Conditional and Opposed Reaction Path Diagrams
for the Analysis of Fluid-Chemistry Interactions

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Introduction. Gardiner [1] observed that "progress in achieving understanding through combustion modeling is now limited by the ability to recognize the implications of what has been computed and to draw conclusions about the underlying reaction mechanisms." This paper considers how to use reaction path diagrams to better understand reacting flow simulations. We are not aware of any comprehensive treatment of these diagrams from this perspective. In exploring the subject we discover some new information about the chemistry of .

Most reaction path diagrams are of a kind called "schematic" [2] because they depict all the theoretically possible reactant-product dependencies in the elementary steps of a chemical mechanism. The diagrams of interest in this paper have path thicknesses that convey quantitative information about the reactions occurring in a fluid-flow simulation. The purpose of these diagrams is to determine which paths may be important in flames. Identifying them is not a purely chemical question, because the answer depends on which species the fluid can bring together to react in quantity.

Integrated Reaction Fluxes. Several methods may be used to determine the thicknesses of paths in reaction path diagrams. Warnatz et al. [2] refer to diagrams obtained by integrating over a flame region as *integral reaction path analysis*. We choose the integrated quantity to be the rate $(mol/cm^3/s)$ at which a selected element moves from one species to another by reaction. This quantifies what has been called a *reaction flux* [3]. When path thicknesses are based on a conserved scalar in this way, then a reaction path diagram has two desirable properties. Consistency: the material removed from the species at the base of a path equals the amount contributed to the species at the head. Conservation: the sum of all paths into a species equals the sum of all paths out from the species. (Species that flow into or out of the domain must also include boundary sources or sinks.).

It is straightforward to determine integrated reaction fluxes. Software to prepare and display

reaction path diagrams is available both from the authors [4] and Cantera [5]. However, the usual manner of stating elementary reactions does not provide sufficient information in all cases. A method supported by Cantera enlarges the specification of elementary reactions to include information about the disposition of individual atoms. The ambiguities typically involve minor species whose reactions do not significantly contribute to the diagrams.

Conditional Reaction Path Analysis. If the volume integrals for path thicknesses are limited to part of the flame, then they are called conditional integrals because they are premised by a condition that picks out the desired region. The resulting *conditional reaction path diagrams* help elucidate fluid-chemistry interactions. When they are conditioned by some property of the fluid, they permit an investigation of the reactions supported by just that fluid regimen.

Example: Conditioning by Stoichiometry. This paper's examples are based on a nitrogen-diluted Burke-Schumann flame. The chemical mechanism and numerical model are described and validated in references [6] [7] [8] [9], where nitrogen reaction path diagrams for atmospheric and fuel nitrogen can be found.

Our first example of conditional reaction path diagrams contrasts the carbon chemistry on the lean and rich sides of the flame. Diffusion flames are known to lie slightly to the rich side of the stoichiometric zones in their mixtures. Figure 1(a) confirms this as the temperature peaks very slightly to the rich side of the stoichiometric surface. Figure 1(b) shows that heat release also correlates with stoichiometry, but in a more complicated way.

In the earliest fully two-dimensional simulations of these flames with detailed chemistry, Smooke et al. [10] observed that CO_2 forms only in the outer layers. They explained the phenomenon by an analysis due to Westbrook and Dryer [11]. To further investigate this finding, Figure 1(c) displays carbon reaction path diagrams for the lean (blue) and rich (red) sides of the flame. This diagram shows that most carbon reactions occur on the rich side of the flame, but the outer layer in which the final step occurs, $CO \rightarrow CO_2$, is almost completely on the lean side. Interestingly, this means that CO is the only carbon species to flow across the stoichiometric line in large amounts.

Example: Conditioning by Downstream Distance. Our next conditional reaction path diagrams compare carbon chemistry at the flame base and downstream. Non-premixed flames have a rich spatial structure [12]. Several flame sheets extend from a common ignition point, and may or may not close at much different heights above the fuel nozzle. Additionally, the concentration
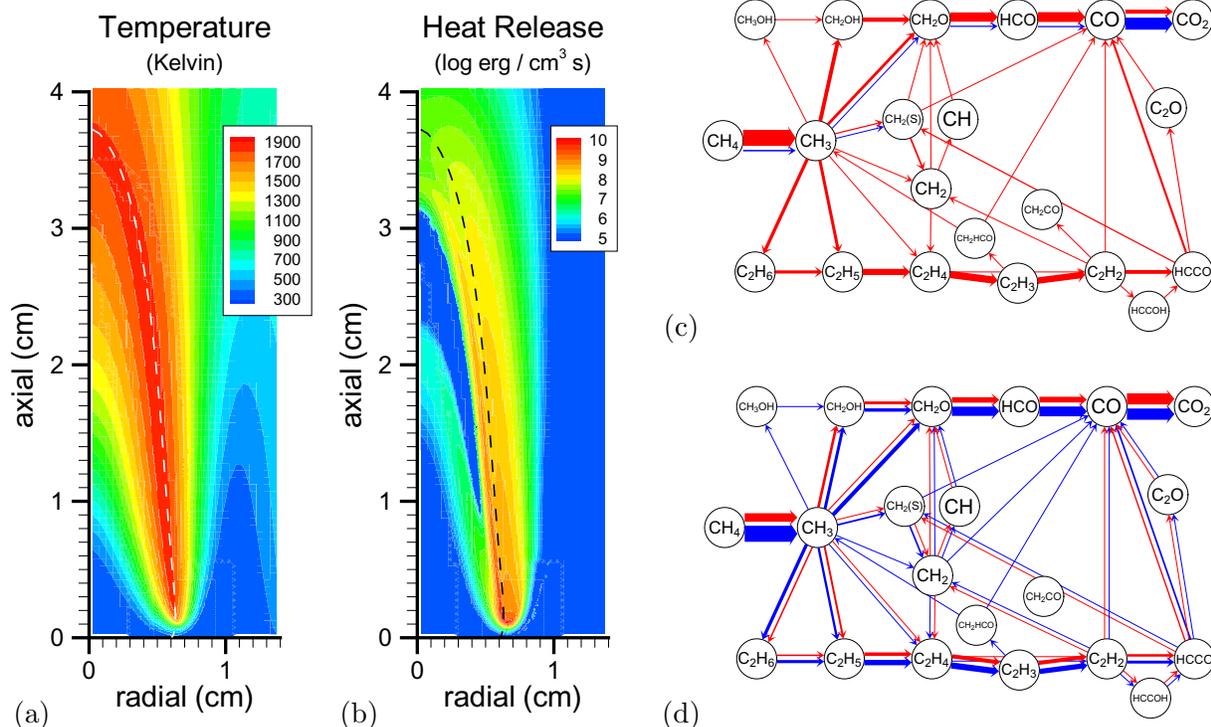
Figure 1: *(a) Temperature and (b) heat release for an axisymmetric Burke-Schumann flame model [8]. Dotted lines mark the stoichiometric sheet. Only the lower third of the domain is shown. (c) Conditional carbon reaction path diagrams for the rich (red) and lean (blue) regions of the flame. (d) Conditional diagrams for the flame base (blue, below 1 cm in axial position) and downstream (red, above 1 cm). Only paths at least 3% of the thickest are drawn.*

of the primary fuel has been observed to become negligible shortly downstream of the flame base. In laboratory-scale flames that are a few centimeters high, a distance of 1 cm often is cited as a rough estimate of the distance beyond which fuel vanishes [10] [13].

These observations suggest that the dominant reactions in a Burke-Schumann flame may be different downstream than at the base. To examine this hypothesis, Figure 1(d) displays reaction path diagrams for the low (blue) and higher (red) parts of the flame. The major carbon paths are clearly mirrored above and below 1 cm, disproving the hypothesis.

Opposed Reaction Paths. It is natural to draw diagrams with opposed paths to represent the reversible nature of reactions, but how to determine the path thicknesses is surprisingly complicated. The full version of this paper enumerates all the the possibilities.

In this abstract, we briefly illustrate opposed paths by using oxygen reaction path diagrams to study chain branching reactions. Figure 2(a) displays the opposed paths that result from treating each direction of a reversible reaction as a separate reaction. Figure 2(b) shows the fully coalesced
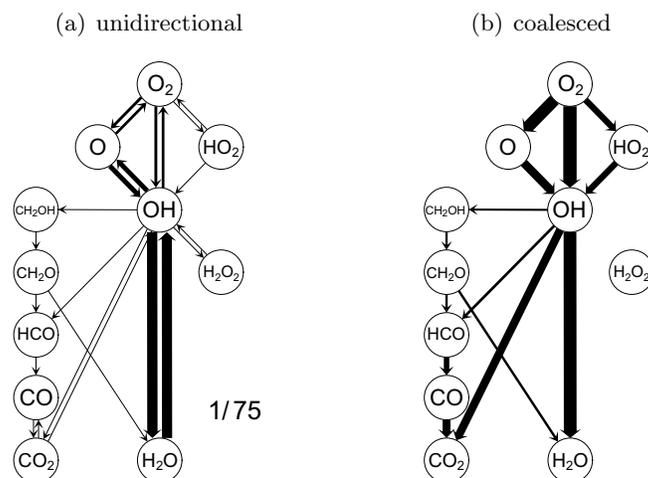
Figure 2: *Oxygen reaction path diagrams (a) based on the unidirectional halves of each reversible reaction, and (b) with only the net direction shown. Figure (a) is drawn to 1/75 the scale of the other; its thickest path is* OH → H$_2$O *at 1.28e-02 (mol/s). The thickest net path in (b) is* O$_2$ → OH *at 2.21e-4 (mol/s). Only arrows at least 10% of the thickest net path are shown.*

paths. These figures reveal the interesting facts that the bulk of the oxygen passes through the OH radical, which is the immediate carbon-less precursor for the oxygen in the carbon-bearing species.

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