# Sensitivity Construction: Gas-Phase Combustion Kinetics

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## Contents

# Nomenclature

**Greek Symbols**

| | |
|---|---|
| $\alpha_{i,j}$ | third-body enhancement factor of species i in reaction j |
| $\nu_{i,j}^{p}$ | product stoichiometric coefficient of species i in reaction j |
| $\nu_{i,j}^{r}$ | reactant stoichiometric coefficient of species i in reaction j |
| $\nu_{i,j}$ | net stoichiometric coefficient of species i in reaction j |
| $\omega_i$ | Net mass rate of production of species i |
| $\rho$ | Mixture mass density |
| $\upsilon$ | Mixture specific volume |
| $\Xi_j$ | Sum of the stoichiometric coefficients of reaction j |
| $\xi_{f,j}$ | Sum of the 'forward' stoichiometric coefficients of reaction j |
| $\xi_{r,j}$ | Sum of the 'reverse' stoichiometric coefficients of reaction j |

**Roman Symbols**

| | |
|---|---|
| $\langle c_i \rangle$ | Molar concentration of species i |
| $\langle c \rangle$ | Mixture molar concentration |
| $\rho_i$ | Molar density of species i |
| $\mathscr{C}_j$ | TBAF (**t**hird-**b**ody **a**nd **f**alloff) component of rate of progress $q_j$ |
| $\mathscr{F}_j$ | Falloff factor of reaction j |
| $\mathscr{R}_j$ | Mass action component of rate of progress $q_j$ |
| $Q$ | Pressure-temperature primitive state vector |
| $u$ | Conserved state vector |
| $V$ | Density-temperature primitive state vector |
| $W$ | Density-pressure primitive state vector |
| $A_j$ | Pre-exponential factor of reaction j |
| $b_j$ | Temperature exponent of reaction j |
| $c_p$ | Specific heat capacity at constant pressure of the mixture |
| $c_v$ | Specific heat capacity at constant volume of the mixture |
| $c_{p_i}$ | Specific heat capacity at constant pressure of species i |
| $c_{TB,j}$ | Third-body-enhanced concentration of reaction j |
| $e$ | Mixture specific internal energy |
| $e_i$ | Specific internal energy of species i |

2

| | |
|---|---|
| $E_{a,j}$ | Activation energy of reaction $j$ |
| $h$ | Mixture specific enthalpy |
| $h_i$ | Specific enthalpy of species $i$ |
| $h_{f,i}^\circ$ | Specific enthalpy of formation of species $i$ at a standard state $T^\circ, p^\circ$ |
| $K_{c,j}$ | Equilibrium constant of reaction $j$ |
| $k_{f,j}$ | Forward reaction rate constant of reaction $j$ |
| $k_{r,j}$ | Reverse reaction rate constant of reaction $j$ |
| $M_{mix}$ | Mixture molar mass |
| $M_i$ | Molar mass of species $i$ |
| $n_r$ | Number of elementary reactions |
| $n_s$ | Number of chemical species |
| $p$ | Pressure |
| $p_{fr,j}$ | Falloff reduced pressure of reaction $j$ |
| $q_j$ | Rate of progress of reaction $j$ |
| $R_{mix}$ | Mixture (specific) gas constant |
| $R_u$ | Universal (molar) gas constant |
| $T$ | Temperature |
| $X_i$ | Mole fraction of species $i$ |
| $Y_i$ | Mass fraction of species $i$ |

# 1 Ideal Gas Mixtures

The *pressure* $p$, *temperature* $T$, and *mixture mass density* $\rho$ are related to the chemical composition of an ideal gas mixture composed $n_s$ species through the *ideal gas law* (IGL),

$$p = \rho R_{\text{mix}} T, \tag{1}$$

where $R_{\text{mix}} \equiv R_u / M_{\text{mix}}$ is the *mixture gas constant*, which depends upon the *universal gas constant* $R_u$ and the *mixture molecular mass* $M_{\text{mix}}$. The mixture molecular mass is computed from the molar masses of each species, $M_i$, through the *mole fractions*, $X_i$, as $M_{\text{mix}} = \sum_{i=1}^{n_s} X_i M_i$. This is related to the *mass fractions* $Y_i$ through

$$M_{\text{mix}} = \sum_{i=1}^{n_s} X_i M_i = \left[ \sum_{i=1}^{n_s} \frac{Y_i}{M_i} \right]^{-1}. \tag{2}$$

The $n_s$ mass and mole fractions are not independent - they are related through $\sum_{i=1}^{n_s} X_i = \sum_{i=1}^{n_s} Y_i = 1$.

Equation 1 can be expressed in many different ways. We might replace the density with the *mixture molar concentration* $\langle c \rangle = \rho / M_{\text{mix}}$ or the *mixture specific volume* $\upsilon = 1/\rho$, giving us the following set of equivalent expressions of the IGL, two of which are further simplified by substituting (2) for the mixture molar mass.

$$
\begin{aligned}
p &= \rho R_{\text{mix}} T = \rho R_u T \sum_{i=1}^{n_s} \frac{Y_i}{M_i}, \\
p\upsilon &= R_{\text{mix}} T = R_u T \sum_{i=1}^{n_s} \frac{Y_i}{M_i}, \\
p &= \langle c \rangle R_u T.
\end{aligned}
\tag{3}
$$

The *species mass density*, $\rho_i = \rho Y_i$, and *species molar concentration* $\langle c_i \rangle = \langle c \rangle X_i$, can be used in this expression with $\rho = \sum_{i=1}^{n_s} \rho_i$ and $\langle c \rangle = \sum_{i=1}^{n_s} \langle c_i \rangle$.

The specific enthalpy $h_i$ of an ideal gas species $i$ is decomposed into chemical and sensible components, respectively,

$$h_i = h_{f,i}^\circ + \int_{T^\circ}^T c_{p,i}(\xi) d\xi, \tag{4}$$

where $h_{f,i}^\circ$ is the specific heat of formation of species $i$ at standard temperature $T^\circ$ and pressure $p^\circ$, and $c_{p,i}$ is the specific heat capacity of species $i$ at constant pressure. The sensible enthalpy is exactly zero at standard conditions. The specific enthalpy of an ideal gas solution is

$$h = \sum_{i=1}^{n_s} Y_i h_i = \sum_{i=1}^{n_s} Y_i h_{f,i}^\circ + \int_{T^\circ}^T c_p(\xi) d\xi, \tag{5}$$

where the mixture specific heat capacity at constant pressure is $c_p = \sum_{i=1}^{n_s} Y_i c_{p,i}$.

The specific internal energy $e_i$ of an ideal gas species $i$ is decomposed similarly. The chemical energy of $i$ is identical to its chemical enthalpy, the heat of formation at STP. However the sensible energy is modified to account for the fact that $e_i = h_i - p/\rho_i$. Thus, while the sensible enthalpy is zero at STP the sensible energy is not. Internal nergy of species $i$ is

$$e_i = h_i - \frac{p}{\rho_i} = h_i - \frac{R_u T}{M_i} = h_{f,i}^\circ + \int_{T^\circ}^T c_{p,i}(\xi) d\xi - \frac{R_u T}{M_i}. \tag{6}$$

For the entire mixture, the internal energy is

$$
\begin{aligned}
e &= \sum_{i=1}^{n_s} Y_i e_i, \\
&= \sum_{i=1}^{n_s} Y_i \left( h_{f,i}^\circ - \frac{R_u T}{M_i} \right) + \int_{T^\circ}^{T} c_p(\xi) d\xi, \\
&= \sum_{i=1}^{n_s} Y_i h_{f,i}^\circ + \int_{T^\circ}^{T} c_p(\xi) d\xi - R_{mix} T, \\
&= \sum_{i=1}^{n_s} Y_i h_{f,i}^\circ + \int_{T^\circ}^{T} c_v(\xi) d\xi - R_{mix} T^\circ.
\end{aligned}
\tag{7}
$$

in which $c_v$ is the mixture's specific heat capacity at constant volume.

## 2 Choosing a Complete, Independent Thermochemical State Representation

To obtain an independent thermochemical state representation, we must carefully choose $n_s - 1$ specifications of the chemical composition and two specifications of bulk mixture quantities. Composition is fixed independently by choosing $n_s - 1$ mole fractions $X_i$, mass fractions $Y_i$, molar concentrations $c_i$, or mass densities $\rho_i$. One cannot independently set all $n_s$ mole/mass fractions because the final fraction is specified by the first $n_s - 1$. Common pairs of the remaining two specifications are: $(\rho, \rho e)$, $(\rho, T)$, $(\rho, p)$, and $(p, T)$. Entropy shows up on occasion.

One must be careful that the thermodynamic state is specified fully. Some examples follow, along with the definition of important state vectors.

**The conserved state variables** The conserved state variables are the following set of volumetric quantities: $(\rho, \rho e, \rho Y_1, \ldots, \rho Y_{n_s - 1})$. This set fully specifies the thermochemical state and allows calculation of all thermodynamic properties. The temperature is computed with $e = \rho e / \rho$, $Y_i = \rho Y_i / \rho$, and the pressure follows. Enthalpy, entropy, free energy, etc. can be computed afterwards. A negative aspect of the conserved state variables is that the temperature solve is iterative because (7) includes temperature as the upper limit on the integral and the heat capacity is typically a polynomial expression of $T$. In addition it is often difficult to compute the sensitivity of functions over the thermochemical state space with respect to the conserved variables.

The conserved state vector is

$$
\mathbf{U} \equiv \begin{pmatrix} \rho \\ \rho e \\ \rho Y_1 \\ \vdots \\ \rho Y_{n_s - 1} \end{pmatrix}.
\tag{8}
$$

**'Primitive' state variables** For the purpose of computing sensitivities to thermochemical state variables it is more convenient to use various 'primitive' state vectors. Such state specifications use $Y_i$ in place of $\rho Y_i$ and use two of pressure, density, and temperature. The three relevant primitive state vectors of

interest here are

$$
\mathbf{V} \equiv \begin{pmatrix} \rho \\ T \\ Y_1 \\ \vdots \\ Y_{n_s-1} \end{pmatrix}, \quad
\mathbf{W} \equiv \begin{pmatrix} \rho \\ p \\ Y_1 \\ \vdots \\ Y_{n_s-1} \end{pmatrix}, \quad
\mathbf{Q} \equiv \begin{pmatrix} p \\ T \\ Y_1 \\ \vdots \\ Y_{n_s-1} \end{pmatrix}.
\tag{9}
$$

**Bad state vector and a surprising fix**   Suppose one wanted to represent the state of a reactor with $(e, h, Y_1, \ldots, Y_{n_s-1})$. This is a problem because the internal energy and enthalpy are only functions of temperature and composition. By specifying composition and $h$ *or* $e$ we can find the temperature, which then specifies the remaining $e$ or $h$. And the result of this set providing an incomplete specification is that we cannot find density or pressure.

A surprising fix to this state representation is to use $\rho e$ instead of $e$ (or the same with the enthalpy instead). Then we can use $h$ and the composition to find the temperature and $e$. Because we specify $\rho e$, however, instead of $e$ alone, we capture the additional dimension and fully specify the state. Calculation of $e$ gives $\rho$, which then allows calculation of pressure.

## 3   Heat Capacity Evaluation

Heat capacity variation with temperature can be expressed in many ways, here we show four common methods. These expressions are valid at the standard state pressure, typically one atmosphere or one bar. The $B_i = -\ln(T) + \frac{M_i}{R_u}\left(s_i - \frac{h_i}{T}\right)$ expressions are included for reference in later sections.

The seven-coefficient NASA polynomial form gives the following expressions for the specific heat capacity at constant pressure, specific enthalpy, and specific entropy of pure species $i$.

**NASA-7**

$$
\begin{aligned}
c_{p,i} &= \frac{R_u}{M_i}\left(a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4\right), \\
\frac{\partial c_{p,i}}{\partial T} &= \frac{R_u}{M_i}\left(a_1 + 2a_2 T + 3a_3 T^2 + 4a_4 T\right), \\
h_i &= \frac{R_u}{M_i}\left(a_0 T + \frac{a_1}{2}T^2 + \frac{a_2}{3}T^3 + \frac{a_3}{4}T^4 + \frac{a_4}{5}T^5 + a_5\right), \\
s_i &= \frac{R_u}{M_i}\left(a_0 \ln(T) + a_1 T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + a_6\right), \\
\frac{h_i}{T} &= \frac{R_u}{M_i}\left(a_0 + \frac{a_1}{2}T + \frac{a_2}{3}T^2 + \frac{a_3}{4}T^3 + \frac{a_4}{5}T^4 + a_5 T^{-1}\right), \\
s_i - \frac{h_i}{T} &= \frac{R_u}{M_i}\left(a_0(\ln(T) - 1) + \frac{a_1}{2}T + \frac{a_2}{6}T^2 + \frac{a_3}{12}T^3 + \frac{a_4}{20}T^4 - a_5 T^{-1} + a_6\right), \\
B_i &= -a_0 + (a_0 - 1)\ln(T) + \frac{a_1}{2}T + \frac{a_2}{6}T^2 + \frac{a_3}{12}T^3 + \frac{a_4}{20}T^4 - a_5 T^{-1} + a_6, \\
\frac{dB_i}{dT} &= (a_0 - 1)T^{-1} + \frac{a_1}{2} + \frac{a_2}{3}T + \frac{a_3}{4}T^2 + \frac{a_4}{5}T^3 + a_5 T^{-2}.
\end{aligned}
\tag{10}
$$

The NASA-9 polynomials take the following forms.

**NASA-9**

$$c_{p,i} = \frac{R_u}{M_i}\left(a_0 T^{-2} + a_1 T^{-1} + a_2 + a_3 T + a_4 T^2 + a_5 T^3 + a_6 T^4\right),$$

$$\frac{\partial c_{p,i}}{\partial T} = \frac{R_u}{M_i}\left(-2a_0 T^{-3} - a_1 T^{-2} + a_3 + 2a_4 T + 3a_5 T^2 + 4a_6 T^3\right),$$

$$h_i = \frac{R_u}{M_i}\left(-a_0 T^{-1} + a_1 \ln(T) + a_2 T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4 + \frac{a_6}{5}T^5 + a_7\right),$$

$$s_i = \frac{R_u}{M_i}\left(-\frac{a_0}{2}T^{-2} - a_1 T^{-1} + a_2 \ln(T) + a_3 T + \frac{a_4}{2}T^2 + \frac{a_5}{3}T^3 + \frac{a_6}{4}T^4 + a_8\right),$$

$$\frac{h_i}{T} = \frac{R_u}{M_i}\left(-a_0 T^{-2} + a_1 \frac{\ln(T)}{T} + a_2 + \frac{a_3}{2}T + \frac{a_4}{3}T^2 + \frac{a_5}{4}T^3 + \frac{a_6}{5}T^4 + a_7 T^{-1}\right),$$

$$s_i - \frac{h_i}{T} = \frac{R_u}{M_i}\left(\frac{a_0}{2}T^{-2} + \ln(T)\left(a_2 - \frac{a_1}{T}\right) - a_2 + a_8 + \frac{a_7 - a_1}{T} + \frac{a_3}{2}T + \frac{a_4}{6}T^2 + \frac{a_5}{12}T^3 + \frac{a_6}{20}T^4\right),$$

$$B_i = \frac{a_0}{2}T^{-2} + \ln(T)\left(a_2 - \frac{a_1}{T} - 1\right) - a_2 + a_8 + \frac{a_7 - a_1}{T} + \frac{a_3}{2}T + \frac{a_4}{6}T^2 + \frac{a_5}{12}T^3 + \frac{a_6}{20}T^4,$$

$$\frac{dB_i}{dT} = -a_0 T^{-3} + \frac{a_2 - 1}{T} + \frac{a_1 \ln(T) - a_7}{T^2} + \frac{a_3}{2} + \frac{a_4}{3}T + \frac{a_5}{4}T^2 + \frac{a_6}{5}T^3.$$

(11)

Finally if a constant heat capacity is specified the relevant expressions are

**Constant $c_p$**

$$c_{p,i} = c_{p,i}^\circ,$$

$$\frac{\partial c_{p,i}}{\partial T} = 0,$$

$$h_i = h_i^\circ + c_{p,i}^\circ(T - T^\circ),$$

$$s_i = s_i^\circ + c_{p,i}^\circ \ln\left(\frac{T}{T^\circ}\right),$$

$$\frac{h_i}{T} = h_i^\circ T^{-1} + c_{p,i}^\circ - c_{p,i}^\circ T^\circ T^{-1},$$

$$s_i - \frac{h_i}{T} = s_i^\circ + c_{p,i}^\circ \ln\left(\frac{T}{T^\circ}\right) + (c_{p,i}^\circ T^\circ - h_i^\circ)T^{-1} - c_{p,i}^\circ,$$

$$B_i = -\ln(T) + \frac{M_i}{R_u}\left(s_i^\circ + c_{p,i}^\circ \ln\left(\frac{T}{T^\circ}\right) + (c_{p,i}^\circ T^\circ - h_i^\circ)T^{-1} - c_{p,i}^\circ\right),$$

$$\frac{dB_i}{dT} = -\frac{1}{T} + \frac{M_i}{R_u T}\left(c_{p,i}^\circ - \frac{c_{p,i}^\circ T^\circ - h_i^\circ}{T}\right).$$

(12)

## 4 Reaction Rates

Here we consider the various forms of reaction rate expressions for homogeneous gas-phase systems. Let $n_s$ and $n_r$ be the number of species and elementary reactions, respectively. The *net mass rate of production* of species $i$, denoted $\omega_i$, is

$$\omega_i = M_i \sum_{j=1}^{n_r} \nu_{i,j} q_j,$$

(13)

where $\nu_{i,j}$ is the *net stoichiometric coefficient* of species $i$ in reaction $j$ and $q_j$ is the *rate of progress* of reaction $j$.

The rate of progress $q_j$ is decomposed into two parts: first, the *mass action component $\mathcal{R}_j$*, and second, the *TBAF component $\mathcal{C}_j$* which contains **t**hird-**b**ody **a**nd **f**alloff effects.

$$q_j = \overset{\text{mass action}}{\mathcal{R}_j} \cdot \overset{\text{3-body + falloff}}{\mathcal{C}_j} . \tag{14}$$

The mass action component consists of *forward* and *reverse rate constants* $k_{f,j}$ and $k_{r,j}$ along with products of species concentrations $c_k$,

$$\mathcal{R}_j = k_{f,j} \prod_{k=1}^{n_s} \langle c_k \rangle^{\nu^f_{k,j}} - k_{r,j} \prod_{k=1}^{n_s} \langle c_k \rangle^{\nu^r_{k,j}} , \tag{15}$$

in which $\nu^f_{i,j}$ and $\nu^r_{i,j}$ are the *forward* and *reverse stoichiometric coefficients* of species $i$ in reaction $j$, respectively.

The forward rate constant is found with a modified Arrhenius expression,

$$k_{f,j} = A_j T^{b_j} \exp\left(-\frac{E_{a,j}}{R_u T}\right) = A_j T^{b_j} \exp\left(-\frac{T_{a,j}}{T}\right), \tag{16}$$

where $A_j$, $b_j$, and $E_{a,j}$ are the pre-exponential factor, temperature exponent, and activation energy of reaction $j$, respectively. $T_{a,j}$ is the 'activation temperature' defined as $E_{a,j}/R_u$. The reverse rate constant of an irreversible reaction is zero. The $k_{r,j}$ of a reversible reaction is found with the *equilibrium constant* $K_{c,j}$, via $k_{r,j} = k_{f,j}/K_{c,j}$. The equilibrium constant is

$$K_{c,j} = \left(\frac{p_{atm}}{R_u}\right)^{\Xi_j} \exp\left(\sum_{k=1}^{n_s} \nu_{k,j} B_k\right), \tag{17}$$

where $\Xi_j \equiv \sum_{k=1}^{n_s} \nu_{k,j}$ and $B_k$ is

$$B_k = -\ln(T) + \frac{M_k}{R_u}\left(s_k - \frac{h_k}{T}\right), \tag{18}$$

which is computed from the heat capacity polynomials. This form is given in §3 for the four types of heat capacity expressions.

The TBAF component $\mathcal{C}_j$ is not so straightforward. There has two nontrivial cases, (1) a three-body reaction and, (2) a unimolecular/recombination falloff reaction. If a reaction is not of a three-body or falloff type, then $\mathcal{C}_j = 1$. For three-body reactions, it is

$$\mathcal{C}_j = \langle c_{TB,j} \rangle = \sum_{i=1}^{n_s} \alpha_{i,j} \langle c_i \rangle, \tag{19}$$

where $\alpha_{i,j}$ is the *third-body enhancement factor* of species $i$ in reaction $j$, and $\langle c_{TB,j} \rangle$ is the *third-body-enhanced concentration* of reaction $j$. $\alpha_{i,j}$ defaults to 1.0 if not specified. For falloff reactions, the TBAF component is

$$\mathcal{C}_j = \frac{p_{fr,j}}{1 + p_{fr,j}} \mathcal{F}_j, \tag{20}$$

in which $p_{fr,j}$ and $\mathcal{F}_j$ are the *falloff reduced pressure* and *falloff blending factor* of reaction $j$, respectively. The falloff reduced pressure is

$$p_{fr,j} = \frac{k_{0,j}}{k_{f,j}} \mathcal{F}_{F,j}, \tag{21}$$

where $k_{0,j}$ is the low-pressure limit rate constant of reaction $j$, evaluated with low-pressure Arrhenius parameters $A_{0,j}$, $b_{0,j}$, $E_{a,0,j}$, and $\mathscr{T}_{F,j}$ is the 'concentration' of the mixture,

$$\mathscr{T}_{F,j} = \begin{cases} \langle c_\ell \rangle, & \text{species } \ell \text{ specified as third-body} \\ \langle c_{TB,j} \rangle, & \text{else} \end{cases}. \tag{22}$$

The falloff blending factor $\mathscr{F}_j$ depends upon the specified falloff form. For the Lindemann approach, $\mathscr{F}_j = 1$. In the Troe form,

$$
\begin{aligned}
\mathscr{F}_j &= \mathscr{F}_{\text{cent}}^{1/(1+(A/B)^2)}, \\
\mathscr{F}_{\text{cent}} &= (1 - a_{\text{Troe}}) \exp\left(-\frac{T}{T^{***}}\right) + a_{\text{Troe}} \exp\left(-\frac{T}{T^*}\right) + \exp\left(-\frac{T^{**}}{T}\right), \\
A &= \log_{10} p_{FR,j} - 0.67 \log_{10} \mathscr{F}_{\text{cent}} - 0.4, \\
B &= 0.806 - 1.1762 \log_{10} \mathscr{F}_{\text{cent}} - 0.14 \log_{10} p_{FR,j},
\end{aligned}
\tag{23}
$$

where $a_{\text{Troe}}$, $T^*$, $T^{**}$, and $T^{***}$ are specified parameters of the Troe form. If $T^{***}$ is unspecified then its term is ignored. Finally, in the SRI form,

$$
\begin{aligned}
\mathscr{F}_j &= dT^e \left(a \exp(-b/T) + \exp(-T/c)\right)^\chi, \\
\chi &= \left(1 + (\log_{10} p_{FR,j})^2\right)^{-1},
\end{aligned}
\tag{24}
$$

where $a, b, c, d, e$ are specified parameters of the SRI form, with defaults $d = 1$ and $e = 0$.

# 5 Sensitivities between State Variables

Before moving to the reaction rates we first consider sensitivities between state variables.

## 5.1 Mixture Molar Mass and Mole/Mass Fractions

Here we aim for the following two sensitivities:

$$\left.\frac{\partial M_{\text{mix}}}{\partial Y_j}\right|_{Y_{k \neq j, n_s}} \quad, \quad \left.\frac{\partial X_i}{\partial Y_j}\right|_{Y_{k \neq j, n_s}}. \tag{25}$$

Relevant expressions are

$$M_{\text{mix}}^{-1} = \sum_{i=1}^{n_s} \frac{Y_i}{M_i}, \quad X_i = Y_i \frac{M_{\text{mix}}}{M_i}. \tag{26}$$

First is the mixture molar mass. Start by computing the convenient derivative,

$$\left.\frac{\partial M_{\text{mix}}^{-1}}{\partial Y_j}\right|_{Y_{k \neq j, n_s}} = \sum_{i=1}^{n_s} \left.\frac{\partial}{\partial Y_j}\right|_{Y_{k \neq j, n_s}} \left(\frac{Y_i}{M_i}\right) = \frac{1}{M_j} - \frac{1}{M_{n_s}}. \tag{27}$$

Next we use the following identity,

$$\frac{\partial f^{-1}}{\partial x} = -f^{-2} \frac{\partial f}{\partial x} \implies \frac{\partial f}{\partial x} = -f^2 \frac{\partial f^{-1}}{\partial x}, \tag{28}$$

to obtain

$$\left.\frac{\partial M_{\text{mix}}}{\partial Y_j}\right|_{Y_{k \neq j, n_s}} = -M_{\text{mix}}^2 \left(\frac{1}{M_j} - \frac{1}{M_{n_s}}\right). \tag{29}$$

9

Now we can do the mole fraction:

$$
\begin{aligned}
\left.\frac{\partial X_i}{\partial Y_j}\right|_{Y_{k \neq j, n_s}} &= \left.\frac{\partial}{\partial Y_j}\right|_{Y_{k \neq j, n_s}} Y_i \frac{M_{mix}}{M_i}, \\
&= \left.\frac{M_{mix}}{M_i} \frac{\partial Y_i}{\partial Y_j}\right|_{Y_{k \neq j, n_s}} + \left.\frac{Y_i}{M_i} \frac{\partial M_{mix}}{\partial Y_j}\right|_{Y_{k \neq j, n_s}}, \\
&= \frac{M_{mix}}{M_i} \left[ (\delta_{i,j} - \delta_{i,n_s}) - Y_i M_{mix} \left( \frac{1}{M_j} - \frac{1}{M_{n_s}} \right) \right].
\end{aligned}
\tag{30}
$$

## 5.2 Molar Concentrations

Here we want sensitivities of molar concentrations (of the mixture and of individual species) to the density, pressure, temperature, and mass fractions.

### 5.2.1 Species Concentration

The molar concentration of species $j$ is

$$
\langle c_j \rangle = \frac{\rho Y_j}{M_j} = \frac{p Y_j M_{mix}}{R_u T M_j}.
\tag{31}
$$

Now we consider the density-temperature primitives $\mathbf{V}$,

$$
\frac{\partial \langle c_j \rangle}{\partial \mathbf{V}} = \left( \left.\frac{\partial \langle c_j \rangle}{\partial \rho}\right|_{T,\{Y\}} \quad \left.\frac{\partial \langle c_j \rangle}{\partial T}\right|_{\rho,\{Y\}} \quad \left.\frac{\partial \langle c_j \rangle}{\partial Y_1}\right|_{\rho,T,Y_{k \neq 1, n_s}} \quad \cdots \quad \left.\frac{\partial \langle c_j \rangle}{\partial Y_{n_s-1}}\right|_{\rho,T,Y_{k \neq n_s-1, n_s}} \right).
\tag{32}
$$

$$
\left.\frac{\partial \langle c_j \rangle}{\partial \rho}\right|_{T,\{Y\}} = \left.\frac{\partial}{\partial \rho}\right|_{T,\{Y\}} \frac{\rho Y_j}{M_j} = \frac{Y_j}{M_j},
\tag{33}
$$

$$
\left.\frac{\partial \langle c_j \rangle}{\partial T}\right|_{\rho,\{Y\}} = \left.\frac{\partial}{\partial T}\right|_{\rho,\{Y\}} \frac{\rho Y_j}{M_j} = 0,
\tag{34}
$$

$$
\left.\frac{\partial \langle c_j \rangle}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k, n_s}} = \left.\frac{\partial}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k, n_s}} \frac{\rho Y_j}{M_j} = \frac{\rho}{M_j} \left.\frac{\partial Y_j}{\partial Y_k}\right|_{Y_{\ell \neq k, n_s}} = \frac{\rho}{M_j} (\delta_{j,k} - \delta_{j,n_s}).
\tag{35}
$$

This last one can also be written as

$$
\left.\frac{\partial \langle c_j \rangle}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k, n_s}} = \frac{\rho}{M_j} \cdot
\begin{cases}
+1 & , k = j \\
-1 & , \forall k : j = n_s \\
0 & , k \neq j, j \neq n_s
\end{cases}.
\tag{36}
$$

### 5.2.2 Mixture Concentration

The mixture molar concentration is

$$
\langle c \rangle = \frac{\rho}{M_{mix}} = \rho \sum_{i=1}^{n_s} \frac{Y_i}{M_i}.
\tag{37}
$$

For the density-temperature primitives $\mathbf{V}$,

$$
\frac{\partial \langle c \rangle}{\partial \mathbf{V}} = \left( \left.\frac{\partial \langle c \rangle}{\partial \rho}\right|_{T,\{Y\}} \quad \left.\frac{\partial \langle c \rangle}{\partial T}\right|_{\rho,\{Y\}} \quad \left.\frac{\partial \langle c \rangle}{\partial Y_1}\right|_{\rho,T,Y_{k \neq 1, n_s}} \quad \cdots \quad \left.\frac{\partial \langle c \rangle}{\partial Y_{n_s-1}}\right|_{\rho,T,Y_{k \neq n_s-1, n_s}} \right).
\tag{38}
$$

$$
\left.\frac{\partial \langle c \rangle}{\partial \rho}\right|_{T,\{Y\}} = \left.\frac{\partial}{\partial \rho}\right|_{T,\{Y\}} \frac{\rho}{M_{mix}} = \frac{1}{M_{mix}},
\tag{39}
$$

$$\left.\frac{\partial \langle c \rangle}{\partial T}\right|_{\rho,\{Y\}} = \left.\frac{\partial}{\partial T}\right|_{\rho,\{Y\}} \frac{\rho}{M_{\text{mix}}} = 0, \tag{40}$$

$$\left.\frac{\partial \langle c \rangle}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k,n_s}} = \left.\frac{\partial}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k,n_s}} \rho \sum_{i=1}^{n_s} \frac{Y_i}{M_i} = \rho \left(\frac{1}{M_k} - \frac{1}{M_{n_s}}\right). \tag{41}$$

## 5.3 Why density-temperature-mass primitives?

Before moving on we note that the primitive state $V = (\rho, T, \{Y\})^{\intercal}$ is likely the most efficient choice for deriving sensitivities of reaction rate expressions. Temperature is practically necessary as it fixes rate constant and equilibrium constant expressions whenever $T$ is held constant during partial differentiation. If we instead used pressure and density, for instance, then temperature would float and the rate constants would be sensitive to changes in *every* variable in the state vector! Mass fractions are not quite as convenient as mole fractions when computing sensitivities of molar concentrations, but the widespread usage of mass fractions in simulation codes means we would need an expensive dense matrix transformation to appropriately convert sensitivities derived with mole fractions. And finally the species concentration derived above shows that density is *far* more convenient than pressure. If the pressure is held constant in (35) then the density varies when *any* mass fraction is changed (unless the species has the same molar mass as the $n_s$-th species), resulting in dense coupling between the species concentrations and species mass fractions. As shown above, however, using the density gives a very sparse coupling, with each mass fraction impacting only two species concentrations, its own and the $n_s$-th species'.

# 6 Sensitivities of the Production & Reaction Rates

Here we derive the sensitivity of each rate of progress $q_j$ and the species production rates $\omega_i$ to the density-temperature primitive state vector, $V$. The production rates are straightforward given the reaction rates,

$$\left.\frac{\partial \omega_i}{\partial V_k}\right|_{V_{j \neq k}} = M_i \sum_{j=1}^{n_r} \nu_{i,j} \left.\frac{\partial q_j}{\partial V_k}\right|_{V_{j \neq k}}. \tag{42}$$

For the reaction rates, first we use the product rule to split the mass action and three-body and falloff terms, which we then deal with separately.

$$\left.\frac{\partial q_j}{\partial V_k}\right|_{V_{\ell \neq k}} = \mathscr{C}_j \left.\frac{\partial \mathscr{R}_j}{\partial V_k}\right|_{V_{\ell \neq k}} + \mathscr{R}_j \left.\frac{\partial \mathscr{C}_j}{\partial V_k}\right|_{V_{\ell \neq k}}. \tag{43}$$

## 6.1 Mass Action Component

This section derives

$$\frac{\partial \mathscr{R}_j}{\partial V} = \left(\left.\frac{\partial \mathscr{R}_j}{\partial \rho}\right|_{T,\{Y\}} \quad \left.\frac{\partial \mathscr{R}_j}{\partial T}\right|_{\rho,\{Y\}} \quad \left.\frac{\partial \mathscr{R}_j}{\partial Y_1}\right|_{\rho,T,Y_{k \neq 1,n_s}} \quad \cdots \quad \left.\frac{\partial \mathscr{R}_j}{\partial Y_{n_s-1}}\right|_{\rho,T,Y_{k \neq n_s-1,n_s}}\right). \tag{44}$$

First we split the mass action term into forward and reverse terms.

$$\mathscr{R}_j = \mathscr{R}_{f,j} - \mathscr{R}_{r,j},$$
$$\mathscr{R}_{f,j} = k_{f,j} \prod_{k=1}^{n_s} \langle c_k \rangle^{\nu_{k,j}^f},$$
$$\mathscr{R}_{r,j} = k_{r,j} \prod_{k=1}^{n_s} \langle c_k \rangle^{\nu_{k,j}^r}. \tag{45}$$

11

Now for the forward term. This should be simplified for quick evaluation in several common cases, wherein only three species A, B, and C are involved, to avoid a for-loop in the product:

$$
\begin{aligned}
\text{ONE:} \quad & \mathscr{R}_{f,j} = k_{f,j} \langle c_A \rangle, \\
\text{TWO:} \quad & \mathscr{R}_{f,j} = k_{f,j} \langle c_A \rangle^2, \\
\text{ONE\_ONE:} \quad & \mathscr{R}_{f,j} = k_{f,j} \langle c_A \rangle \langle c_B \rangle, \\
\text{ONE\_ONE\_ONE:} \quad & \mathscr{R}_{f,j} = k_{f,j} \langle c_A \rangle \langle c_B \rangle \langle c_C \rangle, \\
\text{TWO\_ONE:} \quad & \mathscr{R}_{f,j} = k_{f,j} \langle c_A \rangle^2 \langle c_B \rangle, \\
\text{ONE\_TWO:} \quad & \mathscr{R}_{f,j} = k_{f,j} \langle c_A \rangle \langle c_B \rangle^2, \\
\text{GENERAL:} \quad & \mathscr{R}_{f,j} = k_{f,j} \prod_{k=1}^{n_s} \langle c_k \rangle^{\nu_{k,j}^f}.
\end{aligned}
\tag{46}
$$

For the density sensitivity we start by writing the forward term as

$$
\mathscr{R}_{f,j} = k_{f,j} \prod_{k=1}^{n_s} \langle c_k \rangle^{\nu_{k,j}^f} = k_{f,j} \langle c \rangle^{\xi_{f,j}} \prod_{k=1}^{n_s} X_k^{\nu_{k,j}^f},
\tag{47}
$$

where $\xi_{f,j} = \sum_{i=1}^{n_s} \nu_{i,j}^f$ is the sum of all forward stoichiometric coefficients. The density sensitivity is then

$$
\left. \frac{\partial \mathscr{R}_{f,j}}{\partial \rho} \right|_{T,\{Y\}} = k_{f,j} \left. \frac{\partial \langle c \rangle^{\xi_{f,j}}}{\partial \rho} \right|_{T,\{Y\}} \prod_{k=1}^{n_s} X_k^{\nu_{k,j}^f} = k_{f,j} \frac{\xi_{f,j} \langle c \rangle^{\xi_{f,j}-1}}{M_{mix}} \prod_{k=1}^{n_s} X_k^{\nu_{k,j}^f},
\tag{48}
$$

which simplifies to

$$
\left. \frac{\partial \mathscr{R}_{f,j}}{\partial \rho} \right|_{T,\{Y\}} = \frac{\xi_{f,j}}{\langle c \rangle M_{mix}} \mathscr{R}_{f,j}.
\tag{49}
$$

The temperature sensitivity is simple because we fix the composition and density. Only the rate constant remains sensitive to temperature:

$$
\left. \frac{\partial \mathscr{R}_{f,j}}{\partial T} \right|_{\rho,\{Y\}} = \left. \frac{\partial k_{f,j}}{\partial T} \right|_{\rho,\{Y\}} \langle c \rangle^{\xi_{f,j}} \prod_{k=1}^{n_s} X_k^{\nu_{k,j}^f},
\tag{50}
$$

The modified Arrhenius rate constant has sensitivity

$$
\left. \frac{\partial k_{f,j}}{\partial T} \right|_{\rho,\{Y\}} = \frac{k_{f,j}}{T} \left( b_j + \frac{T_{a,j}}{T} \right),
\tag{51}
$$

and so $\mathscr{R}_{f,j}$ has

$$
\left. \frac{\partial \mathscr{R}_{f,j}}{\partial T} \right|_{\rho,\{Y\}} = \frac{\mathscr{R}_{f,j}}{T} \left( b_j + \frac{T_{a,j}}{T} \right).
\tag{52}
$$

For the mass fraction sensitivities of $\mathscr{R}_{f,j}$ we will present results for the various simplifications given in (46). First, define the following shorthand:

$$
\text{dcAdY}\ell = \begin{cases} +1 & , \text{index}(A) = \ell \\ -1 & , \forall \ell : \text{index}(A) = n_s \\ 0 & , \text{index}(A) \neq \ell, \text{index}(A) \neq n_s \end{cases}.
\tag{53}
$$

Now we give the simplified and general form sensitivities:

$$
\text{ONE:} \quad \left. \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell} \right|_{\rho,T,Y_{k \neq \ell,n_s}} = k_{f,j} \left. \frac{\partial \langle c_A \rangle}{\partial Y_\ell} \right|_{\rho,T,Y_{k \neq \ell,n_s}} = k_{f,j} \frac{\rho}{M_A} \text{dcAdY}\ell.
\tag{54}
$$

12

$$\text{TWO:} \quad \left.\frac{\partial \mathcal{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = 2\left\langle c_A\right\rangle k_{f,j} \frac{\rho}{M_A} \text{dcAdY}\ell. \tag{55}$$

$$\text{ONE\_ONE:} \quad \left.\frac{\partial \mathcal{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \frac{\rho}{M_A}\left\langle c_B\right\rangle \text{dcAdY}\ell + \frac{\rho}{M_B}\left\langle c_A\right\rangle \text{dcBdY}\ell. \tag{56}$$

$$\text{ONE\_ONE\_ONE:} \quad \left.\frac{\partial \mathcal{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \frac{\rho}{M_A}\left\langle c_B\right\rangle\left\langle c_C\right\rangle \text{dcAdY}\ell + \frac{\rho}{M_B}\left\langle c_A\right\rangle\left\langle c_C\right\rangle \text{dcBdY}\ell + \frac{\rho}{M_C}\left\langle c_A\right\rangle\left\langle c_B\right\rangle \text{dcCdY}\ell. \tag{57}$$

$$\text{TWO\_ONE:} \quad \left.\frac{\partial \mathcal{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = 2\frac{\rho}{M_A}\left\langle c_A\right\rangle\left\langle c_B\right\rangle \text{dcAdY}\ell + \frac{\rho}{M_B}\left\langle c_A\right\rangle^2 \text{dcBdY}\ell. \tag{58}$$

$$\text{ONE\_TWO:} \quad \left.\frac{\partial \mathcal{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \frac{\rho}{M_A}\left\langle c_B\right\rangle^2 \text{dcAdY}\ell + 2\frac{\rho}{M_B}\left\langle c_A\right\rangle\left\langle c_B\right\rangle \text{dcBdY}\ell. \tag{59}$$

$$\text{GENERAL:} \quad \left.\frac{\partial \mathcal{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = k_{f,j} \cdot \left( \nu_{1,j}^f \frac{\rho}{M_1} \text{dc1dY}\ell \left\langle c_1\right\rangle^{\nu_{1,j}^f - 1} \prod_{k=2}^{n_s} \left\langle c_k\right\rangle^{\nu_{k,j}^f} + \right.$$
$$\nu_{2,j}^f \frac{\rho}{M_2} \text{dc2dY}\ell \left\langle c_2\right\rangle^{\nu_{2,j}^f - 1} \prod_{k=1\neq 2}^{n_s} \left\langle c_k\right\rangle^{\nu_{k,j}^f} + \tag{60}$$
$$\vdots$$
$$\left. \nu_{n_s,j}^f \frac{\rho}{M_{n_s}} \text{dc} n_s \text{dY}\ell \left\langle c_{n_s}\right\rangle^{\nu_{n_s,j}^f - 1} \prod_{k=1}^{n_s-1} \left\langle c_k\right\rangle^{\nu_{k,j}^f} \right)$$

The above sensitivities are a bit tricky to compute efficiently. In the case that no reactant is the $n_s$-th species, then only a single term survives the partial differentiation with respect to $Y_\ell$. But if the $n_s$-th species is a reactant, then there will be an additional term. And the $n_s$-th species concentration is sensitive to all species mass fractions, so this additional term influences every other species. For example, the ONE_ONE case with index$(A) = n_s$ and index$(B) \neq n_s$ has sensitivity to $Y_\ell$,

$$\left.\frac{\partial}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} (k_{f,j}\left\langle c_A\right\rangle\left\langle c_B\right\rangle) = k_f\left\langle c_B\right\rangle \frac{\rho}{M_A} \left.\frac{\partial Y_A}{\partial Y_\ell}\right|_{Y_{k\neq\ell,n_s}} + k_f\left\langle c_A\right\rangle \frac{\rho}{M_B} \left.\frac{\partial Y_B}{\partial Y_\ell}\right|_{Y_{k\neq\ell,n_s}},$$
$$= -k_f\left\langle c_B\right\rangle \frac{\rho}{M_A} + k_f\left\langle c_A\right\rangle \frac{\rho}{M_B} \left.\frac{\partial Y_B}{\partial Y_\ell}\right|_{Y_{k\neq\ell,n_s}}, \tag{61}$$
$$= \begin{cases} -k_f\left\langle c_B\right\rangle \frac{\rho}{M_A} + k_f\left\langle c_A\right\rangle \frac{\rho}{M_B} & ,\ell = \text{index}(B), \\ -k_f\left\langle c_B\right\rangle \frac{\rho}{M_A} & ,\ell \neq \text{index}(B). \end{cases}$$

To compute sensitivities of $\mathcal{R}_{f,j}$ to mass fractions one can use a two-stage procedure to account for the $n_s$-th species being a reactant.

1. Calculate sensitivities of $\mathcal{R}_{f,j}$ to all reactant species mass fractions, ignoring the $n_s$-th species if it is a reactant.

2. If species $n_s$ is a reactant, then calculate the $n_s$ term such as $-k_f\left\langle c_B\right\rangle \frac{\rho}{M_A}$ in the above ONE_ONE example. Add this term to the already-computed $\partial \mathcal{R}_{f,j}/\partial Y_\ell$ terms for *all* species. This must be done for all species, not just all reactants.

### 6.1.1 Summary of Sensitivities of the Forward Reaction Rate

<div align="center">

**Sensitivities of $\mathscr{R}_{f,j}$ to $\rho$, $T$**

</div>

$$\left.\frac{\partial \mathscr{R}_{f,j}}{\partial \rho}\right|_{T,\{Y\}} = \frac{\xi_{f,j}}{\langle c \rangle \, M_{\text{mix}}} \mathscr{R}_{f,j}. \tag{62}$$

$$\left.\frac{\partial \mathscr{R}_{f,j}}{\partial T}\right|_{\rho,\{Y\}} = \frac{\mathscr{R}_{f,j}}{T}\left(b_j + \frac{T_{a,j}}{T}\right). \tag{63}$$

<div align="center">

*PART 1/2 of* sensitivities of $\mathscr{R}_{f,j}$ to $Y_\ell$, ignoring $n_s$ as reactant

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$$\text{ONE}: \quad \left.\frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \begin{cases} k_{f,j}\frac{\rho}{M_A}, & \ell = \text{index}(A), \\ 0, & \text{else}. \end{cases} \tag{64}$$

$$\text{TWO}: \quad \left.\frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \begin{cases} 2k_{f,j}\frac{\rho}{M_A}\langle c_A \rangle, & \ell = \text{index}(A), \\ 0, & \text{else}. \end{cases} \tag{65}$$

$$\text{ONE\_ONE}: \quad \left.\frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \begin{cases} k_{f,j}\frac{\rho}{M_A}\langle c_B \rangle, & \ell = \text{index}(A), \\ k_{f,j}\frac{\rho}{M_B}\langle c_A \rangle, & \ell = \text{index}(B), \\ 0, & \text{else}. \end{cases} \tag{66}$$

$$\text{ONE\_ONE\_ONE}: \quad \left.\frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \begin{cases} k_{f,j}\frac{\rho}{M_A}\langle c_B \rangle \langle c_C \rangle, & \ell = \text{index}(A), \\ k_{f,j}\frac{\rho}{M_B}\langle c_A \rangle \langle c_C \rangle, & \ell = \text{index}(B), \\ k_{f,j}\frac{\rho}{M_C}\langle c_A \rangle \langle c_B \rangle, & \ell = \text{index}(C), \\ 0, & \text{else}. \end{cases} \tag{67}$$

$$\text{TWO\_ONE}: \quad \left.\frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \begin{cases} 2k_{f,j}\frac{\rho}{M_A}\langle c_A \rangle \langle c_B \rangle, & \ell = \text{index}(A), \\ k_{f,j}\frac{\rho}{M_B}\langle c_A \rangle^2, & \ell = \text{index}(B), \\ 0, & \text{else}. \end{cases} \tag{68}$$

$$\text{ONE\_TWO}: \quad \left.\frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \begin{cases} k_{f,j}\frac{\rho}{M_A}\langle c_B \rangle^2, & \ell = \text{index}(A), \\ 2k_{f,j}\frac{\rho}{M_B}\langle c_A \rangle \langle c_B \rangle, & \ell = \text{index}(B), \\ 0, & \text{else}. \end{cases} \tag{69}$$

$$\text{GENERAL}: \quad \left.\frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\right|_{\rho,T,Y_{k\neq\ell,n_s}} = \nu_{\ell,j}^f \frac{\rho}{M_\ell}\langle c_\ell \rangle^{\nu_{\ell,j}^f - 1} \prod_{k=1,k\neq\ell}^{n_s} \langle c_k \rangle^{\nu_{k,j}^f} \tag{70}$$

Note that the $+ =$ indicates that we are adding the RHS to the LHS, not setting LHS = RHS. Also note that there are no conditions on $\ell$ here - the RHS addition is to occur for all species, $\ell \in [1, 2, \ldots, n_s - 1]$.

$$\texttt{ONE:} \quad \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} + = \begin{cases} -k_{f,j} \frac{\rho}{M_{n_s}}, & \text{index}(A) = n_s, \\ 0, & \text{else}. \end{cases} \tag{71}$$

$$\texttt{TWO:} \quad \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} + = \begin{cases} -2k_{f,j} \frac{\rho}{M_{n_s}} \langle c_{n_s} \rangle, & \text{index}(A) = n_s, \\ 0, & \text{else}. \end{cases} \tag{72}$$

$$\texttt{ONE\_ONE:} \quad \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} + = \begin{cases} k_{f,j} \frac{\rho}{M_{n_s}} \langle c_B \rangle, & \text{index}(A) = n_s, \\ k_{f,j} \frac{\rho}{M_{n_s}} \langle c_A \rangle, & \text{index}(B) = n_s, \\ 0, & \text{else}. \end{cases} \tag{73}$$

$$\texttt{ONE\_ONE\_ONE:} \quad \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} + = \begin{cases} -k_{f,j} \frac{\rho}{M_{n_s}} \langle c_B \rangle \langle c_C \rangle, & \text{index}(A) = n_s, \\ -k_{f,j} \frac{\rho}{M_{n_s}} \langle c_A \rangle \langle c_C \rangle, & \text{index}(B) = n_s, \\ -k_{f,j} \frac{\rho}{M_{n_s}} \langle c_A \rangle \langle c_B \rangle, & \text{index}(C) = n_s, \\ 0, & \text{else}. \end{cases} \tag{74}$$

$$\texttt{TWO\_ONE:} \quad \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} + = \begin{cases} -2k_{f,j} \frac{\rho}{M_{n_s}} \langle c_{n_s} \rangle \langle c_B \rangle, & \text{index}(A) = n_s, \\ -k_{f,j} \frac{\rho}{M_{n_s}} \langle c_A \rangle^2, & \text{index}(B) = n_s, \\ 0, & \text{else}. \end{cases} \tag{75}$$

$$\texttt{ONE\_TWO:} \quad \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} + = \begin{cases} -k_{f,j} \frac{\rho}{M_{n_s}} \langle c_B \rangle^2, & \text{index}(A) = n_s, \\ -2k_{f,j} \frac{\rho}{M_{n_s}} \langle c_A \rangle \langle c_{n_s} \rangle, & \text{index}(B) = n_s, \\ 0, & \text{else}. \end{cases} \tag{76}$$

$$\texttt{GENERAL:} \quad \frac{\partial \mathscr{R}_{f,j}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} + = -\nu^f_{n_s,j} \frac{\rho}{M_{n_s}} \langle c_{n_s} \rangle^{\nu^f_{n_s,j}-1} \prod_{k=1}^{n_s-1} \langle c_k \rangle^{\nu^f_{k,j}} \tag{77}$$

Now we consider the reverse rate $\mathscr{R}_{r,j}$. In the case that a reverse Arrhenius rate constant is given, the expression is identical to the above for $\mathscr{R}_{f,j}$ with all f scripts changed to r. In the common case of an equilibrium constant being used, however, then the density and mass fraction sensitivities still remain the same but sensitivity to temperature is quite different:

$$\frac{\partial k_{r,j}}{\partial T} = \frac{\partial}{\partial T}\left(\frac{k_{f,j}}{K_{c,j}}\right) = \frac{1}{K_{c,j}}\frac{\partial k_{f,j}}{\partial T} - \frac{k_{f,j}}{K_{c,j}^2}\frac{\partial K_{c,j}}{\partial T} = \frac{1}{K_{c,j}}\frac{\partial k_{f,j}}{\partial T} - \frac{k_{r,j}}{K_{c,j}}\frac{\partial K_{c,j}}{\partial T}, \tag{78}$$

which can be computed as part of $\mathscr{R}_{r,j}$ as

$$\left.\frac{\partial \mathscr{R}_{r,j}}{\partial T}\right|_{\rho,\{Y\}} = \frac{\mathscr{R}_{r,j}}{k_{r,j}}\left.\frac{\partial k_{r,j}}{\partial T}\right|_{\rho,\{Y\}} = \mathscr{R}_{r,j}\left(\frac{1}{k_{f,j}}\frac{\partial k_{f,j}}{\partial T} - \frac{1}{K_{c,j}}\frac{\partial K_{c,j}}{\partial T}\right). \tag{79}$$

The sensitivity of the forward rate constant is completed above. The derivative of the equilibrium constant,

$$\frac{\partial K_{c,j}}{\partial T} = K_{c,j}\sum_{k=1}^{n_s}\nu_{k,j}\frac{\partial B_k}{\partial T}, \tag{80}$$

depends upon the heat capacity model. $\partial B_k/\partial T$ is given for each model in §3. With straightforward simplification the sensitivity of the reverse reaction rate (mass action component only) to temperature is

$$\left.\frac{\partial \mathscr{R}_{r,j}}{\partial T}\right|_{\rho,\{Y\}} = \frac{\mathscr{R}_{r,j}}{k_{r,j}}\left.\frac{\partial k_{r,j}}{\partial T}\right|_{\rho,\{Y\}} = \mathscr{R}_{r,j}\left(\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T}\right) - \sum_{k=1}^{n_s}\nu_{k,j}\frac{\partial B_k}{\partial T}\right). \tag{81}$$

### 6.1.2 Summary of Sensitivities of the Reverse Reaction Rate

<div style="border:1px solid">

**Sensitivities of $\mathscr{R}_{r,j}$**

The sensitivities to $\rho$ and $Y_i$ are identical in form to those of the forward rate given in §6.1.1. The only change that is required is to replace all $f$ with $r$ to use the right stoichiometric coefficients. If reverse Arrhenius parameters are given, then the temperature sensitivity is identical in form as well.

The sensitivities to temperature for a reversible reaction that uses an equilibrium constant are below.

$$\left.\frac{\partial \mathscr{R}_{r,j}}{\partial T}\right|_{\rho,\{Y\}} = \mathscr{R}_{f,j}\left(\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T}\right) - \sum_{k=1}^{n_s} \nu_{k,j}\frac{\partial B_k}{\partial T}\right). \tag{82}$$

For NASA-7 heat capacity polynomials:

$$\texttt{NASA-7}: \quad \frac{\partial B_k}{\partial T} = (a_0 - 1)T^{-1} + \frac{a_1}{2} + \frac{a_2}{3}T + \frac{a_3}{4}T^2 + \frac{a_4}{5}T^3 + a_5 T^{-2}, \tag{83}$$

where the coefficients must be the dimensionless values and chosen appropriately for the temperature range. For a constant heat capacity:

$$\texttt{Const\_Cp}: \quad \frac{\partial B_k}{\partial T} = \frac{1}{T}\left[\frac{M_i}{R_u}\left(c_{p,i}^\circ - \frac{c_{p,i}^\circ T^\circ - h_i^\circ}{T}\right) - 1\right], \tag{84}$$

where the 'coefficients' are given in dimensional form.

</div>

## 6.2 TBAF Component

This section derives

$$\frac{\partial \mathcal{C}_j}{\partial \mathbf{V}} = \left( \frac{\partial \mathcal{C}_j}{\partial \rho} \bigg|_{T,\{Y\}} \quad \frac{\partial \mathcal{C}_j}{\partial T} \bigg|_{\rho,\{Y\}} \quad \frac{\partial \mathcal{C}_j}{\partial Y_1} \bigg|_{\rho,T,Y_{k \neq 1, n_s}} \quad \cdots \quad \frac{\partial \mathcal{C}_j}{\partial Y_{n_s-1}} \bigg|_{\rho,T,Y_{k \neq n_s-1, n_s}} \right). \tag{85}$$

### 6.2.1 Elementary Reactions

For elementary reactions, $\mathcal{C}_j = 1$ and the sensitivities are all zero.

### 6.2.2 Three-Body Reactions

For three-body reactions the TBAF component sensitivities are simple, as $\mathcal{C}_j = \langle c \rangle_{TB,j}$. To optimize calculation of $\langle c \rangle_{TB,j}$, however, we write it in a different manner:

$$\langle c \rangle_{TB,j} = \sum_{i=1}^{n_s} \alpha_{i,j} \langle c \rangle_i = \hat{\alpha} \langle c \rangle + \sum_{i=1}^{n_s} \alpha'_{i,j} \langle c \rangle_i, \tag{86}$$

where $\hat{\alpha}$ is the base third body efficiency and $\alpha'_{i,j} \equiv \alpha_{i,j} - \hat{\alpha}$ is the offset that is only nonzero for a small subset of species (likely). This allows us to perform a smaller summation over nonzero $\alpha'_{i,j}$. The sensitivities are

$$\frac{\partial \mathcal{C}_j}{\partial \rho} \bigg|_{T,\{Y\}} = \hat{\alpha} \frac{\partial \langle c \rangle}{\partial \rho} \bigg|_{T,\{Y\}} + \sum_{i=1}^{n_s} \alpha'_{i,j} \frac{\partial \langle c \rangle_i}{\partial \rho} \bigg|_{T,\{Y\}},$$

$$= \frac{\hat{\alpha}}{M_{mix}} + \sum_{i=1}^{n_s} \alpha'_{i,j} \frac{Y_i}{M_i}, \tag{87}$$

$$\frac{\partial \mathcal{C}_j}{\partial T} \bigg|_{\rho,\{Y\}} = \hat{\alpha} \frac{\partial \langle c \rangle}{\partial T} \bigg|_{\rho,\{Y\}} + \sum_{i=1}^{n_s} \alpha'_{i,j} \frac{\partial \langle c \rangle_i}{\partial T} \bigg|_{\rho,\{Y\}} = 0, \tag{88}$$

$$\frac{\partial \mathcal{C}_j}{\partial Y_k} \bigg|_{\rho,T,Y_{\ell \neq k, n_s}} = \hat{\alpha} \frac{\partial \langle c \rangle}{\partial Y_k} \bigg|_{\rho,T,Y_{\ell \neq k, n_s}} + \sum_{i=1}^{n_s} \alpha'_{i,j} \frac{\partial \langle c \rangle_i}{\partial Y_k} \bigg|_{\rho,T,Y_{\ell \neq k, n_s}},$$

$$= \hat{\alpha} \rho \left( \frac{1}{M_k} - \frac{1}{M_{n_s}} \right) + \rho \sum_{i=1}^{n_s} \frac{\alpha'_{i,j}}{M_i} \begin{cases} +1 & , k = j \\ -1 & , \forall k : j = n_s \\ 0 & , k \neq j, j \neq n_s \end{cases}. \tag{89}$$

Because of the coupling between the $n_s$-th species to all others, if it is a third-body with $\alpha' \neq 0$ then we have to use a two-stage evaluation similar to the mass action terms (see §6.1.1). As an example, consider the case below with three third bodies, one of which is the $n_s$-th species.

$$\frac{\partial \mathcal{C}_j}{\partial Y_k} \bigg|_{\rho,T,Y_{\ell \neq k, n_s}} = \hat{\alpha} \rho \left( \frac{1}{M_k} - \frac{1}{M_{n_s}} \right) + \rho \left( \frac{\alpha'_{A,j}}{M_A} \frac{\partial Y_A}{\partial Y_\ell} \bigg|_{Y_{\ell \neq k, n_s}} \right) +$$

$$\rho \left( \frac{\alpha'_{B,j}}{M_B} \frac{\partial Y_B}{\partial Y_\ell} \bigg|_{Y_{\ell \neq k, n_s}} \right) +$$

$$\rho \left( \frac{\alpha'_{n_s,j}}{M_{n_s}} \frac{\partial Y_{n_s}}{\partial Y_\ell} \bigg|_{Y_{\ell \neq k, n_s}} \right), \tag{90}$$

which simplifies to

$$\frac{\partial \mathcal{C}_j}{\partial Y_k} \bigg|_{\rho,T,Y_{\ell \neq k, n_s}} = \underbrace{\hat{\alpha} \rho \left( \frac{1}{M_k} - \frac{1}{M_{n_s}} \right) + \rho \left( \frac{\alpha'_{A,j}}{M_A} \delta_{index(A),k} + \frac{\alpha'_{B,j}}{M_B} \delta_{index(B),k} \right)}_{\text{stage 1}} - \underbrace{\rho \frac{\alpha'_{n_s,j}}{M_{n_s}}}_{\text{stage 2}}. \tag{91}$$

### 6.2.3 Summary of Sensitivities of the TBAF Term of Three-Body Reactions

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**Sensitivities of $\mathscr{C}_j$ for Three-Body Reactions**

$$\left.\frac{\partial \mathscr{C}_j}{\partial \rho}\right|_{T,\{Y\}} = \frac{\hat{\alpha}}{M_{\text{mix}}} + \sum_{i=1}^{n_s} \alpha'_{i,j} \frac{Y_i}{M_i}. \tag{92}$$

$$\left.\frac{\partial \mathscr{C}_j}{\partial T}\right|_{\rho,\{Y\}} = 0. \tag{93}$$

Stage 1 of mass fraction sensitivities, ignoring $n_s$ as a third-body with $\alpha'_{n_s,j} \neq 0$:

$$\left.\frac{\partial \mathscr{C}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k, n_s}} = \hat{\alpha}\rho \left( \frac{1}{M_k} - \frac{1}{M_{n_s}} \right) + \rho \frac{\alpha'_{k,j}}{M_k}. \tag{94}$$

Stage 2 of mass fraction sensitivities, to proceed only if species $n_s$ is a third-body with $\alpha'_{n_s,j} \neq 0$. The '$- =$' indicates that $\rho \frac{\alpha'_{n_s,j}}{M_{n_s}}$ is to be subtracted from the LHS.

$$\left.\frac{\partial \mathscr{C}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k, n_s}} - = \rho \frac{\alpha'_{n_s,j}}{M_{n_s}}. \tag{95}$$

</div>

### 6.2.4 Unimolecular/recombination Falloff Reactions

Here

$$\mathscr{C}_j = \frac{p_{fr,j}}{1+p_{fr,j}}\mathscr{F}_j = \left(1+p_{fr,j}^{-1}\right)^{-1}\mathscr{F}_j, \tag{96}$$

where $\mathscr{F}_j$ is the falloff blending factor, dependent upon the falloff form. The sensitivity to $V_i$ is

$$\left.\frac{\partial\mathscr{C}_j}{\partial V_i}\right|_{V_{k\neq i}} = \left(1+p_{fr,j}^{-1}\right)^{-1}\left.\frac{\partial\mathscr{F}_j}{\partial V_i}\right|_{V_{k\neq i}} + \mathscr{F}_j\frac{1}{(1+p_{fr,j})^2}\left.\frac{\partial p_{fr,j}}{\partial V_i}\right|_{V_{k\neq i}} \tag{97}$$

The falloff-reduced pressure is

$$p_{fr,j} = \frac{k_{0,j}}{k_{f,j}}\mathscr{T}_{F,j}, \tag{98}$$

and $\mathscr{T}_{F,j} = \langle c_{TB,j}\rangle$ is the concentration of the mixture including three body enhancement.

In general the sensitivity of $p_{fr,j}$ is

$$\left.\frac{\partial p_{fr,j}}{\partial V_i}\right|_{V_{k\neq i}} = p_{fr,j}\left(\frac{1}{k_{0,j}}\left.\frac{\partial k_{0,j}}{\partial V_i}\right|_{V_{k\neq i}} - \frac{1}{k_{f,j}}\left.\frac{\partial k_{f,j}}{\partial V_i}\right|_{V_{k\neq i}} + \frac{1}{\mathscr{T}_{F,j}}\left.\frac{\partial\mathscr{T}_{F,j}}{\partial V_i}\right|_{V_{k\neq i}}\right). \tag{99}$$

More specifically, we have

$$\begin{aligned}\left.\frac{\partial p_{fr,j}}{\partial T}\right|_{\rho,\{Y\}} &= p_{fr,j}\left(\frac{1}{k_{0,j}}\frac{\partial k_{0,j}}{\partial T} - \frac{1}{k_{f,j}}\frac{\partial k_{f,j}}{\partial T}\right), \\ &= p_{fr,j}\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T} + b_{0,j} + \frac{T_{a,0,j}}{T}\right),\end{aligned} \tag{100}$$

$$\left.\frac{\partial p_{fr,j}}{\partial\rho}\right|_{T,\{Y\}} = p_{fr,j}\frac{1}{\mathscr{T}_{F,j}}\left.\frac{\partial\mathscr{T}_{F,j}}{\partial\rho}\right|_{T,\{Y\}} = p_{fr,j}\frac{1}{\mathscr{T}_{F,j}}\left[\frac{\hat{\alpha}}{M_{mix}} + \sum_{i=1}^{n_s}\alpha'_{i,j}\frac{Y_i}{M_i}\right], \tag{101}$$

$$\begin{aligned}\left.\frac{\partial p_{fr,j}}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}} &= p_{fr,j}\frac{1}{\mathscr{T}_{F,j}}\left.\frac{\partial\mathscr{T}_{F,j}}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}}, \\ &= p_{fr,j}\frac{\rho}{\mathscr{T}_{F,j}}\left[\hat{\alpha}\left(\frac{1}{M_k} - \frac{1}{M_{n_s}}\right) + \sum_{i=1}^{n_s}\frac{\alpha'_{i,j}}{M_i}\begin{cases}+1 &, k=j \\ -1 &, \forall k:j=n_s \\ 0 &, k\neq j, j\neq n_s\end{cases}\right]\end{aligned} \tag{102}$$

**Lindemann Falloff** The Lindemann blending factor is $\mathscr{F}_j = 1$ and has zero derivatives. Sensitivities of $\mathscr{C}_j$ follow.

$$\left.\frac{\partial\mathscr{C}_j}{\partial T}\right|_{\rho,\{Y\}} = \frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T} + b_{0,j} + \frac{T_{a,0,j}}{T}\right), \tag{103}$$

$$\left.\frac{\partial\mathscr{C}_j}{\partial\rho}\right|_{T,\{Y\}} = \frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{1}{\mathscr{T}_{F,j}}\left[\frac{\hat{\alpha}}{M_{mix}} + \sum_{i=1}^{n_s}\alpha'_{i,j}\frac{Y_i}{M_i}\right], \tag{104}$$

$$\left.\frac{\partial\mathscr{C}_j}{\partial\rho}\right|_{T,\{Y\}} = \frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{\rho}{\mathscr{T}_{F,j}}\left[\hat{\alpha}\left(\frac{1}{M_k} - \frac{1}{M_{n_s}}\right) + \sum_{i=1}^{n_s}\frac{\alpha'_{i,j}}{M_i}\begin{cases}+1 &, k=j \\ -1 &, \forall k:j=n_s \\ 0 &, k\neq j, j\neq n_s\end{cases}\right], \tag{105}$$

### 6.2.5 Summary of Sensitivities of the TBAF Term of Lindemann Falloff Reactions

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**Sensitivities of $\mathscr{C}_j$ for Lindemann Falloff Reactions**

$$\left.\frac{\partial \mathscr{C}_j}{\partial T}\right|_{\rho,\{Y\}} = \frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T} + b_{0,j} + \frac{T_{a,0,j}}{T}\right). \tag{106}$$

$$\left.\frac{\partial \mathscr{C}_j}{\partial \rho}\right|_{T,\{Y\}} = \frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{1}{\mathscr{T}_{F,j}}\left[\frac{\hat{\alpha}}{M_{mix}} + \sum_{i=1}^{n_s}\alpha'_{i,j}\frac{Y_i}{M_i}\right]. \tag{107}$$

Stage 1 of mass fraction sensitivities, ignoring $n_s$ as a third-body with $\alpha'_{n_s,j} \neq 0$:

$$\left.\frac{\partial \mathscr{C}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k,n_s}} = \frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{\rho}{\mathscr{T}_{F,j}}\left[\hat{\alpha}\left(\frac{1}{M_k} - \frac{1}{M_{n_s}}\right) + \frac{\alpha'_{k,j}}{M_k}\right]. \tag{108}$$

Stage 2 of mass fraction sensitivities, to proceed only if species $n_s$ is a third-body with $\alpha'_{n_s,j} \neq 0$. The '$-=$' indicates that the RHS is to be subtracted from the LHS.

$$\left.\frac{\partial \mathscr{C}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k,n_s}} -= \frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{\rho}{\mathscr{T}_{F,j}}\frac{\alpha'_{n_s,j}}{M_{n_s}}. \tag{109}$$

</div>

**Troe Falloff**

$$\mathscr{F}_j = \mathscr{F}_{\text{cent}}^{1/(1+(A/B)^2)},$$

$$\mathscr{F}_{\text{cent}} = (1 - a_{\text{Troe}}) \exp\left(-\frac{T}{T^{***}}\right) + a_{\text{Troe}} \exp\left(-\frac{T}{T^*}\right) + \exp\left(-\frac{T^{**}}{T}\right), \tag{110}$$

$$A = \log_{10} p_{FR,j} - 0.67 \log_{10} \mathscr{F}_{\text{cent}} - 0.4,$$

$$B = 0.806 - 1.1762 \log_{10} \mathscr{F}_{\text{cent}} - 0.14 \log_{10} p_{FR,j},$$

This involves derivatives of the following functional form,

$$\frac{d}{dx}\left(x^{g(x)}\right) = x^{g(x)}\left(\frac{g(x)}{x} + \ln(x)\frac{dg}{dx}\right), \tag{111}$$

which is found with implicit differentiation after using the natural log of $x^{g(x)}$. Writing $\mathscr{F}_j = \mathscr{F}_{\text{cent}}^{g(p_{fr,j}, \mathscr{F}_{\text{cent}})}$ where $g(p_{fr,j}, \mathscr{F}_{\text{cent}}) \equiv 1/(1 + (A/B)^2)$, allows one to find

$$\frac{\partial \mathscr{F}_j}{\partial x} = \mathscr{F}_j\left(g\frac{1}{\mathscr{F}_{\text{cent}}}\frac{\partial \mathscr{F}_{\text{cent}}}{\partial x} + \ln(\mathscr{F}_{\text{cent}})\frac{\partial g}{\partial x}\right). \tag{112}$$

Then we have the following:

$$\frac{\partial \mathscr{F}_{\text{cent}}}{\partial T}\bigg|_{\rho,\{Y\}} = \frac{a_{\text{Troe}} - 1}{T^{***}}\exp\left(-\frac{T}{T^{***}}\right) - \frac{a_{\text{Troe}}}{T^*}\exp\left(-\frac{T}{T^*}\right) + \frac{T^{**}}{T^2}\exp\left(-\frac{T^{**}}{T}\right), \tag{113}$$

where the absence of a $T^{***}$ parameter removes the first term - this is where setting $T^{***} = 0$ by default is *not* appropriate! Sensitivities to other state variables are

$$\frac{\partial \mathscr{F}_{\text{cent}}}{\partial \rho}\bigg|_{T,\{Y\}} = 0, \tag{114}$$

$$\frac{\partial \mathscr{F}_{\text{cent}}}{\partial Y_\ell}\bigg|_{\rho,T,Y_{k \neq \ell,n_s}} = 0. \tag{115}$$

For $g = 1/(1 + (A/B)^2)$ we have

$$\frac{\partial g}{\partial x} = -2g^2\frac{A}{B^3}\left(B\frac{\partial A}{\partial x} - A\frac{\partial B}{\partial x}\right), \tag{116}$$

$$\frac{\partial A}{\partial x} = \frac{1}{\ln 10}\frac{1}{p_{fr,j}}\frac{\partial p_{fr,j}}{\partial x} - \frac{0.67}{\ln 10}\frac{1}{\mathscr{F}_{\text{cent}}}\frac{\partial \mathscr{F}_{\text{cent}}}{\partial x}, \tag{117}$$

$$\frac{\partial B}{\partial x} = -\frac{1.1762}{\ln 10}\frac{1}{\mathscr{F}_{\text{cent}}}\frac{\partial \mathscr{F}_{\text{cent}}}{\partial x} - \frac{0.14}{\ln 10}\frac{1}{p_{fr,j}}\frac{\partial p_{fr,j}}{\partial x}, \tag{118}$$

which can be filled with the sensitivities of $\mathscr{F}_{\text{cent}}$ derived above and of $p_{fr,j}$ earlier. We can simplify a bit upfront,

$$\frac{\partial g}{\partial x} = -\frac{2g^2}{\ln 10}\frac{A}{B^3}\left[(B + 0.14A)\frac{1}{p_{fr,j}}\frac{\partial p_{fr,j}}{\partial x} - (0.67B - 1.1762A)\frac{1}{\mathscr{F}_{\text{cent}}}\frac{\partial \mathscr{F}_{\text{cent}}}{\partial x}\right], \tag{119}$$

which simplifies nicely because $\mathscr{F}_{\text{cent}}$ is not a function of density or composition.

$$\frac{\partial g}{\partial \rho}\bigg|_{T,\{Y\}} = -\frac{2g^2}{\ln 10}\frac{A}{B^3}(B + 0.14A)\frac{1}{p_{fr,j}}\frac{\partial p_{fr,j}}{\partial \rho}\bigg|_{T,\{Y\}}, \tag{120}$$

$$\left.\frac{\partial g}{\partial T}\right|_{\rho,\{Y\}} = -\frac{2g^2}{\ln 10}\frac{A}{B^3}\left[(B+0.14A)\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T} + b_{0,j} + \frac{T_{a,0,j}}{T}\right) - (0.67B - 1.1762A)\frac{1}{\mathscr{F}_{cent}}\left.\frac{\partial \mathscr{F}_{cent}}{\partial T}\right|_{\rho,\{Y\}}\right],$$

$$\tag{121}$$

$$\left.\frac{\partial g}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}} = -\frac{2g^2}{\ln 10}\frac{A}{B^3}(B+0.14A)\frac{1}{p_{fr,j}}\left.\frac{\partial p_{fr,j}}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}}. \tag{122}$$

Now we can go back to the blending factor:

$$\left.\frac{\partial \mathscr{F}_j}{\partial \rho}\right|_{T,\{Y\}} = \mathscr{F}_j \ln(\mathscr{F}_{cent})\left.\frac{\partial g}{\partial \rho}\right|_{T,\{Y\}}, \tag{123}$$

$$\left.\frac{\partial \mathscr{F}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}} = \mathscr{F}_j \ln(\mathscr{F}_{cent})\left.\frac{\partial g}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}}, \tag{124}$$

$$\left.\frac{\partial \mathscr{F}_j}{\partial T}\right|_{\rho,\{Y\}} = \mathscr{F}_j\left(g\frac{1}{\mathscr{F}_{cent}}\left.\frac{\partial \mathscr{F}_{cent}}{\partial T}\right|_{\rho,\{Y\}} + \ln(\mathscr{F}_{cent})\left.\frac{\partial g}{\partial T}\right|_{\rho,\{Y\}}\right). \tag{125}$$

And finally the sensitivities of the entire TBAF term:

$$\left.\frac{\partial \mathscr{C}_j}{\partial \rho}\right|_{T,\{Y\}} = \left(1 + p_{fr,j}^{-1}\right)^{-1}\mathscr{F}_j \ln(\mathscr{F}_{cent})\left.\frac{\partial g}{\partial \rho}\right|_{T,\{Y\}} + \mathscr{F}_j\frac{1}{(1+p_{fr,j})^2}\left.\frac{\partial p_{fr,j}}{\partial \rho}\right|_{T,\{Y\}},$$

$$= \left[-\left(1 + p_{fr,j}^{-1}\right)^{-1}\mathscr{F}_j \ln(\mathscr{F}_{cent})\frac{2g^2}{\ln 10}\frac{A}{B^3}(B+0.14A)\frac{1}{p_{fr,j}} + \mathscr{F}_j\frac{1}{(1+p_{fr,j})^2}\right]\left.\frac{\partial p_{fr,j}}{\partial \rho}\right|_{T,\{Y\}},$$

$$\tag{126}$$

$$\left.\frac{\partial \mathscr{C}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}} = \left[-\left(1 + p_{fr,j}^{-1}\right)^{-1}\mathscr{F}_j \ln(\mathscr{F}_{cent})\frac{2g^2}{\ln 10}\frac{A}{B^3}(B+0.14A)\frac{1}{p_{fr,j}} + \mathscr{F}_j\frac{1}{(1+p_{fr,j})^2}\right]\left.\frac{\partial p_{fr,j}}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}},$$

$$\tag{127}$$

and

$$\left.\frac{\partial \mathscr{C}_j}{\partial T}\right|_{\rho,\{Y\}} = \left(1 + p_{fr,j}^{-1}\right)^{-1}\left.\frac{\partial \mathscr{F}_j}{\partial T}\right|_{\rho,\{Y\}} + \mathscr{F}_j\frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T} + b_{0,j} + \frac{T_{a,0,j}}{T}\right), \tag{128}$$

where the temperature sensitivities ($\mathscr{F}$, $g$, and $\mathscr{F}_{cent}$) are found above.

### 6.2.6 Summary of Sensitivities of the TBAF Term of Troe Falloff Reactions

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**Sensitivities of $\mathscr{C}_j$ for Troe Falloff Reactions**

Compute and store

$$\left.\frac{\partial \mathscr{F}_{\text{cent}}}{\partial T}\right|_{\rho,\{Y\}} = \frac{a_{\text{Troe}}-1}{T^{***}} \exp\left(-\frac{T}{T^{***}}\right) - \frac{a_{\text{Troe}}}{T^*} \exp\left(-\frac{T}{T^*}\right) + \frac{T^{**}}{T^2} \exp\left(-\frac{T^{**}}{T}\right), \qquad (129)$$

ignoring individual terms if the corresponding $T^*$, $T^{**}$, or $T^{***}$ parameter is not specified by the mechanism. This is not equivalent to setting a default value of zero, because, for instance $T^{***} = 0$ results in division by zero.

Compute and store

$$\left.\frac{\partial g}{\partial T}\right|_{\rho,\{Y\}} = -\frac{2g^2}{\ln 10}\frac{A}{B^3}\left[(B+0.14A)\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T} + b_{0,j} + \frac{T_{a,0,j}}{T}\right) - (0.67B - 1.1762A)\frac{1}{\mathscr{F}_{\text{cent}}}\left.\frac{\partial \mathscr{F}_{\text{cent}}}{\partial T}\right.\right], \qquad (130)$$

and

$$\left.\frac{\partial \mathscr{F}_j}{\partial T}\right|_{\rho,\{Y\}} = \mathscr{F}_j\left(g\frac{1}{\mathscr{F}_{\text{cent}}}\left.\frac{\partial \mathscr{F}_{\text{cent}}}{\partial T}\right|_{\rho,\{Y\}} + \ln(\mathscr{F}_{\text{cent}})\left.\frac{\partial g}{\partial T}\right|_{\rho,\{Y\}}\right). \qquad (131)$$

$$\left.\frac{\partial \mathscr{C}_j}{\partial T}\right|_{\rho,\{Y\}} = \left(1+p_{fr,j}^{-1}\right)^{-1}\left.\frac{\partial \mathscr{F}_j}{\partial T}\right|_{\rho,\{Y\}} + \mathscr{F}_j\frac{p_{fr,j}}{(1+p_{fr,j})^2}\frac{1}{T}\left(b_j + \frac{T_{a,j}}{T} + b_{0,j} + \frac{T_{a,0,j}}{T}\right). \qquad (132)$$

Compute and store a temporary,

$$\texttt{tmp} = \frac{1}{\mathscr{T}_j}\left[-2\left(1+p_{fr,j}^{-1}\right)^{-1}\mathscr{F}_j\ln(\mathscr{F}_{\text{cent}})\frac{g^2}{\ln(10)}\frac{A}{B^3}(B+0.14A) + p_{fr,j}\mathscr{F}_j\frac{1}{(1+p_{fr,j})^2}\right]. \qquad (133)$$

$$\left.\frac{\partial \mathscr{C}_j}{\partial \rho}\right|_{T,\{Y\}} = \texttt{tmp}\left(\frac{\hat{\alpha}}{M_{\text{mix}}} + \sum_{i=1}^{n_s}\frac{\alpha'_{i,j}}{M_i}Y_i\right). \qquad (134)$$

Stage 1 of mass fraction sensitivities, ignoring $n_s$ as a third-body with $\alpha'_{n_s,j} \neq 0$:

$$\left.\frac{\partial \mathscr{C}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}} = \texttt{tmp}\cdot\rho\left[\hat{\alpha}\left(\frac{1}{M_k} - \frac{1}{M_{n_s}}\right) + \frac{\alpha'_{k,j}}{M_k}\right]. \qquad (135)$$

Stage 2 of mass fraction sensitivities, to proceed only if species $n_s$ is a third-body with $\alpha'_{n_s,j} \neq 0$. The '$-=$' indicates that the RHS is to be subtracted from the LHS.

$$\left.\frac{\partial \mathscr{C}_j}{\partial Y_k}\right|_{\rho,T,Y_{\ell\neq k,n_s}} -= \texttt{tmp}\cdot\rho\frac{\alpha'_{n_s,j}}{M_{n_s}}. \qquad (136)$$

</div>

# 7 Common RHS Sensitivities

In this section we derive the sensitivities of common right-hand-side vectors representing chemistry in ODEs/PDEs. Sensitivities are derived with respect to $\mathbf{V} = (\rho, T, Y_1, \ldots, Y_{n_s-1})^{\intercal}$. The RHS vectors may include densities, heat capacities, enthalpies, etc., which require more differentiation but nothing on the scale of the species production rates considered earlier. The idea here is to get sensitivities of full RHS vectors in terms of the production rate sensitivities.

## 7.1 Chemical Part of Conserved State Variable RHS

The conserved state vector and corresponding RHS vector are below. The sensitivities of $\omega_i$ are directly applicable to this RHS.

$$
\mathbf{U} \equiv \begin{pmatrix} \rho \\ \rho e_t \\ \rho Y_1 \\ \vdots \\ \rho Y_{n_s-1} \end{pmatrix}, \quad \mathbf{RHS} \equiv \begin{pmatrix} 0 \\ 0 \\ \omega_1 \\ \vdots \\ \omega_{n_s-1} \end{pmatrix}.
\tag{137}
$$

## 7.2 Pressure-based Primitive RHS Vector for Flamelet Equations

In this case the state vector $\mathbf{Q}$ and RHS are

$$
\mathbf{Q} \equiv \begin{pmatrix} p \\ T \\ Y_1 \\ \vdots \\ Y_{n_s-1} \end{pmatrix}, \quad \mathbf{RHS} \equiv \begin{pmatrix} 0 \\ -\frac{1}{\rho c_p} \sum_{i=1}^{n_s} \omega_i h_i \\ \omega_1/\rho \\ \vdots \\ \omega_{n_s-1}/\rho \end{pmatrix}.
\tag{138}
$$

The matrix of interest here is

$$
\frac{\partial \mathbf{RHS}}{\partial \mathbf{V}} = \begin{bmatrix} \mathbf{0}^{\intercal} \\ \frac{\partial}{\partial \mathbf{V}}\left(-\frac{1}{\rho c_p} \sum_{i=1}^{n_s} \omega_i h_i\right) \\ \frac{\partial \omega_1/\rho}{\partial \mathbf{V}} \\ \vdots \\ \frac{\partial \omega_{n_s-1}/\rho}{\partial \mathbf{V}} \end{bmatrix}.
\tag{139}
$$

The species terms:

$$
\left.\frac{\partial \omega_i/\rho}{\partial \rho}\right|_{T,\{Y\}} = -\frac{\omega_i}{\rho^2} + \frac{1}{\rho} \left.\frac{\partial \omega_i}{\partial \rho}\right|_{T,\{Y\}},
\tag{140}
$$

$$
\left.\frac{\partial \omega_i/\rho}{\partial T}\right|_{\rho,\{Y\}} = \frac{1}{\rho} \left.\frac{\partial \omega_i}{\partial T}\right|_{\rho,\{Y\}},
\tag{141}
$$

$$
\left.\frac{\partial \omega_i/\rho}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k, n_s}} = \frac{1}{\rho} \left.\frac{\partial \omega_i}{\partial Y_k}\right|_{\rho,T,Y_{\ell \neq k, n_s}}.
\tag{142}
$$

The temperature term:

$$\frac{\partial}{\partial\rho}\bigg|_{T,\{Y\}}\left(-\frac{1}{\rho c_p}\sum_{i=1}^{n_s}\omega_i h_i\right) = \frac{1}{\rho^2 c_p}\sum_{i=1}^{n_s}\omega_i h_i - \frac{1}{\rho c_p}\sum_{i=1}^{n_s}h_i\frac{\partial\omega_i}{\partial\rho}\bigg|_{T,\{Y\}},$$

$$= -\frac{\mathbf{RHS}_T}{\rho} - \frac{1}{\rho c_p}\sum_{i=1}^{n_s}h_i\frac{\partial\omega_i}{\partial\rho}\bigg|_{T,\{Y\}}, \tag{143}$$

$$\frac{\partial}{\partial T}\bigg|_{\rho,\{Y\}}\left(-\frac{1}{\rho c_p}\sum_{i=1}^{n_s}\omega_i h_i\right) = -\frac{1}{\rho}\left[\frac{1}{c_p^2}\frac{\partial c_p}{\partial T}\bigg|_{\{Y\}}\sum_{i=1}^{n_s}\omega_i h_i + \frac{1}{c_p}\sum_{i=1}^{n_s}\left(h_i\frac{\partial\omega_i}{\partial T}\bigg|_{\rho,\{Y\}} + \omega_i c_{p,i}\right)\right], \tag{144}$$

$$\frac{\partial}{\partial Y_k}\bigg|_{\rho,T,Y_{\ell\neq k,n_s}}\left(-\frac{1}{\rho c_p}\sum_{i=1}^{n_s}\omega_i h_i\right) = \mathbf{RHS}_T\frac{c_{p,n_s} - c_{p,k}}{c_p} - \frac{1}{\rho c_p}\sum_{i=1}^{n_s}h_i\frac{\partial\omega_i}{\partial Y_k}\bigg|_{\rho,T,Y_{\ell\neq k,n_s}}. \tag{145}$$

The sensitivity of $c_p$ to temperature is

$$\frac{\partial c_p}{\partial T}\bigg|_{\{Y\}} = \sum_{i=1}^{n_s}Y_i\frac{\partial c_{p,i}}{\partial T}, \tag{146}$$

where the sensitivity of the species heat capacity is provided in §3.

26

# 8  Conserved State Variable Sensitivities

To find $\partial\phi/\partial\mathbf{U}$ where $\phi$ is some variable of interest and $\mathbf{U} = (\rho, \rho e, \rho Y_1, \rho Y_2, \ldots)^\mathsf{T}$ is the conserved state vector, we use a transformation matrix to avoid nasty/ambiguous derivatives. First, as done above, compute $\partial\phi/\partial\mathbf{V}$. Then simply use the state Jacobian matrix (note that if $\phi$ is a scalar, then $\partial\phi/\partial\mathbf{V}$ is a *row* vector),

$$\frac{\partial\phi}{\partial\mathbf{U}} = \frac{\partial\phi}{\partial\mathbf{V}}\frac{\partial\mathbf{V}}{\partial\mathbf{U}}. \tag{147}$$

To form a full matrix of sensitivities to $\mathbf{U}$, apply this transformation to each row. Below we show the transformation matrices and give an efficient form of the sparse vector-matrix right-multiplication of $\partial\mathbf{V}/\partial\mathbf{U}$ on an arbitrary vector.

The state Jacobian is

$$\frac{\partial\mathbf{U}}{\partial\mathbf{V}} = \begin{bmatrix} 1 & 0 & 0 & 0 & \cdots \\ e & \rho c_v & \rho\theta_1 & \cdots & \rho\theta_{n_s-1} \\ Y_1 & 0 & \rho & 0 & \cdots \\ \vdots & \vdots & & \ddots & 0 \\ Y_{n_s-1} & 0 & \cdots & 0 & \rho \end{bmatrix}, \tag{148}$$

where $\theta_i \equiv e_i - e_{n_s}$ and $e_i = h_i - R_u T/M_i$. The inverse matrix used to transform $\mathbf{V}$ sensitivities to $\mathbf{U}$ is

$$\frac{\partial\mathbf{V}}{\partial\mathbf{U}} = \begin{bmatrix} 1 & 0 & 0 & 0 & \cdots \\ -\Theta/(\rho c_v) & 1/(\rho c_v) & -\theta_1/(\rho c_v) & \cdots & -\theta_{n_s-1}/(\rho c_v) \\ -Y_1/\rho & 0 & 1/\rho & 0 & \cdots \\ \vdots & \vdots & & \ddots & 0 \\ -Y_{n_s-1}/\rho & 0 & \cdots & 0 & 1/\rho \end{bmatrix}, \tag{149}$$

where $\Theta \equiv e - \sum_{i=1}^{n_s-1} Y_i\theta_i = e_{n_s}$.

The vector-matrix product $\mathbf{b} = \mathbf{f} \cdot \partial\mathbf{V}/\partial\mathbf{U}$ may be efficiently computed without forming the sparse transformation matrix:

$$\begin{aligned}
\mathbf{b} &= \begin{pmatrix} b_1 & b_2 & \cdots & b_{n_s+1} \end{pmatrix} \\[4pt]
&= \begin{pmatrix} f_1 & f_2 & \cdots & f_{n_s+1} \end{pmatrix} \begin{bmatrix} 1 & 0 & 0 & 0 & \cdots \\ -\Theta/(\rho c_v) & 1/(\rho c_v) & -\theta_1/(\rho c_v) & \cdots & -\theta_{n_s-1}/(\rho c_v) \\ -Y_1/\rho & 0 & 1/\rho & 0 & \cdots \\ \vdots & \vdots & & \ddots & 0 \\ -Y_{n_s-1}/\rho & 0 & \cdots & 0 & 1/\rho \end{bmatrix}, \\[4pt]
&= \frac{1}{\rho c_v} \begin{pmatrix} \rho c_v f_1 - \left[ f_2\Theta + \sum_{i=1}^{n_s-1} Y_i f_{2+i} c_v \right] \\ f_2 \\ f_3 c_v - f_2\theta_1 \\ f_4 c_v - f_2\theta_2 \\ \vdots \\ f_{j+2} c_v - f_2\theta_j \\ \vdots \\ f_{n_s+1} c_v - f_2\theta_{n_s-1} \end{pmatrix}^\mathsf{T}.
\end{aligned} \tag{150}$$

This may also be written as

$$
b_i = \frac{1}{\rho c_v} \cdot \begin{cases} \rho c_v f_1 - \left[ f_2 \Theta + \sum_{i=1}^{n_s-1} Y_i f_{2+i} c_v \right] & \text{if } i = 1, \\ f_2 & \text{if } i = 2, \\ f_{i+2} c_v - f_2 \theta_i & \text{if } i > 2. \end{cases} \tag{151}
$$

Right multiplication of a row by $\partial \mathbf{U}/\partial \mathbf{V}$ can be accomplished by

$$
b_i = \begin{cases} f_1 + e b_2 + \sum_{k=1}^{n_s-1} Y_k f_{2+k} & \text{if } i = 1, \\ \rho c_v f_2 & \text{if } i = 2, \\ \rho \theta_{j-2} f_2 + \rho f_j & \text{if } i > 2. \end{cases} \tag{152}
$$

# 9 Pressure-based Primitive State Variable Sensitivities

To find $\partial \phi / \partial \mathbf{Q}$ where $\phi$ is some variable of interest and $\mathbf{Q} = (p, T, Y_1, \ldots, Y_{n_s-1})^\intercal$ is the conserved state vector, we use a transformation matrix to avoid nasty/ambiguous derivatives. First, as done above, compute $\partial \phi / \partial \mathbf{V}$. Then simply use the state Jacobian matrix (note that if $\phi$ is a scalar, then $\partial \phi / \partial \mathbf{V}$ is a *row* vector),

$$
\frac{\partial \phi}{\partial \mathbf{Q}} = \frac{\partial \phi}{\partial \mathbf{V}} \frac{\partial \mathbf{V}}{\partial \mathbf{Q}}. \tag{153}
$$

To form a full matrix of sensitivities to $\mathbf{Q}$, apply this transformation to each row.

The transformation matrix is

$$
\frac{\partial \mathbf{V}}{\partial \mathbf{Q}} = \begin{bmatrix} \frac{\partial \rho}{\partial p}\big|_{T,\{Y\}} & \frac{\partial \rho}{\partial T}\big|_{p,\{Y\}} & \frac{\partial \rho}{\partial Y_1}\big|_{p,T,Y_{k \neq 1, n_s}} & \frac{\partial \rho}{\partial Y_2}\big|_{p,T,Y_{k \neq 2, n_s}} & \cdots & \frac{\partial \rho}{\partial Y_{n_s-1}}\big|_{p,T,Y_{k \neq n_s-1, n_s}} \\ 0 & 1 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 1 \end{bmatrix}
$$

$$
= \begin{bmatrix} \rho/p & -\rho/T & -\rho M_{\text{mix}} \left( \frac{1}{M_1} - \frac{1}{M_{n_s}} \right) & -\rho M_{\text{mix}} \left( \frac{1}{M_2} - \frac{1}{M_{n_s}} \right) & \cdots & -\rho M_{\text{mix}} \left( \frac{1}{M_{n_s-1}} - \frac{1}{M_{n_s}} \right) \\ 0 & 1 & 0 & 0 & \cdots & 0 \\ 0 & 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \cdots & 1 \end{bmatrix}. \tag{154}
$$

The inverse of the transformation is

$$
\frac{\partial \mathbf{Q}}{\partial \mathbf{V}} =
\begin{bmatrix}
\left.\frac{\partial p}{\partial \rho}\right|_{T,\{Y\}} & \left.\frac{\partial p}{\partial T}\right|_{\rho,\{Y\}} & \left.\frac{\partial p}{\partial Y_1}\right|_{\rho,T,Y_{k\neq 1,n_s}} & \left.\frac{\partial p}{\partial Y_2}\right|_{\rho,T,Y_{k\neq 2,n_s}} & \cdots & \left.\frac{\partial p}{\partial Y_{n_s-1}}\right|_{\rho,T,Y_{k\neq n_s-1,n_s}} \\
0 & 1 & 0 & 0 & \cdots & 0 \\
0 & 0 & 1 & 0 & \cdots & 0 \\
0 & 0 & 0 & 1 & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & 0 & \cdots & 1
\end{bmatrix}
$$

$$
=
\begin{bmatrix}
R_{\text{mix}}T & R_{\text{mix}}\rho & R_u\rho T\left(\frac{1}{M_1}-\frac{1}{M_{n_s}}\right) & R_u\rho T\left(\frac{1}{M_2}-\frac{1}{M_{n_s}}\right) & \cdots & R_u\rho T\left(\frac{1}{M_{n_s-1}}-\frac{1}{M_{n_s}}\right) \\
0 & 1 & 0 & 0 & \cdots & 0 \\
0 & 0 & 1 & 0 & \cdots & 0 \\
0 & 0 & 0 & 1 & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & 0 & \cdots & 1
\end{bmatrix}.
$$

$$(155)$$

Right multiplication of a row by $\partial \mathbf{V}/\partial \mathbf{Q}$ can be accomplished by

$$
b_i = \begin{cases}
f_1\rho/p & \text{if } i = 1, \\
-f_1\rho/T + f_2 & \text{if } i = 2, \\
-\rho M_{\text{mix}}\left(\frac{1}{M_{i-2}}-\frac{1}{M_{n_s}}\right)f_1 + f_i & \text{if } i > 2,
\end{cases}
\tag{156}
$$

and right multiplication of a row by $\partial \mathbf{Q}/\partial \mathbf{V}$ may be performed with

$$
b_i = \begin{cases}
R_{\text{mix}}Tf_1 & \text{if } i = 1, \\
R_{\text{mix}}\rho f_1 + f_2 & \text{if } i = 2, \\
R_u\rho T\left(\frac{1}{M_{i-2}}-\frac{1}{M_{n_s}}\right)f_1 + f_i & \text{if } i > 2.
\end{cases}
\tag{157}
$$