow field, advection and reaction terms no longer balance at $O(1)$, and the reaction system loses its plug flow character.

Many other authors (e.g., [118,119]) have considered more specifically the diverse behaviors inherent in Eq. (1) for flow-reactor-like conditions, and it is not our intention to replicate their results here. However, the case where $\varepsilon \rightarrow 1$, $P_{ei} \rightarrow 1$ and $D_{a,n} = O(1)$ is particularly interesting in anticipation of the discussion in the next section. Under appropriate radial boundary conditions, these assumptions represent the equation of an idealized laminar premixed reaction wave (flame) propagating at $U_m$. In keeping with earlier terminology, the flame thickness is $L$, although this may be significantly smaller than the length scale representing a reactor. Alternatively, the fixed reactor length $L$ can be considered the characteristic dimension so that $\varepsilon \ll 1$ and $P_{ei} \ll 1$, as in the laminar plug flow reactor example given above. In real reactors, the
reaction wave character may depart significantly from that of an ideal uni-dimensional flame as a result of interactions with the reactor walls. For these conditions, a reaction wave solution is admitted by \( Da_t \gg 1 \). Either of these interpretations seems an apt description of the laminar flow reactor results described in the next section.

5.2. Laminar flow reactor subject to significant interior/boundary complexity

Some very recent experimental flow reactor studies have focused on species characterization in complex reaction systems through application of molecular beam sampling or development of new species-specific diagnostics, for example, \([66,67,69]\). Each of these studies assumed isothermal, laminar reaction conditions were approached in experiments through flow preheating to the nominal reaction temperature (as in Fig. 3), isothermal reactor walls surrounding the reaction section, and low Reynolds number flow conditions. Moreover, each study applied a plug flow assumption to interpret the experimental laminar flow observations. All of the studies were conducted at atmospheric pressure conditions, in contrast to many previously cited studies of elementary reaction kinetics or the recent low pressure complex kinetic research of Qi \([49]\).

In light of our preceding discussions, two-dimensional axisymmetric analysis \([120]\) of DME oxidation observations in the laminar flow tube experiment of Guo et al. \([67]\) is further detailed here to illustrate the significant complexity that radial and axial diffusive coupling may impose on interpretation of reactor results. For this experimental configuration, \( Pe \) for DME based on diffusion in the primarily He diluent is on the order of 20, while the flow Reynolds number is of order 10, suggesting that both radial and axial gradients may be significant in interpreting experimental data depending on the Damköhler number. The analyses presented below also clearly illustrate additional complications arising from kinetic complexities in local chemical time scales produced by two-stage reactivity of the fuel. Dimethyl ether is particularly appropriate for demonstrating these effects, as the transport data and reaction model are reasonably well characterized \([52]\).

To assess departure from the ideal plug flow assumption, an experiment of \([67]\) is modeled using an in-house multi-dimensional, steady state, laminar reacting flow model. Detailed DME/O\(_2\)/He oxidation chemistry \([52]\) was employed in the simulations. Thermodynamic and transport properties were evaluated using the CHEMKIN and TRANSPORT packages \([121]\) and multi-component diffusion was considered. The OpenFOAM \([29]\) framework was used for solving the coupled systems of governing equations.

Present simulations assume an ideal initialization of the reaction system, i.e., isothermal, non-reacting conditions at the reactor inlet and a uniformly distributed mass inflow rate with magnitude prescribed by the experimental conditions \([67]\). The quartz reactor tube described in the experiment was tightly jacketed within a copper sleeve, and the assembly was placed inside an electrically heated tube furnace to generate a uniform tube wall temperature. Thus, the wall is modeled as an isothermal surface. The predictions for centerline parameters at the exit of the reactor are compared with results of ideal plug flow simulations employing both adiabatic and isothermal assumptions, obtained using SENKIN \([122]\).

The residence time of these latter calculations was set to 1.7 s, on the basis of a plug flow representation of the experiment. Simulations are presented here for a broad range of isothermal wall (and initial gas) temperatures from 500 to 750 K and for an initial DME/O\(_2\)/He mixture mole fraction composition of 0.02/0.1/0.88.

Fig. 8 shows the predicted steady state temperature contours for different prescribed wall (and inlet) temperature conditions of 500, 550, 615 and 750 K. The temperature contours clearly show that at the fuel loadings of these experiments, a reaction wave develops \((Da_t \neq O(1))\) as boundary temperature is increased. At 500 K, the predicted axial gas temperature is essentially uniform in the entire flow tube section, though reactant conversion is negligible. As the reactant and wall temperatures increase to 550 K, a reaction wave is established at the mid section of the tube with an up to \(\sim 150\) K increase in the local temperature. This wave moves upstream closer to the flow tube entrance section as the boundary temperature

![Fig. 8. Predicted temperature profiles for different isothermal wall temperature boundary conditions (noted by the left-hand value in each color scale) for DME oxidation in flow tube arrangements (DME/O\(_2\)/He 0.02/0.1/0.88, 1 atm). For interpretation of the color scales in the figure legends, the reader is referred to the online version of this article.)](image)
increases. In addition to the relocation of the reaction wave, the difference in the peak temperature relative to the isothermal reaction temperature elsewhere is diminished as $T$ increases. Fig. 9 reveals clear axial gradients (and with Fig. 8, implies radial gradients) in longitudinal velocity, temperature, and species concentration. In some conditions, these gradients are large enough to support significant local axial diffusion. The resulting wave structure shares phenomenological similarity to a laminar premixed flame, thickened and stabilized by heat losses to the reactor wall. In the context of the reaction wave development, there exists the possibility of radical interactions with the reactor walls, which thus far have been ignored. The wall reactions can affect the local reactivity of the system. Additional simulations including wall reactions are currently under investigation.

Importantly, as with other fixed sampling location reactors referenced in Figs. 2 and 3, the rich details of the interior domain of the reacting flow field suggested by the results in Figs. 8 and 9 cannot be discerned by sampling of either species or temperature at the reactor exit. Moreover, the reaction gradient occurs sufficiently early within the reactor section that downstream diffusion results in small radial and axial gradients at the sampling location, frustrating any experimental diagnosis of processes occurring inside of the reactor. Despite the fact that only minimal reaction occurs downstream of the reaction wave, the inability to characterize the spatial/temporal coordinate or products of the reaction wave creates significantly ill-posed initial conditions should the plug flow initial value problem be invoked to describe the slowly reacting flow downstream of the wave.

DME, O$_2$, CH$_3$OCHO and CH$_2$O mole fractions at the exit plane of the flow tube behave non-monotonically with reaction temperature, indicating negative temperature coefficient behavior characteristic of two-stage chemical kinetic phenomena. Fig. 10 compares the two-dimensional simulation results to the associated adiabatic and isothermal zero-dimensional predictions for CH$_2$O at the sampling location, which is on the centerline at the reactor exit plane. Results show that the two-dimensional interpretation of the flow tube experiments substantially affects predicted species fractions at the exit plane, and for no condition do the three simulated CH$_2$O profiles agree well. The largest discrepancies among the simulations occur between 550 and 650 K, where reaction wave development is most prominent.

The two-dimensional nature of the reaction zone is further detailed in Figs. 11 and 12. These figures display the axial CH$_2$O and H$_2$O$_2$ profiles (respectively) as a function of initial reaction (isothermal wall) temperature. The axial profile characteristics vary in a complex non-linear manner with changes in boundary temperature that are not reflected in observations at the reactor exit. The computational data also display axially varying radial distributions in temperature (Fig. 8) and species (not shown). These results further confirm the potential pitfalls in using this type of “reactivity” kinetic data for testing model predictive behavior, for an inappropriate application of a plug flow interpretation cannot discern the complexities of the experimental observations over the experimental reactor time scale.

**Fig. 9.** Predicted centerline ($r = 0$) a) axial velocity, b) temperature, and c) DME mole fraction profiles for different isothermal wall boundary conditions assumed in two-dimensional axisymmetric modeling of DME flow tube oxidation (DME/O$_2$/He 0.02/0.1/0.88, 1 atm).

**Fig. 10.** Predicted reactor exit CH$_2$O reactivity profiles for two-dimensional axisymmetric modeling as well as zero-dimensional isothermal and adiabatic assumptions (DME/O$_2$/He = 0.02/0.1/0.88, 1 atm).
The present findings extend to other flow reactor experiments: multi-dimensional effects may lead to significant departures from classical plug flow reactor interpretation. The coupled effects of advection, species-specific diffusion, and condition-specific reaction kinetics cannot be neglected without due consideration. Accordingly, thorough consideration of both the initialization and reactor interior/boundary is critical to properly interpreting flow reactor experiments and for their use in validating detailed kinetic model predictions.

As shown above, changes in chemical time scales due to the multi-stage kinetics of DME can produce violations of IVP interpretation of predictions. This observation can be generalized to other kinetic behaviors associated with combustion chemistry that similarly impact chemical time scales. For example, the crossing of a critical branching condition as a reaction proceeds, causing very high local reaction gradients (e.g., Ref. [90]). Another example arises during the transition between hydrocarbon + OH reactions and CO + OH during hydrocarbon oxidation. As the hydrocarbon and its reactive fragments are consumed, there are strong gradients produced by the oxidation of the CO present into CO$_2$, as observed, for example, in the oxidation of DME [123] or methanol [124].

Fig. 11. Centerline CH$_2$O profiles from two-dimensional axisymmetric modeling as a function of isothermal wall temperature [DME/O$_2$/He = 0.02/0.1/0.88, 1 atm].

Fig. 12. Centerline H$_2$O$_2$ profiles from two-dimensional axisymmetric modeling as a function of isothermal wall temperature [DME/O$_2$/He = 0.02/0.1/0.88, 1 atm].

6. Closure

This discourse has been directed toward assisting those interested in the design and analysis of flow reactor experiments for the study of complex reacting systems. The main goals of flow reactor studies are to develop and test predictive chemical kinetic models. The application of such studies to provide stable species histories as a function of reaction progress (as demonstrated in the literature since the early 1970s) provides substantial constraint for formulating the mechanistic construction of detailed kinetic models as well as quantitative assessment of their predictive quality. Rapidly evolving advancements in optical diagnostics, molecular beam/VUV photoionization mass spectrometry, and extractive sampling/multi-dimensional gas chromatography all promise to further enrich flow reactor speciation characterizations, particularly for highly reactive species. As important to advancing our fundamental understanding as these experimental enhancements will likely be, their impact will depend strongly on well-characterized flow reactor design and operational procedures, as well as accurate modeling of the experimental conditions. The latter issue has been the principal subject addressed in this paper.

Much as in shock tube, rapid compression machine, and jet-stirred reactor approaches, the initialization process assumed in comparing computational predictions with experimental measurements represents an inherent difficulty in interpreting flow reactor results. We have discussed in detail how several experimental initialization approaches evident in the literature can lead to misinterpretation of kinetic model predictions premised on ideal initial conditions. Further, we have also discussed techniques for modeling such initialization perturbations. These generally compare the simulated and experimental regions of strong reaction gradient, which provides insight on the chemical kinetic source term and serves to constrain kinetic model development.

There is no general method of initialization that is accurate for all chemical kinetic systems or flow reactor designs, and each method must be carefully vetted for each reaction study and condition investigated. We have shown that, in some cases, all of the methods yield comparable and satisfactory initialization while, in others, each may contribute significant uncertainties in interpretation. We cannot overemphasize that the veracity of each of these assessments are reaction system-dependent and cannot be assessed well without assuming a construct for the detailed chemical kinetic processes. Because of the sensitivities of the predicted/experimental comparisons to the initialization method, we do not recommend the use of flow reactors as a means of investigating the fundamental kinetics controlling absolute chemical reaction times, but only for yielding relative reaction time scales for regions where interpretation of reaction gradients are to be compared with computational predictions.

In a majority of the published literature, plug flow interpretation is applied to the region of flow reactor axial reaction gradients to be analyzed independent of the method chosen for initializing the computational predictions. Plug flow interpretation is most desirable as it permits a simple interconversion of reaction distances to reaction time through the axial velocity distribution, allowing homogeneous kinetic interpretations to be applied directly to the experimental data analysis. The attributes of making this assumption permit the use of large chemical models and accommodate elementary sensitivity, feature sensitivity, reaction pathway analysis, and computational singular perturbation methodologies for analysis without incurring prohibitive computational costs. However, the plug flow assumption is frequently applied without a careful vetting of potential sources of departure from this behavior...
as a result of significant axial and/or radial gradients in species, momentum, and/or temperature; non-idealities imposed by the reactor wall boundaries, such as surface reaction and/or heat transfer; or changes in chemical reaction time scales with extent of reaction, initial reactant concentrations, pressure, and reaction temperature.

A classification of flow reactor departures from ideal plug flow on the basis of reactor dimensional scales, laminar/turbulent and developing/fully-developed flow properties, and chemical time scales has been presented to provide some background for reader interpretation of literature results. Finally, a specific laminar flow reactor example has been analyzed to demonstrate the coupled nature of all of the above sources of departure of plug flow behavior. If significant radial distributions in reaction scalars result, then ambiguities exist in interpretation of line-of-sight optical diagnostic measurements, extractive point-sampling, and total quenched exit flow measurements. As experimental reaction parameters such as temperature, pressure, and initial reactant concentrations are changed, changes in relevant chemical kinetic time scales can also produce local failure of plug flow interpretation. Thus, the testing of assumptions must be constantly re-evaluated as model refinements occur and operating conditions are changed.

Finally, it has been shown that data generated using measurements with fixed reaction time as a function of initial reaction temperature can obscure departures from plug flow interpretation resulting from changes in chemical time scales.

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