1 State Variables

$$[C]_k = \frac{n_k}{V} \tag{1}$$

$$\Phi = \{T, V, n[1], n[2] \ldots n[-1 + Ns()]\} \tag{2}$$

$$\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \left\{ \frac{\mathrm{d}T}{\mathrm{d}t}, \frac{\mathrm{d}V}{\mathrm{d}t}, \frac{\mathrm{d}n}{\mathrm{d}t}[1], \frac{\mathrm{d}n}{\mathrm{d}t}[2] \ldots \frac{\mathrm{d}n}{\mathrm{d}t}[-1 + Ns()] \right\} \tag{3}$$

2 Source Terms

$$\frac{\mathrm{d}n}{\mathrm{d}t}_k = V\dot{\omega}_k \tag{4}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1} H_k \dot{\omega}_k}{\sum_{k=1} [C]_k C_{p_k}} \tag{5}$$

From conservation of mass:

$$m = \sum_{k=1} W_k n_k \tag{6}$$

$$0 = \sum_{k=1} W_k \frac{\mathrm{d}n}{\mathrm{d}t}_k \tag{7}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{1}{W} \sum_{k=1}^{-1+} W_k \frac{\mathrm{d}n}{\mathrm{d}t}_k \tag{8}$$

$$n = \frac{VP}{T} \tag{9}$$

Thus...

$$\dot{\omega} = -\frac{1}{W} \sum_{k=1}^{-1+} W_k \dot{\omega}_k \tag{10}$$

And...

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{1}{\sum_{k=1} [C]_k C_{p_k}} \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W} \right) \dot{\omega}_k \tag{11}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \sum_{k=1} \frac{\mathrm{d}n}{\mathrm{d}t}_k \tag{12}$$

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \sum_{k=1}^{-1+} \left(1 - \frac{W_k}{W} \right) \frac{\mathrm{d}n}{\mathrm{d}t}_k \tag{13}$$

From the ideal gas law:

$$\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{}{P} \left(T\frac{\mathrm{d}n}{\mathrm{d}t} + \frac{\mathrm{d}T}{\mathrm{d}t} n \right) \tag{14}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t} = V \left(\frac{T}{P} \sum_{k=1}^{-1+} \left(1 - \frac{W_k}{W} \right) \dot{\omega}_k + \frac{1}{T} \frac{\mathrm{d}T}{\mathrm{d}t} \right) \tag{15}$$

2.1 Other defns

$$[C] = \frac{P}{T} \tag{16}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t} = V\left(\frac{1}{[C]}\sum_{k=1}^{-1+}\left(1 - \frac{W_k}{W}\right)\dot{\omega}_k + \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t}\right) \tag{17}$$

$$[C] = [C] - \sum_{k=1}^{-1+}[C]_k \tag{18}$$

$$[C] = -\sum_{k=1}^{-1+}[C]_k + \frac{P}{T} \tag{19}$$

$$W = \sum_{k=1} W_k X_k \tag{20}$$

$$W = \frac{1}{[C]}\sum_{k=1} W_k [C]_k \tag{21}$$

$$[C] = -\sum_{k=1}^{-1+}[C]_k + \frac{P}{T} \tag{22}$$

$$W = \frac{1}{[C]}\left(\left([C] - \sum_{k=1}^{-1+}[C]_k\right)W + \sum_{k=1}^{-1+} W_k [C]_k\right) \tag{23}$$

$$W = W + \frac{1}{[C]}\sum_{k=1}^{-1+}\left(-W + W_k\right)[C]_k \tag{24}$$

3 Thermo Definitions

$$C_{p,k}{}^{\circ} = C_{p_k} \tag{25}$$

$$C_{p_k} = \left(T\left(T\left(T\left(Ta_{k,4} + a_{k,3}\right) + a_{k,2}\right) + a_{k,1}\right) + a_{k,0}\right) \tag{26}$$

$$C_{p_k} = T^4 a_{k,4} + T^3 a_{k,3} + T^2 a_{k,2} + T a_{k,1} + a_{k,0} \tag{27}$$

$$\frac{\mathrm{d}C_p}{\mathrm{d}T}_k = \left(4T^3 a_{k,4} + 3T^2 a_{k,3} + 2T a_{k,2} + a_{k,1}\right) \tag{28}$$

$$\frac{\mathrm{d}C_p}{\mathrm{d}T}_k = \left(T \left(T \left(4 T a_{k,4} + 3 a_{k,3}\right) + 2 a_{k,2}\right) + a_{k,1}\right) \tag{29}$$

$$\bar{c_p} = \sum_{k=1} \frac{n_k C_{p_k}}{n} \tag{30}$$

$$C_{v,k}{}^{\circ} = C_{v\,k} \tag{31}$$

$$C_{v\,k} = \left(T \left(T \left(T \left(T a_{k,4} + a_{k,3}\right) + a_{k,2}\right) + a_{k,1}\right) + a_{k,0} - 1\right) \tag{32}$$

$$C_{v\,k} = T^{4} a_{k,4} + T^{3} a_{k,3} + T^{2} a_{k,2} + T a_{k,1} + a_{k,0} - \tag{33}$$

$$\frac{\mathrm{d}C_v}{\mathrm{d}T}_k = \left(4 T^{3} a_{k,4} + 3 T^{2} a_{k,3} + 2 T a_{k,2} + a_{k,1}\right) \tag{34}$$

$$\frac{\mathrm{d}C_v}{\mathrm{d}T}_k = \left(T \left(T \left(4 T a_{k,4} + 3 a_{k,3}\right) + 2 a_{k,2}\right) + a_{k,1}\right) \tag{35}$$

$$\bar{c_v} = \sum_{k=1} \frac{n_k C_{v\,k}}{n} \tag{36}$$

$$H_k^{\circ} = H_k \tag{37}$$

$$H_k = \left(T \left(T \left(T \left(T \left(\frac{T a_{k,4}}{5} + \frac{a_{k,3}}{4}\right) + \frac{a_{k,2}}{3}\right) + \frac{a_{k,1}}{2}\right) + a_{k,0}\right) + a_{k,5}\right) \tag{38}$$

$$H_k = \frac{T^{5} a_{k,4}}{5} + \frac{T^{4} a_{k,3}}{4} + \frac{T^{3} a_{k,2}}{3} + \frac{T^{2} a_{k,1}}{2} + T a_{k,0} + a_{k,5} \tag{39}$$

$$\frac{\mathrm{d}H}{\mathrm{d}T}_k = \left(T \left(T \left(T \left(T a_{k,4} + a_{k,3}\right) + a_{k,2}\right) + a_{k,1}\right) + a_{k,0}\right) \tag{40}$$

$$H_k = U_k + \frac{PV}{n} \tag{41}$$

$$U_k = -T + H_k \tag{42}$$

$$U_k = \left(T \left(T \left(T \left(T \left(\frac{T a_{k,4}}{5} + \frac{a_{k,3}}{4}\right) + \frac{a_{k,2}}{3}\right) + \frac{a_{k,1}}{2}\right) + a_{k,0}\right) - T + a_{k,5}\right) \tag{43}$$

$$\frac{\mathrm{d}U}{\mathrm{d}T}_k = \left(T \left(T \left(T \left(T a_{k,4} + a_{k,3}\right) + a_{k,2}\right) + a_{k,1}\right) + a_{k,0} - 1\right) \tag{44}$$

$$\begin{aligned} S_k^{\circ} &= S_k \\ &= \left(T \left(T \left(T \left(\frac{T a_{k,4}}{4} + \frac{a_{k,3}}{3}\right) + \frac{a_{k,2}}{2}\right) + a_{k,1}\right) + \log{\left(T \right)} a_{k,0} + a_{k,6}\right) \end{aligned} \tag{45}$$

4 Definitions

$$\nu_{k,i} = \nu''_{k,i} - \nu'_{k,i} \tag{46}$$

$$\dot{\omega}_k = \sum_{i=1} \nu_{k,i} q_i \tag{47}$$

$$q_i = R_i c_i \tag{48}$$

$$\dot{\omega}_k = \sum_{i=1} \nu_{k,i} R_i c_i \tag{49}$$

5 Rate of Progress

$$R_i = R_{f\,i} - R_{r\,i} \tag{50}$$

$$R_{f\,i} = k_{f\,i} \prod_{k=1} [C]_k^{\nu'_{k,i}} \tag{51}$$

$$R_{r\,i} = k_{r\,i} \prod_{k=1} [C]_k^{\nu''_{k,i}} \tag{52}$$

6 Third-body effect

$$c_i = 1 \quad \text{for elementary reactions} \tag{53}$$

$$c_i = [X]_i \quad \text{for third-body enhanced reactions} \tag{54}$$

$$c_i = \frac{F_i P_{r,i}}{P_{r,i} + 1} \quad \text{for unimolecular/recombination falloff reactions} \tag{55}$$

$$c_i = \frac{F_i}{P_{r,i} + 1} \quad \text{for chemically-activated bimolecular reactions} \tag{56}$$

7 Forward Reaction Rate

$$k_{f\,i} = T^{\beta_i} \exp\left(-\frac{E_{a\,i}}{T}\right) A_i \tag{57}$$

8 Equilibrium Constants

$$K_{ci} = \left(\left(\frac{P_{atm}}{T}\right)^{\sum_{k=1}\nu_{k,i}}\right) K_{p_i} \tag{58}$$

$$K_{p_i} = \exp(\frac{\Delta S_k^\circ}{} - \frac{\Delta H_k^\circ}{T}) \tag{59}$$

$$K_{p_i} = \exp\left(\sum_{k=1} \nu_{ki}\left(\frac{S_k^\circ}{} - \frac{H_k^\circ}{T}\right)\right) \tag{60}$$

$$K_{ci} = \left(\left(\frac{P_{atm}}{}\right)^{\sum_{k=1}\nu_{k,i}}\right) \exp\left(\sum_{k=1} \nu_{k,i} B_k\right) \tag{61}$$

$$B_k = \frac{S_k^\circ}{} - \frac{H_k^\circ}{T} - ln(T) \tag{62}$$

$$\begin{aligned} B_k = T\left(T\left(T\left(\frac{Ta_{k,4}}{20} + \frac{a_{k,3}}{12}\right) + \frac{a_{k,2}}{6}\right) + \frac{a_{k,1}}{2}\right) \\ + (a_{k,0} - 1)\log(T) - a_{k,0} + a_{k,6} - \frac{a_{k,5}}{T} \end{aligned} \tag{63}$$

9 Reverse Reaction Rate

$$k_{ri} = \frac{k_{f\,i}}{K_{ci}} \quad \text{if non-explicit} \tag{64}$$

$$R_{ri} = T^{\beta_{r\,i}} \exp\left(-\frac{E_{a,r_i}}{T}\right) A_{ri} \prod_{k=1} [C]_k^{\nu''_{k,i}} \quad \text{if explicit} \tag{65}$$

10 Third-Body Efficiencies

$$[X]_i = \sum_{k=1} \alpha_{k,i}[C]_k \tag{66}$$

$$[X]_i = [C] + \sum_{k=1} (\alpha_{k,i} - 1)[C]_k \tag{67}$$

$$[X]_i = [C] + (\alpha_{,i} - 1)\left(-\sum_{k=1}^{-1+} [C]_k + \frac{P}{T}\right) + \sum_{k=1}^{-1+} (\alpha_{k,i} - 1)[C]_k \tag{68}$$

$$[X]_i = [C]\alpha_{,i} + \sum_{k=1}^{-1+} \left(-\alpha_{,i} + \alpha_{k,i}\right)[C]_k \quad \text{for mixture as third-body} \tag{69}$$

$$[X]_i = [C] \quad \text{for all } \alpha_{ki} = 1 \tag{70}$$

$$[X]_i = \left([C] - \sum_{k=1}^{-1+} [C]_k\right)\delta_m + \left(-\delta_m + 1\right)[C]_m \quad \text{for a single species third-body} \tag{71}$$

11 Falloff Reactions

$$k_{0,i} = T^{\beta_0} A_0 \exp\left(-\frac{E_{a,0}}{T}\right) \tag{72}$$

$$k_{\infty,i} = T^{\beta_\infty} A_\infty \exp\left(-\frac{E_{a,\infty}}{T}\right) \tag{73}$$

$$P_{r,i} = \frac{[X]_i k_{0,i}}{k_{\infty,i}} \quad \text{for the mixture as the third-body} \tag{74}$$

$$P_{r,i} = \frac{k_{0,i}}{k_{\infty,i}} \left(\left([C] - \sum_{k=1}^{-1+} [C]_k\right)\delta_m + \left(-\delta_m + 1\right)[C]_m\right) \quad \text{for species } m \text{ as the third-body} \tag{75}$$

$$P_{r,i} = \frac{[C] k_{0,i}}{k_{\infty,i}} \quad \text{for for all } \alpha_{i,j} = 1 \tag{76}$$

$$F_i = 1 \quad \text{for Lindemann} \tag{77}$$

$$F_i = F_{cent}^{\frac{1}{\frac{A_{Troe}^2}{B_{Troe}^2} + 1}} \quad \text{for Troe} \tag{78}$$

$$F_i = T^e d \left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)^X \quad \text{for SRI} \tag{79}$$

$$F_{cent} = a \exp\left(-\frac{T}{T^*}\right) + (-a + 1)\exp\left(-\frac{T}{T^{***}}\right) + \exp\left(-\frac{T^{**}}{T}\right) \tag{80}$$

$$A_{Troe} = -\frac{0.67 \log\left(F_{cent}\right)}{\log(10)} + \frac{\log\left(P_{r,i}\right)}{\log(10)} - 0.4 \tag{81}$$

$$B_{Troe} = -\frac{1.1762 \log\left(F_{cent}\right)}{\log(10)} - \frac{0.14 \log\left(P_{r,i}\right)}{\log(10)} + 0.806 \tag{82}$$

$$X = \frac{1}{\frac{\log^2\left(P_{r,i}\right)}{\log^2(10)} + 1} \tag{83}$$

12 Pressure-Dependent Reactions

For PLog reactions

$$k_1 = T^{\beta_1} A_1 \exp\left(\frac{E_{a_1}}{T}\right) \quad \text{at } P_1 \tag{84}$$

$$k_2 = T^{\beta_2} A_2 \exp\left(\frac{E_{a_2}}{T}\right) \quad \text{at } P_2 \tag{85}$$

$$\log\left(k_{f\,i}\right) = \frac{\left(-\log\left(k_1\right) + \log\left(k_2\right)\right)\left(-\log\left(P_1\right) + \log\left(P\right)\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \log\left(k_1\right) \tag{86}$$

For Chebyshev reactions

$$\frac{\log\left(k_{f\,i}\right)}{\log\left(10\right)} = \sum_{\substack{1\leq l\leq N_P\\ 1\leq j\leq N_T}} T_{j-1}\left(\tilde{T}\right) T_{l-1}\left(\tilde{P}\right) \eta_{l,j} \tag{87}$$

$$\tilde{T} = \frac{-\frac{1}{T_{min}} - \frac{1}{T_{max}} + \frac{2}{T}}{-\frac{1}{T_{min}} + \frac{1}{T_{max}}} \tag{88}$$

$$\tilde{P} = \frac{-\log\left(P_{max}\right) - \log\left(P_{min}\right) + 2\log\left(P\right)}{\log\left(P_{max}\right) - \log\left(P_{min}\right)} \tag{89}$$

13 Derivatives

$$\frac{\partial q}{\partial T}_i = R_i \frac{\partial c}{\partial T}_i + \frac{\partial R}{\partial T}_i c_i \tag{90}$$

$$\frac{\partial \dot{\omega}}{\partial T}_k = \sum_{i=1} \left(\nu_{k,i} R_i \frac{\partial c}{\partial T}_i + \nu_{k,i} \frac{\partial R}{\partial T}_i c_i\right) \tag{91}$$

$$\frac{\partial q}{\partial n[k]}_i = R_i \frac{\partial c}{\partial n[j]}_i + \frac{\partial R}{\partial n[j]}_i c_i \tag{92}$$

$$\frac{\partial \dot{\omega}}{\partial n[j]}_k = \sum_{i=1} \left(\nu_{k,i} R_i \frac{\partial c}{\partial n[j]}_i + \nu_{k,i} \frac{\partial R}{\partial n[j]}_i c_i\right) \tag{93}$$

$$\frac{\partial q}{\partial V}_i = R_i \frac{\partial c}{\partial V}_i + \frac{\partial R}{\partial V}_i c_i \tag{94}$$

$$\frac{\partial \dot{\omega}}{\partial V}_k = \sum_{i=1} \left(\nu_{k,i} R_i \frac{\partial c}{\partial V}_i + \nu_{k,i} \frac{\partial R}{\partial V}_i c_i\right) \tag{95}$$

14 Rate of Progress Derivatives

14.1 Molar Derivatives

$$\frac{d}{dn_k} R_f = \left(\frac{\partial}{\partial n_j} \prod_{k=1} [C]_k^{\nu'_{k,i}} \right) k_{f\,i} \tag{96}$$

$$\frac{\partial [C_k]}{\partial n_j} = \frac{\delta_{jk}}{V} \tag{97}$$

$$\frac{\partial [C_{Ns}]}{\partial n_j} = -\frac{1}{V} \tag{98}$$

$$\frac{\partial [C_{Ns}]^{\nu'_{Ns,i}}}{\partial [n_j]} = -\frac{\left(\left(-\sum_{k=1}^{-1+} \frac{n_k}{V} + \frac{P}{T} \right)^{\nu'_{,i}} \right) \nu'_{,i} \sum_{k=1}^{-1+} \frac{\delta_{jk}}{V}}{-\sum_{k=1}^{-1+} \frac{n_k}{V} + \frac{P}{T}} \tag{99}$$

$$\frac{\partial [C_{Ns}]^{\nu'_{Ns,i}}}{\partial n_j} = -\frac{\nu'_{,i}}{V} [C]^{\nu'_{,i}-1} \tag{100}$$

$$\frac{\partial R_f}{\partial n[j]}_i = k_{f\,i} \sum_{k=1} \left(-\frac{\delta_k}{V} + \frac{\delta_{jk}}{V} \right) \nu'_{k,i} [C]_k^{\nu'_{k,i}-1} \prod_{\substack{1 \leq l \leq k-1 \\ k+1 \leq l \leq}} [C]_l^{\nu'_{l,i}} \tag{101}$$

$$\frac{\partial R_f}{\partial n[j]}_i = \frac{k_{f\,i}}{V} \left(-\nu'_{,i} [C]^{\nu'_{,i}-1} \prod_{l=1}^{-1+} [C]_l^{\nu'_{l,i}} + \nu'_{j,i} [C]_j^{\nu'_{j,i}-1} \prod_{\substack{1 \leq l \leq j-1 \\ j+1 \leq l \leq}} [C]_l^{\nu'_{l,i}} \right) \tag{102}$$

$$S'_l = \nu'_{l,i} [C]_l^{\nu'_{l,i}-1} \prod_{\substack{1 \leq l \leq l-1 \\ l+1 \leq l \leq}} [C]_l^{\nu'_{l,i}} \tag{103}$$

$$\frac{\partial R_f}{\partial n[j]}_i = \frac{k_{f\,i}}{V} \left(-S' + S'_j \right) \tag{104}$$

$$\frac{\partial R_r}{\partial n[j]}_i = k_{r\,i} \sum_{k=1} \left(-\frac{\delta_k}{V} + \frac{\delta_{jk}}{V} \right) \nu''_{k,i} [C]_k^{\nu''_{k,i}-1} \prod_{\substack{1 \leq l \leq k-1 \\ k+1 \leq l \leq}} [C]_l^{\nu''_{l,i}} \tag{105}$$

$$\frac{\partial R_r}{\partial n[j]}_i = \frac{k_{r\,i}}{V} \left(-\nu''_{,i} [C]^{\nu''_{,i}-1} \prod_{l=1}^{-1+} [C]_l^{\nu''_{l,i}} + \nu''_{j,i} [C]_j^{\nu''_{j,i}-1} \prod_{\substack{1 \leq l \leq j-1 \\ j+1 \leq l \leq}} [C]_l^{\nu''_{l,i}} \right) \tag{106}$$

$$S''_l = \nu''_{l,i} [C]_l^{\nu''_{l,i}-1} \prod_{\substack{1 \le l \le l-1 \\ l+1 \le l \le}} [C]_l^{\nu''_{l,i}} \tag{107}$$

$$\frac{\partial R_r}{\partial n[j]}_i = \frac{k_{r\,i}}{V} \left(-S'' + S''_j\right) \tag{108}$$

For all reversible reactions

$$\frac{\partial R}{\partial n[j]}_i = -\frac{k_{r\,i}}{V} \left(-S'' + S''_j\right) + \frac{k_{f\,i}}{V} \left(-S' + S'_j\right) \tag{109}$$

14.2 Temperature Derivative

$$R_f = k_{f\,i} \prod_{k=1} [C]_k^{\nu'_{k,i}} \tag{110}$$

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \frac{k_{f\,i}}{T} \left(\beta_i + \frac{E_{a\,i}}{T}\right) \tag{111}$$

$$R_f = \left(\left(-\sum_{k=1}^{-1+} [C]_k + \frac{P}{T}\right)^{\nu'_{,i}}\right) k_{f\,i} \prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}} \tag{112}$$

$$\begin{aligned} \frac{\partial R_f}{\partial T}_i = & \left(\left(-\sum_{k=1}^{-1+} [C]_k + \frac{P}{T}\right)^{\nu'_{,i}}\right) \frac{\mathrm{d}k_f}{\mathrm{d}T}_i \prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}} \\ & - \frac{P \left(\left(-\sum_{k=1}^{-1+} [C]_k + \frac{P}{T}\right)^{\nu'_{,i}}\right) \nu'_{,i} k_{f\,i} \prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}}}{T^2 \left(-\sum_{k=1}^{-1+} [C]_k + \frac{P}{T}\right)} \end{aligned} \tag{113}$$

$$\frac{\partial R_f}{\partial T}_i = \frac{\mathrm{d}k_f}{\mathrm{d}T}_i \prod_{k=1} [C]_k^{\nu'_{k,i}} - \frac{[C]\nu'_{,i}}{T} [C]^{\nu'_{,i}-1} k_{f\,i} \prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}} \tag{114}$$

$$\frac{\partial R_f}{\partial T}_i = -\frac{[C]S'}{T} k_{f\,i} + \frac{R_{f\,i}}{T} \left(\beta_i + \frac{E_{a\,i}}{T}\right) \tag{115}$$

For reactions with explicit reverse Arrhenius coefficients

$$\frac{\partial R_r}{\partial T}_i = -\frac{[C]S''}{T} k_{r\,i} + \frac{R_{r\,i}}{T} \left(\beta_{r\,i} + \frac{E_{a,r\,i}}{T}\right) \tag{116}$$

$$\frac{\partial R}{\partial T}_i = \frac{[C]S''}{T} k_{r\,i} - \frac{[C]S'}{T} k_{f\,i} + \frac{R_{f\,i}}{T} \left(\beta_i + \frac{E_{a\,i}}{T}\right) - \frac{R_{r\,i}}{T} \left(\beta_{r\,i} + \frac{E_{a,r\,i}}{T}\right) \tag{117}$$

For non-explicit reversible reactions

$$\frac{\mathrm{d}k_r}{\mathrm{d}T}_i = -\frac{k_{f\,i}}{K_{ci}^2}\frac{\mathrm{d}K_c}{\mathrm{d}T}_i + \frac{1}{K_{ci}}\frac{\mathrm{d}k_f}{\mathrm{d}T}_i \tag{118}$$

$$\frac{\mathrm{d}k_r}{\mathrm{d}T}_i = \left(-\frac{1}{K_{ci}}\frac{\mathrm{d}K_c}{\mathrm{d}T}_i + \frac{1}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\right) k_{r\,i} \tag{119}$$

$$\frac{\mathrm{d}K_c}{\mathrm{d}T}_i = K_{ci}\sum_{k=1}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k \tag{120}$$

$$\frac{\mathrm{d}k_r}{\mathrm{d}T}_i = \left(-\sum_{k=1}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\right) k_{r\,i} \tag{121}$$

$$\frac{\partial R_r}{\partial T}_i = \left(-\sum_{k=1}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\right) R_{r\,i} - \frac{[C]S''}{T}k_{r\,i} \tag{122}$$

$$\frac{\partial R_r}{\partial T}_i = \left(-\sum_{k=1}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\right) R_{r\,i} - \frac{[C]S''}{T}k_{r\,i} \tag{123}$$

$$\begin{aligned}\frac{\partial R}{\partial T}_i = -&\left(-\sum_{k=1}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\right) R_{r\,i} \\ &+ \frac{[C]S''}{T}k_{r\,i} - \frac{[C]S'}{T}k_{f\,i} + \frac{R_{f\,i}}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\end{aligned} \tag{124}$$

$$\frac{\mathrm{d}B}{\mathrm{d}T}_k = T\left(T\left(\frac{Ta_{k,4}}{5} + \frac{a_{k,3}}{4}\right) + \frac{a_{k,2}}{3}\right) + \frac{a_{k,1}}{2} + \frac{1}{T}\left(a_{k,0} - 1 + \frac{a_{k,5}}{T}\right) \tag{125}$$

14.3 Volume derivatives

$$\frac{\partial [C]}{\partial V}_k = -\frac{[C]_k}{V} \tag{126}$$

$$\frac{\partial [C]}{\partial V} = \frac{1}{V}\sum_{k=1}^{-1+}[C]_k \tag{127}$$

$$\frac{\partial [C_{Ns}]^{\nu'_{Ns,i}}}{\partial V} = \frac{\nu'_{k,i}}{V}\left([C] - [C]\right)[C]^{\nu'_{k,i}-1} \tag{128}$$

$$\text{True} \tag{129}$$

$$R_{f\,i} = \left(\left(-\sum_{k=1}^{-1+} [C]_k + \frac{P}{T} \right)^{\nu'_{,i}} \right) k_{f\,i} \prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}} \tag{130}$$

$$\begin{aligned} \frac{\partial R_f}{\partial V}_i = & -\frac{\nu'_{,i}[C]^{\nu'_{,i}}}{[C]} k_{f\,i} \left(\prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}} \right) \sum_{k=1}^{-1+} \frac{\partial [C]}{\partial V}_k \\ & + [C]^{\nu'_{,i}} k_{f\,i} \sum_{k=1}^{-1+} \frac{\nu'_{k,i}[C]_k^{\nu'_{k,i}}}{[C]_k} \frac{\partial [C]}{\partial V}_k \prod_{\substack{1 \le l \le k-1 \\ k+1 \le l \le -1+}} [C]_l^{\nu'_{l,i}} \end{aligned} \tag{131}$$

$$\begin{aligned} \frac{\partial R_f}{\partial V}_i = & -\frac{\nu'_{,i}[C]^{\nu'_{,i}}}{[C]} k_{f\,i} \left(\prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}} \right) \sum_{k=1}^{-1+} -\frac{[C]_k}{V} \\ & + [C]^{\nu'_{,i}} k_{f\,i} \sum_{k=1}^{-1+} -\frac{\nu'_{k,i}[C]_k^{\nu'_{k,i}}}{V} \prod_{\substack{1 \le l \le k-1 \\ k+1 \le l \le -1+}} [C]_l^{\nu'_{l,i}} \end{aligned} \tag{132}$$

$$\frac{\partial R_f}{\partial V}_i = -\frac{\nu'_{,i}[C]^{\nu'_{,i}}}{[C]} k_{f\,i} \left(\prod_{k=1}^{-1+} [C]_k^{\nu'_{k,i}} \right) \sum_{k=1}^{-1+} -\frac{[C]_k}{V} - \frac{[C]^{\nu'_{,i}} k_{f\,i}}{V} \left(\prod_{l=1}^{-1+} [C]_l^{\nu'_{l,i}} \right) \sum_{k=1}^{-1+} \nu'_{k,i} \tag{133}$$

$$\frac{\partial R_f}{\partial V}_i = \frac{[C]S'}{V} k_{f\,i} - \frac{\nu'_{,i}[C]^{\nu'_{,i}}}{V} k_{f\,i} \prod_{l=1}^{-1+} [C]_l^{\nu'_{l,i}} - \frac{[C]^{\nu'_{,i}} k_{f\,i}}{V} \left(\prod_{l=1}^{-1+} [C]_l^{\nu'_{l,i}} \right) \sum_{k=1}^{-1+} \nu'_{k,i} \tag{134}$$

$$\frac{\partial R_f}{\partial V}_i = \frac{[C]S'}{V} k_{f\,i} - \frac{R_{f\,i}}{V} \sum_{k=1} \nu'_{k,i} \tag{135}$$

$$R_{r\,i} = \left(\left(-\sum_{k=1}^{-1+} [C]_k + \frac{P}{T} \right)^{\nu''_{,i}} \right) k_{r\,i} \prod_{k=1}^{-1+} [C]_k^{\nu''_{k,i}} \tag{136}$$

$$\begin{aligned} \frac{\partial R_r}{\partial V}_i = & -\frac{\nu''_{,i}[C]^{\nu''_{,i}}}{[C]} k_{r\,i} \left(\prod_{k=1}^{-1+} [C]_k^{\nu''_{k,i}} \right) \sum_{k=1}^{-1+} \frac{\partial [C]}{\partial V}_k \\ & + [C]^{\nu''_{,i}} k_{r\,i} \sum_{k=1}^{-1+} \frac{\nu''_{k,i}[C]_k^{\nu''_{k,i}}}{[C]_k} \frac{\partial [C]}{\partial V}_k \prod_{\substack{1 \le l \le k-1 \\ k+1 \le l \le -1+}} [C]_l^{\nu''_{l,i}} \end{aligned} \tag{137}$$

$$
\begin{aligned}
\frac{\partial R_r}{\partial V}_i = &-\frac{\nu''_{,i}[C]^{\nu''_{,i}}}{[C]} k_{r\,i} \left(\prod_{k=1}^{-1+} [C]_k^{\nu''_{k,i}} \right) \sum_{k=1}^{-1+} -\frac{[C]_k}{V} \\
&+ [C]^{\nu''_{,i}} k_{r\,i} \sum_{k=1}^{-1+} -\frac{\nu''_{k,i}[C]_k^{\nu''_{k,i}}}{V} \prod_{\substack{1 \le l \le k-1 \\ k+1 \le l \le -1+}} [C]_l^{\nu''_{l,i}}
\end{aligned}
\tag{138}
$$

$$
\frac{\partial R_r}{\partial V}_i = -\frac{\nu''_{,i}[C]^{\nu''_{,i}}}{[C]} k_{r\,i} \left(\prod_{k=1}^{-1+} [C]_k^{\nu''_{k,i}} \right) \sum_{k=1}^{-1+} -\frac{[C]_k}{V} - \frac{[C]^{\nu''_{,i}} k_{r\,i}}{V} \left(\prod_{l=1}^{-1+} [C]_l^{\nu''_{l,i}} \right) \sum_{k=1}^{-1+} \nu''_{k,i}
\tag{139}
$$

$$
\frac{\partial R_r}{\partial V}_i = \frac{[C]S''}{V} k_{r\,i} - \frac{\nu''_{,i}[C]^{\nu''_{,i}}}{V} k_{r\,i} \prod_{l=1}^{-1+} [C]_l^{\nu''_{l,i}} - \frac{[C]^{\nu''_{,i}} k_{r\,i}}{V} \left(\prod_{l=1}^{-1+} [C]_l^{\nu''_{l,i}} \right) \sum_{k=1}^{-1+} \nu''_{k,i}
\tag{140}
$$

$$
\frac{\partial R_r}{\partial V}_i = \frac{[C]S''}{V} k_{r\,i} - \frac{R_{r\,i}}{V} \sum_{k=1} \nu''_{k,i}
\tag{141}
$$

15 Third-Body/Falloff Derivatives

15.1 Elementary reactions

$$
\frac{\partial c}{\partial T}_i = 0
\tag{142}
$$

$$
\frac{\partial c}{\partial n[j]}_i = 0
\tag{143}
$$

$$
\frac{\partial c}{\partial V}_i = 0
\tag{144}
$$

15.2 Third-body enhanced reactions

$$
\frac{\partial [X]_i}{\partial T} = -\frac{[C]\alpha_{,i}}{T}
\tag{145}
$$

$$
\frac{\partial [X]_i}{\partial n[j]} = \frac{1}{V} \left(-\alpha_{,i} + \alpha_{j,i} \right)
\tag{146}
$$

$$
\frac{\partial [X]_i}{\partial V} = \frac{1}{V} \left([C]\alpha_{,i} - [X]_i \right)
\tag{147}
$$

For species m as the third-body

$$\frac{\partial c}{\partial T}_i = -\frac{\delta_m}{T}[C] \tag{148}$$

$$\frac{\partial c}{\partial n[j]}_i = \frac{1}{V}\left(-\delta_m \delta_{jm} - \delta_m + \delta_{jm}\right) \tag{149}$$

$$\frac{\partial c}{\partial n[j]}_i = \frac{1}{V}\left(-\delta_m + \delta_{jm}\right) \tag{150}$$

$$\frac{\partial c}{\partial V}_i = -\delta_m \sum_{k=1}^{-1+} -\frac{[C]_k}{V} - \frac{[C]_m}{V}\left(-\delta_m + 1\right) \tag{151}$$

$$\frac{\partial c}{\partial V}_i = \frac{\delta_m}{V}\left([C] - [C]\right) + \frac{[C]_m}{V}\left(\delta_m - 1\right) \tag{152}$$

If all $\alpha_{j,i} = 1$ for all species j

$$\frac{\partial c}{\partial T}_i = -\frac{[C]}{T} \tag{153}$$

$$\frac{\partial c}{\partial n[j]}_i = 0 \tag{154}$$

$$\frac{\partial c}{\partial V}_i = 0 \tag{155}$$

15.3 Unimolecular/recombination fall-off reactions

$$\frac{\partial c}{\partial T}_i = \frac{1}{P_{r,i}+1}\left(P_{r,i}\frac{\partial F_i}{\partial T} + \frac{\partial P_{r,i}}{\partial T}\left(F_i - c_i\right)\right) \tag{156}$$

$$\frac{\partial c}{\partial n[j]}_i = \frac{1}{P_{r,i}+1}\left(P_{r,i}\frac{\partial F_i}{\partial n[j]} + \frac{\partial P_{r,i}}{\partial n[j]}\left(F_i - c_i\right)\right) \tag{157}$$

$$\frac{\partial c}{\partial V}_i = \frac{1}{P_{r,i}+1}\left(P_{r,i}\frac{\partial F_i}{\partial V} + \frac{\partial P_{r,i}}{\partial V}\left(F_i - c_i\right)\right) \tag{158}$$

15.4 Chemically-activated bimolecular reactions

$$\frac{\partial c}{\partial T}_i = \frac{1}{P_{r,i}+1}\left(\frac{\partial F_i}{\partial T} - \frac{\partial P_{r,i}}{\partial T}c_i\right) \tag{159}$$

$$\frac{\partial c}{\partial n[j]}_i = \frac{1}{P_{r,i}+1}\left(\frac{\partial F_i}{\partial n[j]} - \frac{\partial P_{r,i}}{\partial n[j]}c_i\right) \tag{160}$$

$$\frac{\partial c}{\partial V}_i = \frac{1}{P_{r,i}+1}\left(\frac{\partial F_i}{\partial V} - \frac{\partial P_{r,i}}{\partial V}c_i\right) \tag{161}$$

15.5 Reduced Pressure derivatives

For the mixture as the third body

$$\frac{\partial P_{r,i}}{\partial T} = \frac{P_{r,i}}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) - \frac{[C]k_{0,i}\alpha_{,i}}{Tk_{\infty,i}} \tag{162}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{k_{0,i}\left(-\alpha_{,i} + \alpha_{j,i}\right)}{Vk_{\infty,i}} \tag{163}$$

$$\frac{\partial P_{r,i}}{\partial V} = -\frac{P_{r,i}}{V} + \frac{[C]k_{0,i}\alpha_{,i}}{Vk_{\infty,i}} \tag{164}$$

Simplifying:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T,mix} + \bar{\theta}_{P_{r,i},\partial T,mix} \tag{165}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{\bar{\theta}_{P_{r,i},\partial n_j,mix}}{Vk_{\infty,i}}k_{0,i} \tag{166}$$

$$\frac{\partial P_{r,i}}{\partial V} = P_{r,i}\Theta_{P_{r,i},\partial V,mix} + \bar{\theta}_{P_{r,i},\partial V,mix} \tag{167}$$

$$\Theta_{P_{r,i},\partial T,mix} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \tag{168}$$

$$\bar{\theta}_{P_{r,i},\partial T,mix} = -\frac{[C]k_{0,i}\alpha_{,i}}{Tk_{\infty,i}} \tag{169}$$

$$\bar{\theta}_{P_{r,i},\partial n_j,mix} = -\alpha_{,i} + \alpha_{j,i} \tag{170}$$

$$\Theta_{P_{r,i},\partial V,mix} = -\frac{1}{V} \tag{171}$$

$$\bar{\theta}_{P_{r,i},\partial V,mix} = \frac{[C]k_{0,i}\alpha_{,i}}{Vk_{\infty,i}} \tag{172}$$

For species m as the third-body

$$\frac{\partial P_{r,i}}{\partial T} = \frac{P_{r,i}}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) - \frac{[C]k_{0,i}\delta_m}{Tk_{\infty,i}} \tag{173}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{k_{0,i}}{Vk_{\infty,i}}\left(-\delta_m + \delta_{jm}\right) \tag{174}$$

$$\frac{\partial P_{r,i}}{\partial V} = -\frac{P_{r,i}}{V} + \frac{[C]k_{0,i}\delta_m}{Vk_{\infty,i}} \tag{175}$$

Simplifying:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T,spec} + \bar{\theta}_{P_{r,i},\partial T,spec} \tag{176}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{\bar{\theta}_{P_{r,i},\partial n_j,spec}}{V k_{\infty,i}} k_{0,i} \tag{177}$$

$$\frac{\partial P_{r,i}}{\partial V} = P_{r,i}\Theta_{P_{r,i},\partial V,spec} + \bar{\theta}_{P_{r,i},\partial V,spec} \tag{178}$$

$$\Theta_{P_{r,i},\partial T,spec} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \tag{179}$$

$$\bar{\theta}_{P_{r,i},\partial T,spec} = -\frac{[C]k_{0,i}\delta_m}{T k_{\infty,i}} \tag{180}$$

$$\bar{\theta}_{P_{r,i},\partial n_j,spec} = -\delta_m + \delta_{jm} \tag{181}$$

$$\Theta_{P_{r,i},\partial V,spec} = -\frac{1}{V} \tag{182}$$

$$\bar{\theta}_{P_{r,i},\partial V,spec} = \frac{[C]k_{0,i}\delta_m}{V k_{\infty,i}} \tag{183}$$

If all $\alpha_{j,i} = 1$ for all species j

$$\frac{\partial P_{r,i}}{\partial T} = \frac{P_{r,i}}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \tag{184}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = 0 \tag{185}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = 0 \tag{186}$$

Simplifying:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T,unity} \tag{187}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \bar{\theta}_{P_{r,i},\partial n_j,unity} \tag{188}$$

$$\frac{\partial P_{r,i}}{\partial V} = \bar{\theta}_{P_{r,i},\partial V,unity} \tag{189}$$

$$\Theta_{P_{r,i},\partial T,unity} = \frac{1}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \tag{190}$$

$$\bar{\theta}_{P_{r,i},\partial T,unity} = 0 \tag{191}$$

$$\bar{\theta}_{P_{r,i},\partial n_j,unity} = 0 \tag{192}$$

$$\Theta_{P_{r,i},\partial V,unity} = 0 \tag{193}$$

$$\bar{\theta}_{P_{r,i},\partial V,unity} = 0 \tag{194}$$

Thus we write:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T} \tag{195}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}}{Vk_{\infty,i}} \tag{196}$$

$$\frac{\partial P_{r,i}}{\partial V} = P_{r,i}\Theta_{P_{r,i},\partial V} + \bar{\theta}_{P_{r,i},\partial V} \tag{197}$$

For

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \quad \text{if mix} \tag{198a}$$

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \quad \text{if species} \tag{198b}$$

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \quad \text{if unity} \tag{198c}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\alpha_{,i}}{Tk_{\infty,i}} \quad \text{if mix} \tag{199a}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\delta_m}{Tk_{\infty,i}} \quad \text{if species} \tag{199b}$$

$$\bar{\theta}_{P_{r,i},\partial T} = 0 \quad \text{if unity} \tag{199c}$$

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\alpha_{,i} + \alpha_{j,i} \quad \text{if mix} \tag{200a}$$

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\delta_m + \delta_{jm} \quad \text{if species} \tag{200b}$$

$$\bar{\theta}_{P_{r,i},\partial n_j} = 0 \quad \text{if unity} \tag{200c}$$

$$\Theta_{P_{r,i},\partial V} = -\frac{1}{V} \quad \text{if mix} \tag{201a}$$

$$\Theta_{P_{r,i},\partial V} = -\frac{1}{V} \quad \text{if species} \tag{201b}$$

$$\Theta_{P_{r,i},\partial V} = 0 \quad \text{if unity} \tag{201c}$$

$$\bar{\theta}_{P_{r,i},\partial V} = \frac{[C]k_{0,i}\alpha_{,i}}{Vk_{\infty,i}} \quad \text{if mix} \tag{202a}$$

$$\bar{\theta}_{P_{r,i},\partial V} = \frac{[C]k_{0,i}\delta_m}{Vk_{\infty,i}} \quad \text{if species} \tag{202b}$$

$$\bar{\theta}_{P_{r,i},\partial V} = 0 \quad \text{if unity} \tag{202c}$$

15.6 Falloff Blending Factor derivatives

For Lindemann reactions

$$\frac{\partial F_i}{\partial T} = 0 \tag{203}$$

$$\frac{\partial F_i}{\partial n[j]} = 0 \tag{204}$$

$$\frac{\partial F_i}{\partial V} = 0 \tag{205}$$

For Troe reactions

$$\frac{\partial F_i}{\partial T} = \frac{\partial F_i}{\partial F_{cent}} \frac{\mathrm{d}F_{cent}}{\mathrm{d}T} + \frac{\partial F_i}{\partial P_{r,i}} \frac{\partial P_{r,i}}{\partial T} \tag{206}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{\partial F_i}{\partial P_{r,i}} \frac{\partial P_{r,i}}{\partial n[j]} \tag{207}$$

$$\frac{\partial F_i}{\partial V} = \frac{\partial F_i}{\partial P_{r,i}} \frac{\partial P_{r,i}}{\partial V} \tag{208}$$

where

$$\frac{\partial F_i}{\partial F_{cent}} = \frac{F_i}{\frac{A_{Troe}^2}{B_{Troe}^2} + 1} \left(\frac{2 A_{Troe} \log\left(F_{cent}\right)}{B_{Troe}^2 \left(\frac{A_{Troe}^2}{B_{Troe}^2} + 1\right)} \left(\frac{A_{Troe}}{B_{Troe}} \frac{\partial B_{Troe}}{\partial F_{cent}} - \frac{\partial A_{Troe}}{\partial F_{cent}} \right) + \frac{1}{F_{cent}} \right) \tag{209}$$

$$\frac{\mathrm{d}F_{cent}}{\mathrm{d}T} = -\frac{a}{T^{*}} \exp\left(-\frac{T}{T^{*}}\right) - \frac{\exp\left(-\frac{T}{T^{***}}\right)}{T^{***}} (-a+1) + \frac{T^{**}}{T^2} \exp\left(-\frac{T^{**}}{T}\right) \tag{210}$$

$$\frac{\partial F_i}{\partial P_{r,i}} = \frac{2 F_i A_{Troe} \log\left(F_{cent}\right)}{B_{Troe}^2 \left(\frac{A_{Troe}^2}{B_{Troe}^2} + 1\right)^2} \left(\frac{A_{Troe}}{B_{Troe}} \frac{\partial B_{Troe}}{\partial P_{r,i}} - \frac{\partial A_{Troe}}{\partial P_{r,i}} \right) \tag{211}$$

And

$$\frac{\partial A_{Troe}}{\partial F_{cent}} = -\frac{0.67}{F_{cent} \log\left(10\right)} \tag{212}$$

$$\frac{\partial B_{Troe}}{\partial F_{cent}} = -\frac{1.1762}{F_{cent} \log\left(10\right)} \tag{213}$$

$$\frac{\partial A_{Troe}}{\partial P_{r,i}} = \frac{1}{P_{r,i} \log\left(10\right)} \tag{214}$$

$$\frac{\partial B_{Troe}}{\partial P_{r,i}} = -\frac{0.14}{P_{r,i} \log\left(10\right)} \tag{215}$$

Thus

$$\frac{\partial F_i}{\partial F_{cent}} = -\frac{F_i B_{Troe}}{F_{cent}\left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)}\left(2A_{Troe}\left(1.1762A_{Troe} - 0.67B_{Troe}\right)\log(F_{cent}) - B_{Troe}\left(A_{Troe}^2 + B_{Troe}^2\right)\log(10)\right) \tag{216}$$

$$\frac{\partial F_i}{\partial P_{r,i}} = -\frac{2F_i A_{Troe}\left(\frac{0.14A_{Troe}}{B_{Troe}} + 1\right)\log(F_{cent})}{B_{Troe}^2 P_{r,i}\left(\frac{A_{Troe}^2}{B_{Troe}^2} + 1\right)^2 \log(10)} \tag{217}$$

And

$$\frac{\partial F_i}{\partial T} = F_i \Theta_{F_i,\partial T} \tag{218}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{F_i k_{0,i} \Theta_{F_i,\partial n_j}}{V k_{\infty,i}} \bar{\theta}_{P_{r,i},\partial n_j} \tag{219}$$

$$\frac{\partial F_i}{\partial V} = F_i \Theta_{F_i,\partial V} \tag{220}$$

Where

$$\Theta_{F_i,\partial T} = -\frac{B_{Troe}}{F_{cent} P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)}\Bigg(2A_{Troe}F_{cent}\left(0.14A_{Troe} + B_{Troe}\right)\left(P_{r,i}\Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right)\log(F_{cent}) + P_{r,i}\frac{\mathrm{d}F_{cent}}{\mathrm{d}T}\left(2A_{Troe}\left(1.1762A_{Troe} - 0.67B_{Troe}\right)\log(F_{cent}) - B_{Troe}\left(A_{Troe}^2 + B_{Troe}^2\right)\log(10)\right)\Bigg) \tag{221}$$

$$\Theta_{F_i,\partial n_j} = -\frac{2A_{Troe}B_{Troe}\left(0.14A_{Troe} + B_{Troe}\right)\log(F_{cent})}{P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)} \tag{222}$$

$$\Theta_{F_i,\partial V} = -\frac{2A_{Troe}B_{Troe}\log(F_{cent})}{P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)}\left(0.14A_{Troe} + B_{Troe}\right)\left(P_{r,i}\Theta_{P_{r,i},\partial V} + \bar{\theta}_{P_{r,i},\partial V}\right) \tag{223}$$

For SRI reactions

$$\frac{\partial F_i}{\partial T} = F_i\left(\frac{X\left(-\frac{\exp\left(-\frac{T}{c}\right)}{c} + \frac{ab}{T^2}\exp\left(-\frac{b}{T}\right)\right)}{a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)} + \frac{\partial P_{r,i}}{\partial T}\frac{\mathrm{d}X}{\mathrm{d}P_{r,i}}\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right) + \frac{e}{T}\right) \tag{224}$$

$$\frac{\partial F_i}{\partial n[j]} = F_i \frac{\partial P_{r,i}}{\partial n[j]} \frac{\mathrm{d}X}{\mathrm{d}P_{r,i}} \log\left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right) \tag{225}$$

$$\frac{\partial F_i}{\partial V} = F_i \frac{\partial P_{r,i}}{\partial V} \frac{\mathrm{d}X}{\mathrm{d}P_{r,i}} \log\left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right) \tag{226}$$

Where

$$\frac{\mathrm{d}X}{\mathrm{d}P_{r,i}} = -\frac{2X^2 \log(P_{r,i})}{P_{r,i}\log^2(10)} \tag{227}$$

$$\frac{\partial X}{\partial n_j} = \frac{\partial P_{r,i}}{\partial n[j]} \frac{\mathrm{d}X}{\mathrm{d}P_{r,i}} \tag{228}$$

And

$$\frac{\partial F_i}{\partial T} = F_i \Theta_{F_i,\partial T} \tag{229}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{F_i k_{0,i} \Theta_{F_i,\partial n_j}}{V k_{\infty,i}} \bar{\theta}_{P_{r,i},\partial n_j} \tag{230}$$

$$\frac{\partial F_i}{\partial V} = F_i \Theta_{F_i,\partial V} \tag{231}$$

Where

$$\begin{aligned}\Theta_{F_i,\partial T} = &-\frac{X\left(\frac{\exp\left(-\frac{T}{c}\right)}{c} - \frac{ab}{T^2}\exp\left(-\frac{b}{T}\right)\right)}{a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)} + \frac{e}{T} \\ &- \frac{2X^2\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2(10)}\left(P_{r,i}\Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right)\log(P_{r,i})\end{aligned} \tag{232}$$

$$\Theta_{F_i,\partial n_j} = -\frac{2X^2\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2(10)}\log(P_{r,i}) \tag{233}$$

$$\begin{aligned}\Theta_{F_i,\partial V} = &-\frac{2X^2\log(P_{r,i})}{P_{r,i}\log^2(10)}\left(P_{r,i}\Theta_{P_{r,i},\partial V}\right. \\ &\left.+\bar{\theta}_{P_{r,i},\partial V}\right)\log\left(\left(a\exp\left(\frac{T}{c}\right) + \exp\left(\frac{b}{T}\right)\right)\exp\left(-\frac{T}{c} - \frac{b}{T}\right)\right)\end{aligned} \tag{234}$$

Simplifying:

$$\frac{\partial F_i}{\partial T} = F_i \Theta_{F_i,\partial T} \tag{235}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{F_i k_{0,i} \Theta_{F_i,\partial n_j}}{V k_{\infty,i}} \bar{\theta}_{P_{r,i},\partial n_j} \tag{236}$$

$$\frac{\partial F_i}{\partial V} = F_i \Theta_{F_i,\partial V} \tag{237}$$

Where:

$$\Theta_{F_i,\partial T} = 0 \quad \text{if Lindemann} \tag{238a}$$

$$\begin{aligned}\Theta_{F_i,\partial T} = &-\frac{B_{Troe}}{F_{cent} P_{r,i} \left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)} \Big(2 A_{Troe} F_{cent} \left(0.14 A_{Troe}\right.\\ &\left. + B_{Troe}\right) \left(P_{r,i} \Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right) \log(F_{cent})\\ &+ P_{r,i} \frac{\mathrm{d}F_{cent}}{\mathrm{d}T} \left(2 A_{Troe} \left(1.1762 A_{Troe} - 0.67 B_{Troe}\right) \log(F_{cent})\right.\\ &\left. - B_{Troe} \left(A_{Troe}^2 + B_{Troe}^2\right) \log(10)\right)\Big) \quad \text{if Troe}\end{aligned} \tag{238b}$$

$$\begin{aligned}\Theta_{F_i,\partial T} = &-\frac{X \left(\frac{\exp\left(-\frac{T}{c}\right)}{c} - \frac{ab}{T^2} \exp\left(-\frac{b}{T}\right)\right)}{a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)} + \frac{e}{T}\\ &- \frac{2X^2 \log\left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i} \log^2(10)} \left(P_{r,i} \Theta_{P_{r,i},\partial T}\right.\\ &\left. + \bar{\theta}_{P_{r,i},\partial T}\right) \log(P_{r,i}) \quad \text{if SRI}\end{aligned} \tag{238c}$$

$$\Theta_{F_i,\partial n_j} = 0 \quad \text{if Lindemann} \tag{239a}$$

$$\Theta_{F_i,\partial n_j} = -\frac{2 A_{Troe} B_{Troe} \left(0.14 A_{Troe} + B_{Troe}\right) \log(F_{cent})}{P_{r,i} \left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)} \quad \text{if Troe} \tag{239b}$$

$$\Theta_{F_i,\partial n_j} = -\frac{2X^2 \log\left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i} \log^2(10)} \log(P_{r,i}) \quad \text{if SRI} \tag{239c}$$

$$\Theta_{F_i,\partial V} = 0 \quad \text{if Lindemann} \tag{240a}$$

$$\begin{aligned}\Theta_{F_i,\partial V} = &-\frac{2 A_{Troe} B_{Troe} \log(F_{cent})}{P_{r,i} \left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)} \left(0.14 A_{Troe} + B_{Troe}\right) \left(P_{r,i} \Theta_{P_{r,i},\partial V}\right.\\ &\left. + \bar{\theta}_{P_{r,i},\partial V}\right) \quad \text{if Troe}\end{aligned} \tag{240b}$$

$$\begin{aligned}\Theta_{F_i,\partial V} = &-\frac{2X^2 \log(P_{r,i})}{P_{r,i} \log^2(10)} \left(P_{r,i} \Theta_{P_{r,i},\partial V}\right.\\ &\left. + \bar{\theta}_{P_{r,i},\partial V}\right) \log\left(\left(a \exp\left(\frac{T}{c}\right) + \exp\left(\frac{b}{T}\right)\right) \exp\left(-\frac{T}{c} - \frac{b}{T}\right)\right) \quad \text{if SRI}\end{aligned} \tag{240c}$$

15.7 Unimolecular/recombination fall-off reactions (complete)

$$\frac{\partial c}{\partial T}_i = \frac{F_i \bar{\theta}_{P_{r,i},\partial T}}{P_{r,i} + 1} + \left(-\frac{P_{r,i} \Theta_{P_{r,i},\partial T}}{P_{r,i} + 1} + \Theta_{F_i,\partial T} + \Theta_{P_{r,i},\partial T} - \frac{\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i} + 1}\right) c_i \tag{241}$$

$$\frac{\partial c}{\partial n[j]}_i = \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}}{V k_{\infty,i}\left(P_{r,i}+1\right)}\left(F_i\left(P_{r,i}\Theta_{F_i,\partial n_j}+1\right)-c_i\right) \tag{242}$$

$$\frac{\partial c}{\partial V}_i = \frac{F_i\bar{\theta}_{P_{r,i},\partial V}}{P_{r,i}+1} + \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial V}}{P_{r,i}+1} + \Theta_{F_i,\partial V} + \Theta_{P_{r,i},\partial V} - \frac{\bar{\theta}_{P_{r,i},\partial V}}{P_{r,i}+1}\right)c_i \tag{243}$$

15.8 Chemically-activated bimolecular reactions (complete)

$$\frac{\partial c}{\partial T}_i = \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial T}}{P_{r,i}+1} + \Theta_{F_i,\partial T} - \frac{\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1}\right)c_i \tag{244}$$

$$\frac{\partial c}{\partial n[j]}_i = \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}\left(F_i\Theta_{F_i,\partial n_j}-c_i\right)}{V k_{\infty,i}\left(P_{r,i}+1\right)} \tag{245}$$

$$\frac{\partial c}{\partial V}_i = \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial V}}{P_{r,i}+1} + \Theta_{F_i,\partial V} - \frac{\bar{\theta}_{P_{r,i},\partial V}}{P_{r,i}+1}\right)c_i \tag{246}$$

16 Pressure-dependent reaction derivatives

For PLog reactions

$$\begin{aligned}\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \Bigg(\frac{1}{k_1}\frac{\mathrm{d}k_1}{\mathrm{d}T} + \frac{1}{-\log\left(P_1\right)+\log\left(P_2\right)}\Bigg(-\frac{1}{k_1}\frac{\mathrm{d}k_1}{\mathrm{d}T} \\ + \frac{1}{k_2}\frac{\mathrm{d}k_2}{\mathrm{d}T}\Bigg)\left(-\log\left(P_1\right)+\log\left(P\right)\right)\Bigg){k_f}_i\end{aligned} \tag{247}$$

$$\begin{aligned}\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \Bigg(\frac{1}{-\log\left(P_1\right)+\log\left(P_2\right)}\Bigg(-\frac{1}{T}\left(\beta_1+\frac{E_{a_1}}{T}\right) \\ + \frac{1}{T}\left(\beta_2+\frac{E_{a_2}}{T}\right)\Bigg)\left(-\log\left(P_1\right)+\log\left(P\right)\right) + \frac{1}{T}\left(\beta_1+\frac{E_{a_1}}{T}\right)\Bigg){k_f}_i\end{aligned} \tag{248}$$

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \frac{{k_f}_i}{T}\left(\beta_1 + \frac{\left(-\log\left(P_1\right)+\log\left(P\right)\right)\left(-\beta_1+\beta_2-\frac{E_{a_1}}{T}+\frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right)+\log\left(P_2\right)} + \frac{E_{a_1}}{T}\right) \tag{249}$$

$$\begin{aligned}\frac{\partial R_f}{\partial T}_i = -\frac{[C]S'}{T}{k_f}_i + \frac{{R_f}_i}{T}\Bigg(\beta_1 \\ + \frac{\left(-\log\left(P_1\right)+\log\left(P\right)\right)\left(-\beta_1+\beta_2-\frac{E_{a_1}}{T}+\frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right)+\log\left(P_2\right)} + \frac{E_{a_1}}{T}\Bigg)\end{aligned} \tag{250}$$

$$\frac{\mathrm{d}k_r}{\mathrm{d}T}_i = \left(-\sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T} \left(\beta_1 \right.\right.$$
$$\left.\left. + \frac{\left(-\log\left(P_1\right) + \log\left(P\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T} + \frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{T} \right)\right) k_{r\,i} \tag{251}$$

$$\frac{\partial R_r}{\partial T}_i = \left(-\sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T} \left(\beta_1 \right.\right.$$
$$\left.\left. + \frac{\left(-\log\left(P_1\right) + \log\left(P\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T} + \frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{T} \right)\right) R_{r\,i}$$
$$- \frac{[C]S''}{T} k_{r\,i} \tag{252}$$

$$\frac{\partial R}{\partial T}_i = -\left(-\sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T} \left(\beta_1 \right.\right.$$
$$\left.\left. + \frac{\left(-\log\left(P_1\right) + \log\left(P\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T} + \frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{T} \right)\right) R_{r\,i}$$
$$+ \frac{[C]}{T}\left(S'' k_{r\,i} - S' k_{f\,i}\right)$$
$$+ \frac{R_{f\,i}}{T}\left(\beta_1 + \frac{\left(-\log\left(P_1\right) + \log\left(P\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T} + \frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{T} \right) \tag{253}$$

For Chebyshev reactions

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \log(10) k_{f\,i} \sum_{\substack{1\le l\le N_P\\ 1\le j\le N_T}} \frac{\mathrm{d}\tilde{T}}{\mathrm{d}T}\left(j-1\right) T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j} \tag{254}$$

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \log(10) k_{f\,i} \sum_{\substack{1\le l\le N_P\\ 1\le j\le N_T}} -\frac{2T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right)\eta_{l,j}}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)}\left(j-1\right) \tag{255}$$

$$\frac{\partial R_f}{\partial T}_i = \log(10) R_{f\,i} \sum_{\substack{1\le l\le N_P\\ 1\le j\le N_T}} -\frac{2T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right)\eta_{l,j}}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)}\left(j-1\right) - \frac{[C]S'}{T} k_{f\,i} \tag{256}$$

$$\frac{\mathrm{d}k_r}{\mathrm{d}T}_i = -\left(\sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} (j - 1)\, T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}\right) k_{r\,i} \tag{257}$$

$$\frac{\partial R_r}{\partial T}_i = -\left(\sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} (j - 1)\, T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}\right) R_{r\,i} - \frac{[C]S''}{T} k_{r\,i} \tag{258}$$

$$\begin{aligned}\frac{\partial R}{\partial T}_i = &\left(\sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k\right.\\ &\left.+ \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} (j - 1)\, T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}\right) R_{r\,i}\\ &+ \log(10) R_{f\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} - \frac{2T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} (j - 1)\\ &+ \frac{[C]}{T}\left(S'' k_{r\,i} - S' k_{f\,i}\right)\end{aligned} \tag{259}$$

17 Jacobian entries

17.1 Energy Equation

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{1}{\sum_{k=1}[C]_k C_{p_k}} \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \dot{\omega}_k \tag{260}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{-1+}\left(H_k - \frac{W_k H}{W}\right)\dot{\omega}_k}{\left(-\sum_{k=1}^{-1+}[C]_k + \frac{P}{T}\right) C_p + \sum_{k=1}^{-1+}[C]_k C_{p_k}} \tag{261}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \dot{\omega}_k}{[C]C_p + \sum_{k=1}^{-1+} \left(-C_p + C_{p_k}\right) [C]_k} \tag{262}$$

17.2 $\dot{T}$ Derivatives

Molar derivative

$$\begin{aligned}\frac{\partial \dot{T}}{\partial n_j} = &-\frac{\sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \frac{\partial \dot{\omega}}{\partial n[j]}_k}{[C]C_p + \sum_{k=1}^{-1+} -\left(C_p - C_{p_k}\right) [C]_k} \\ &+ \frac{\left(\sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \dot{\omega}_k\right) \sum_{k=1}^{-1+} -\frac{\delta_{jk}}{V} \left(C_p - C_{p_k}\right)}{\left([C]C_p + \sum_{k=1}^{-1+} -\left(C_p - C_{p_k}\right) [C]_k\right)^2}\end{aligned} \tag{263}$$

$$\begin{aligned}\frac{\partial \dot{T}}{\partial n_j} = &\frac{1}{\left(\sum_{k=1} [C]_k C_{p_k}\right)^2} \left(\sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \dot{\omega}_k\right) \sum_{k=1}^{-1+} \\ &-\frac{\delta_{jk}}{V} \left(C_p - C_{p_k}\right) - \frac{1}{\sum_{k=1} [C]_k C_{p_k}} \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \frac{\partial \dot{\omega}}{\partial n[j]}_k\end{aligned} \tag{264}$$

$$\begin{aligned}\frac{\partial \dot{T}}{\partial n_j} = &-\frac{1}{\sum_{k=1} [C]_k C_{p_k}} \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \frac{\partial \dot{\omega}}{\partial n[j]}_k \\ &+ \frac{1}{V\left(\sum_{k=1} [C]_k C_{p_k}\right)^2} \left(-C_p + C_{p_j}\right) \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \dot{\omega}_k\end{aligned} \tag{265}$$

$$\frac{\partial \dot{T}}{\partial n_j} = \frac{1}{\sum_{k=1} [C]_k C_{p_k}} \left(-\sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \frac{\partial \dot{\omega}}{\partial n[j]}_k - \frac{1}{V} \frac{\mathrm{d}T}{\mathrm{d}t} \left(-C_p + C_{p_j}\right)\right) \tag{266}$$

Temperature derivative

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \dot{\omega}_k}{\sum_{k=1}^{-1+} \left(-C_p + C_{p_k}\right) [C]_k + \frac{P C_p}{T}} \tag{267}$$

$$\begin{aligned}\frac{\partial \dot{T}}{\partial T} = &-\frac{1}{\sum_{k=1}^{-1+} \left(-C_p + C_{p_k}\right) [C]_k + \frac{P C_p}{T}} \sum_{k=1}^{-1+} \left(\left(H_k - \frac{W_k H}{W}\right) \frac{\partial \dot{\omega}}{\partial T}_k \right. \\ &\left. + \left(\frac{\mathrm{d}H}{\mathrm{d}T}_k - \frac{W_k}{W} \frac{\mathrm{d}H}{\mathrm{d}T}\right) \dot{\omega}_k\right) \\ &- \frac{1}{\left(\sum_{k=1}^{-1+} \left(-C_p + C_{p_k}\right) [C]_k + \frac{P C_p}{T}\right)^2} \left(-\sum_{k=1}^{-1+} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T} + \frac{\mathrm{d}C_p}{\mathrm{d}T}_k\right) [C]_k \right. \\ &\left. - \frac{P}{T} \frac{\mathrm{d}C_p}{\mathrm{d}T} + \frac{P C_p}{T^2}\right) \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W}\right) \dot{\omega}_k\end{aligned} \tag{268}$$

$$
\begin{aligned}
\frac{\partial\dot{T}}{\partial T} = &-\frac{1}{[C]C_p + \sum_{k=1}^{-1+} \left(-C_p + C_{p\,k}\right)[C]_k} \sum_{k=1}^{-1+} \left(\left(H_k - \frac{W_k H}{W} \right) \frac{\partial\dot{\omega}}{\partial T}_k \right. \\
&\qquad \left. + \left(\frac{\mathrm{d}H}{\mathrm{d}T}_k - \frac{W_k}{W}\frac{\mathrm{d}H}{\mathrm{d}T} \right) \dot{\omega}_k \right) \\
&- \frac{1}{\left([C]C_p + \sum_{k=1}^{-1+} \left(-C_p + C_{p\,k}\right)[C]_k\right)^2} \left(-[C]\frac{\mathrm{d}C_p}{\mathrm{d}T} \right. \\
&\left. - \sum_{k=1}^{-1+} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T} + \frac{\mathrm{d}C_p}{\mathrm{d}T}_k \right)[C]_k + \frac{[C]C_p}{T} \right) \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W} \right) \dot{\omega}_k
\end{aligned}
\tag{269}
$$

$$
\begin{aligned}
\frac{\partial\dot{T}}{\partial T} = &-\frac{1}{\left(\sum_{k=1}[C]_k C_{p\,k}\right)^2} \left(-[C]\frac{\mathrm{d}C_p}{\mathrm{d}T} - \sum_{k=1}^{-1+} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T} + \frac{\mathrm{d}C_p}{\mathrm{d}T}_k \right)[C]_k \right. \\
&\qquad \left. + \frac{[C]C_p}{T} \right) \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W} \right) \dot{\omega}_k \\
&- \frac{1}{\sum_{k=1}[C]_k C_{p\,k}} \sum_{k=1}^{-1+} \left(\left(H_k - \frac{W_k H}{W} \right) \frac{\partial\dot{\omega}}{\partial T}_k + \left(\frac{\mathrm{d}H}{\mathrm{d}T}_k - \frac{W_k}{W}\frac{\mathrm{d}H}{\mathrm{d}T} \right) \dot{\omega}_k \right)
\end{aligned}
\tag{270}
$$

$$
\begin{aligned}
\frac{\partial\dot{T}}{\partial T} = &-\frac{1}{\sum_{k=1}[C]_k C_{p\,k}} \left(\frac{1}{\sum_{k=1}[C]_k C_{p\,k}} \left(-[C]\frac{\mathrm{d}C_p}{\mathrm{d}T} \right. \right. \\
&\left. - \sum_{k=1}^{-1+} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T} + \frac{\mathrm{d}C_p}{\mathrm{d}T}_k \right)[C]_k + \frac{[C]C_p}{T} \right) \sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W} \right) \dot{\omega}_k \\
&\left. + \sum_{k=1}^{-1+} \left(\left(H_k - \frac{W_k H}{W} \right) \frac{\partial\dot{\omega}}{\partial T}_k + \left(\frac{\mathrm{d}H}{\mathrm{d}T}_k - \frac{W_k}{W}\frac{\mathrm{d}H}{\mathrm{d}T} \right) \dot{\omega}_k \right) \right)
\end{aligned}
\tag{271}
$$

$$
\begin{aligned}
\frac{\partial\dot{T}}{\partial T} = &\frac{1}{\sum_{k=1}[C]_k C_{p\,k}} \left(\frac{\mathrm{d}T}{\mathrm{d}t} \left(-[C]\frac{\mathrm{d}C_p}{\mathrm{d}T} - \sum_{k=1}^{-1+} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T} + \frac{\mathrm{d}C_p}{\mathrm{d}T}_k \right)[C]_k + \frac{[C]C_p}{T} \right) \right. \\
&\left. - \sum_{k=1}^{-1+} \left(\left(H_k - \frac{W_k H}{W} \right) \frac{\partial\dot{\omega}}{\partial T}_k + \left(\frac{\mathrm{d}H}{\mathrm{d}T}_k - \frac{W_k}{W}\frac{\mathrm{d}H}{\mathrm{d}T} \right) \dot{\omega}_k \right) \right)
\end{aligned}
\tag{272}
$$

$$
\begin{aligned}
\frac{\partial\dot{T}}{\partial T} = &\frac{1}{\sum_{k=1}[C]_k C_{p\,k}} \left(\frac{\mathrm{d}T}{\mathrm{d}t} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T} \sum_{k=1}[C]_k - \sum_{k=1}^{-1+} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T} + \frac{\mathrm{d}C_p}{\mathrm{d}T}_k \right)[C]_k \right. \right. \\
&\left. \left. + \frac{C_p}{T} \sum_{k=1}[C]_k \right) - \sum_{k=1}^{-1+} \left(\left(H_k - \frac{W_k H}{W} \right) \frac{\partial\dot{\omega}}{\partial T}_k + \left(\frac{\mathrm{d}H}{\mathrm{d}T}_k - \frac{W_k}{W}\frac{\mathrm{d}H}{\mathrm{d}T} \right) \dot{\omega}_k \right) \right)
\end{aligned}
\tag{273}
$$

$$
\begin{aligned}
\frac{\partial \dot{T}}{\partial T} = \frac{1}{\sum_{k=1}[C]_k C_{p_k}} \Bigg(& \frac{\mathrm{d}T}{\mathrm{d}t} \sum_{k=1} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T}_k + \frac{C_p}{T} \right) [C]_k \\
& + \sum_{k=1}^{-1+} \left(\left(-H_k + \frac{W_k H}{W} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(-\frac{\mathrm{d}H}{\mathrm{d}T}_k + \frac{W_k}{W} \frac{\mathrm{d}H}{\mathrm{d}T} \right) \dot{\omega}_k \right) \Bigg)
\end{aligned} \tag{274}
$$

$$
\begin{aligned}
\frac{\partial \dot{T}}{\partial T} = \frac{1}{\sum_{k=1}[C]_k C_{p_k}} \Bigg(& \frac{\mathrm{d}T}{\mathrm{d}t} \sum_{k=1} \left(-\frac{\mathrm{d}C_p}{\mathrm{d}T}_k + \frac{C_p}{T} \right) [C]_k \\
& + \sum_{k=1}^{-1+} \left(\left(-H_k + \frac{W_k H}{W} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(-C_{p_k} + \frac{W_k}{W} \frac{\mathrm{d}H}{\mathrm{d}T} \right) \dot{\omega}_k \right) \Bigg)
\end{aligned} \tag{275}
$$

Volume Derivative

$$
\begin{aligned}
& \frac{\partial \dot{T}}{\partial V} \\
& = \frac{1}{\sum_{k=1}[C]_k C_{p_k}} \left(-\sum_{k=1}^{-1+} \left(H_k - \frac{W_k H}{W} \right) \frac{\partial \dot{\omega}}{\partial V}_k + \frac{1}{V} \frac{\mathrm{d}T}{\mathrm{d}t} \sum_{k=1}^{-1+} \left(-C_p + C_{p_k} \right) [C]_k \right)
\end{aligned} \tag{276}
$$

17.3 $\dot{V}$ Derivatives

Temperature Derivative

$$
\frac{\partial \dot{V}}{\partial T} = \frac{V}{[C]} \sum_{k=1}^{-1+} \left(1 - \frac{W_k}{W} \right) \left(\frac{\partial \dot{\omega}}{\partial T}_k + \frac{\dot{\omega}_k}{T} \right) + \frac{V}{T} \left(\frac{\mathrm{d}\dot{T}}{\mathrm{d}T} - \frac{1}{T} \frac{\mathrm{d}T}{\mathrm{d}t} \right) \tag{277}
$$

Molar Derivative

$$
\frac{\partial \dot{V}}{\partial n[j]} = V \left(\frac{1}{[C]} \sum_{k=1}^{-1+} \left(1 - \frac{W_k}{W} \right) \frac{\partial \dot{\omega}}{\partial n[j]}_k + \frac{1}{T} \frac{\mathrm{d}\dot{T}}{\mathrm{d}n[j]} \right) \tag{278}
$$

Volume Derivative

$$
\frac{\partial \dot{V}}{\partial V} = \frac{1}{[C]} \sum_{k=1}^{-1+} \left(1 - \frac{W_k}{W} \right) \left(V \frac{\partial \dot{\omega}}{\partial V}_k + \dot{\omega}_k \right) + \frac{1}{T} \left(V \frac{\mathrm{d}\dot{T}}{\mathrm{d}V} + \dot{T} \right) \tag{279}
$$

17.4 $\dot{n}_k$ Derivatives

$$
\frac{\partial \dot{n}}{\partial n[j]}_k = V \frac{\partial \dot{\omega}}{\partial n[j]}_k \tag{280}
$$

$$
\frac{\partial \dot{n}}{\partial T}_k = V \frac{\partial \dot{\omega}}{\partial T}_k \tag{281}
$$

$$
\frac{\partial \dot{n}}{\partial V}_k = V \frac{\partial \dot{\omega}}{\partial V}_k + \dot{\omega}_k \tag{282}
$$

18 Jacobian Update Form

18.1 Temperature Derivatives

$$\begin{aligned}\mathcal{J}_{1,1} = \frac{1}{\sum_{k=1}[C]_k C_{p_k}} &\left(\frac{\mathrm{d}T}{\mathrm{d}t}\sum_{k=1}\left(-\frac{\mathrm{d}C_p}{\mathrm{d}T}_k + \frac{C_p}{T}\right)[C]_k\right. \\ &\left.+\sum_{k=1}^{-1+}\left(\left(-C_{p_k} + \frac{W_k}{W}\frac{\mathrm{d}H}{\mathrm{d}T}\right)\dot{\omega}_k + \frac{1}{V}\left(-H_k + \frac{W_k H}{W}\right)\frac{\partial \dot{n}}{\partial T}_k\right)\right)\end{aligned} \tag{283}$$

$$\mathcal{J}_{2,1} = \frac{V}{[C]}\sum_{k=1}^{-1+}\left(1 - \frac{W_k}{W}\right)\left(\frac{1}{V}\frac{\partial \dot{n}}{\partial T}_k + \frac{\dot{\omega}_k}{T}\right) + \frac{V}{T}\left(\frac{\mathrm{d}\dot{T}}{\mathrm{d}T} - \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t}\right) \tag{284}$$

$$\mathcal{J}_{k+2,1} = V\sum_{i=1}\nu_{k,i}\frac{\partial q}{\partial T}_i \tag{285}$$

Converting to update form:

$$\mathcal{J}_{k+2,1} \mathrel{+}= V\nu_{k,i}\frac{\partial q}{\partial T}_i \quad k = 1, \ldots, N_{sp} - 1 \tag{286}$$

18.1.1 Explicit reversible reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} c_i + R_i \frac{\partial c}{\partial T}_i \tag{287}$$

$$\Theta_{\partial T,i} = \frac{[C]S''}{T}k_{r\,i} - \frac{[C]S'}{T}k_{f\,i} + \frac{R_{f\,i}}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right) - \frac{R_{r\,i}}{T}\left(\beta_{r\,i} + \frac{E_{a,r\,i}}{T}\right) \tag{288}$$

18.1.2 Non-explicit reversible reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} c_i + R_i \frac{\partial c}{\partial T}_i \tag{289}$$

$$\begin{aligned}\Theta_{\partial T,i} = -&\left(-\sum_{k=1}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\right)R_{r\,i} \\ &+ \frac{[C]S''}{T}k_{r\,i} - \frac{[C]S'}{T}k_{f\,i} + \frac{R_{f\,i}}{T}\left(\beta_i + \frac{E_{a\,i}}{T}\right)\end{aligned} \tag{290}$$

18.1.3 Pressure-dependent reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} \tag{291}$$

For PLog reactions:

$$\begin{aligned}\Theta_{\partial T,i} = &- \left(- \sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T} \left(\beta_1 \right.\right. \\ &\left.\left. + \frac{\left(-\log\left(P_1\right) + \log\left(P\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T} + \frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{T} \right) \right) R_{r\,i} \\ &+ \frac{[C]}{T}\left(S'' k_{r\,i} - S' k_{f\,i}\right) \\ &+ \frac{R_{f\,i}}{T}\left(\beta_1 + \frac{\left(-\log\left(P_1\right) + \log\left(P\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T} + \frac{E_{a_2}}{T}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{T}\right)\end{aligned} \tag{292}$$

For Chebyshev reactions:

$$\begin{aligned}\Theta_{\partial T,i} = &\left(\sum_{k=1} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k \right. \\ &\left. + \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} \sum_{\substack{1 \le l \le N_P \\ 1 \le j \le N_T}} (j-1)\, T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j} \right) R_{r\,i} \\ &+ \log(10) R_{f\,i} \sum_{\substack{1 \le l \le N_P \\ 1 \le j \le N_T}} - \frac{2 T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} (j-1) \\ &+ \frac{[C]}{T}\left(S'' k_{r\,i} - S' k_{f\,i}\right)\end{aligned} \tag{293}$$

18.1.4 Pressure independent reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} \tag{294}$$

18.1.5 Third-body enhanced reactions

For mixture as third-body:

$$\frac{\partial q}{\partial T}_i = [X]_i \Theta_{\partial T,i} - \frac{[C]\alpha_{,i}}{T} R_i \tag{295}$$

For species m as third-body:

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i}\left(\left(-\delta_m + 1\right)[C]_m + \delta_m[C]\right) - \frac{\delta_m}{T}[C]R_i \tag{296}$$

If all $\alpha_{j,i} = 1$ for all species j:

$$\frac{\partial q}{\partial T}_i = [C]\left(\Theta_{\partial T,i} - \frac{R_i}{T}\right) \tag{297}$$

18.1.6 Unimolecular/recombination fall-off reactions

$$\begin{aligned}\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i}c_i + \Bigg(&\frac{F_i\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1} \\ &+ \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial T}}{P_{r,i}+1} + \Theta_{F_i,\partial T} + \Theta_{P_{r,i},\partial T} - \frac{\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1}\right)c_i\Bigg)R_i\end{aligned} \tag{298}$$

18.1.7 Chemically-activated bimolecular reactions

$$\frac{\partial q}{\partial T}_i = \left(\Theta_{\partial T,i} + \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial T}}{P_{r,i}+1} + \Theta_{F_i,\partial T} - \frac{\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1}\right)R_i\right)c_i \tag{299}$$

18.1.8 Reduced Pressure Derivatives

For mixture as third-body:

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \tag{300}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\alpha_{,i}}{Tk_{\infty,i}} \tag{301}$$

For species m as third-body:

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \tag{302}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\delta_m}{Tk_{\infty,i}} \tag{303}$$

If all $\alpha_{j,i} = 1$ for all species j:

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{T} - \frac{E_{a,\infty}}{T}\right) \tag{304}$$

$$\bar{\theta}_{P_{r,i},\partial T} = 0 \tag{305}$$

18.1.9 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i,\partial T} = 0 \tag{306}$$

For Troe

$$\begin{aligned}\Theta_{F_i,\partial T} = -\frac{B_{Troe}}{F_{cent} P_{r,i} \left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)} \Bigg(& 2 A_{Troe} F_{cent} \left(0.14 A_{Troe} \right.\\ & \left. + B_{Troe}\right) \left(P_{r,i} \Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right) \log\left(F_{cent}\right) \\ & + P_{r,i} \frac{\mathrm{d} F_{cent}}{\mathrm{d} T} \left(2 A_{Troe} \left(1.1762 A_{Troe} - 0.67 B_{Troe}\right) \log\left(F_{cent}\right) \right.\\ & \left. - B_{Troe} \left(A_{Troe}^2 + B_{Troe}^2\right) \log(10)\right)\Bigg)\end{aligned} \tag{307}$$

For SRI

$$\begin{aligned}\Theta_{F_i,\partial T} = & -\frac{X \left(\frac{\exp\left(-\frac{T}{c}\right)}{c} - \frac{ab}{T^2} \exp\left(-\frac{b}{T}\right)\right)}{a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)} + \frac{e}{T} \\ & - \frac{2 X^2 \log\left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i} \log^2(10)} \left(P_{r,i} \Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right) \log\left(P_{r,i}\right)\end{aligned} \tag{308}$$

18.2 Molar Derivatives

$$\begin{aligned}\mathcal{J}_{1,j+2} &= \frac{\partial \dot{T}}{\partial n_j} \\ &= \frac{1}{\sum_{k=1} [C]_k C_{p_k}} \Bigg(- \sum_{k=1}^{-1+} \frac{1}{V} \left(H_k - \frac{W_k H}{W}\right) \frac{\partial \dot{n}}{\partial n[j]}_k \\ & \qquad - \frac{1}{V} \frac{\mathrm{d} T}{\mathrm{d} t} \left(-C_p + C_{p_j}\right)\Bigg)\end{aligned} \tag{309}$$

$$\begin{aligned}\mathcal{J}_{2,j+2} &= \frac{\partial \dot{V}}{\partial n[j]} \\ &= V \left(\frac{1}{[C]} \sum_{k=1}^{-1+} \frac{1}{V} \left(1 - \frac{W_k}{W}\right) \frac{\partial \dot{n}}{\partial n[j]}_k + \frac{1}{T} \frac{\mathrm{d} \dot{T}}{\mathrm{d} n[j]} \right)\end{aligned} \tag{310}$$

$$\begin{aligned}\mathcal{J}_{k+2,j+2} &= \frac{\partial \dot{n}_k}{\partial n_j} \\ &= V \sum_{i=1} \nu_{k,i} \frac{\partial q}{\partial n[j]}_i\end{aligned} \tag{311}$$

Converting to Jacobian Update form:

$$\mathcal{J}_{k+2,j+2} += V\nu_{k,i}\frac{\partial q}{\partial n[j]}_i \tag{312}$$

$$V\frac{\partial q}{\partial n[j]}_k = VR_i\frac{\partial c}{\partial n[j]}_i - \left(\left(-S'' + S''_j\right)k_{ri} - \left(-S' + S'_j\right)k_{fi}\right)c_i \tag{313}$$

18.2.1 Pressure-dependent reactions

$$V\frac{\partial q}{\partial n[j]}_k = -\left(-S'' + S''_j\right)k_{ri} + \left(-S' + S'_j\right)k_{fi} \tag{314}$$

18.2.2 Pressure independent reactions

$$V\frac{\partial q}{\partial n[j]}_k = -\left(-S'' + S''_j\right)k_{ri} + \left(-S' + S'_j\right)k_{fi} \tag{315}$$

18.2.3 Third-body enhanced reactions

For mixture as third-body:

$$V\frac{\partial q}{\partial n[j]}_k = -[X]_i\left(\left(-S'' + S''_j\right)k_{ri} - \left(-S' + S'_j\right)k_{fi}\right) + \left(-\alpha_{,i} + \alpha_{j,i}\right)R_i \tag{316}$$

For species m as third-body:

$$\begin{aligned}V\frac{\partial q}{\partial n[j]}_k =& -\left(\left(-\delta_m+1\right)[C]_m+\delta_m[C]\right)\left(\left(-S''+S''_j\right)k_{ri}-\left(-S'+S'_j\right)k_{fi}\right)\\ &+\left(-\delta_m+\delta_{jm}\right)R_i\end{aligned} \tag{317}$$

If all $\alpha_{j,i} = 1$:

$$V\frac{\partial q}{\partial n[j]}_k = -[C]\left(\left(-S'' + S''_j\right)k_{ri} - \left(-S' + S'_j\right)k_{fi}\right) \tag{318}$$

18.2.4 Falloff Reactions

Unimolecular/recombination fall-off reactions:

$$\begin{aligned}V\frac{\partial q}{\partial n[j]}_i =& \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}R_i}{k_{\infty,i}\left(P_{r,i}+1\right)}\left(F_iP_{r,i}\Theta_{F_i,\partial n_j} + F_i - c_i\right)\\ &+\left(-\left(-S'' + S''_j\right)k_{ri} + \left(-S' + S'_j\right)k_{fi}\right)c_i\end{aligned} \tag{319}$$

18.2.5 Chemically-activated bimolecular reactions

$$\begin{aligned}V\frac{\partial q}{\partial n[j]}_i =& \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}R_i}{k_{\infty,i}\left(P_{r,i}+1\right)}\left(F_i\Theta_{F_i,\partial n_j} - c_i\right)\\ &+\left(-\left(-S'' + S''_j\right)k_{ri} + \left(-S' + S'_j\right)k_{fi}\right)c_i\end{aligned} \tag{320}$$

18.2.6 Reduced Pressure Derivatives

For mixture as third-body:

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\alpha_{,i} + \alpha_{j,i} \tag{321}$$

For species m as third-body:

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\delta_m + \delta_{jm} \tag{322}$$

If all $\alpha_{j,i} = 1$:

$$\bar{\theta}_{P_{r,i},\partial n_j} = 0 \tag{323}$$

18.2.7 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i,\partial n_j} = 0 \tag{324}$$

For Troe

$$\Theta_{F_i,\partial n_j} = -\frac{2A_{Troe}B_{Troe}\left(0.14A_{Troe} + B_{Troe}\right)\log\left(F_{cent}\right)}{P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2\log\left(10\right)} \tag{325}$$

For SRI

$$\Theta_{F_i,\partial n_j} = -\frac{2X^2\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2\left(10\right)}\log\left(P_{r,i}\right) \tag{326}$$

18.3 Volume Derivatives

$$\begin{aligned}
\mathcal{J}_{1,2} &= \frac{\partial \dot{T}}{\partial V} \\
&= \frac{1}{\sum_{k=1}[C]_k C_{p_k}}\left(-\sum_{k=1}^{-1+}\frac{1}{V}\left(H_k - \frac{W_k H}{W}\right)\left(-\dot{\omega}_k + \frac{\partial \dot{n}}{\partial V}_k\right)\right. \\
&\qquad \left. + \frac{1}{V}\frac{\mathrm{d}T}{\mathrm{d}t}\sum_{k=1}^{-1+}\left(-C_p + C_{p_k}\right)[C]_k\right)
\end{aligned} \tag{327}$$

$$\begin{aligned}
\mathcal{J}_{2,2} &= \frac{\partial \dot{V}}{\partial V} \\
&= \frac{1}{[C]}\sum_{k=1}^{-1+}\left(1 - \frac{W_k}{W}\right)\frac{\partial \dot{n}}{\partial V}_k + \frac{1}{T}\left(V\frac{\mathrm{d}\dot{T}}{\mathrm{d}V} + \dot{T}\right)
\end{aligned} \tag{328}$$

$$\begin{aligned}
\mathcal{J}_{k+2,2} &= \frac{\partial \dot{n_k}}{\partial V} \\
&= \sum_{i=1}\left(V\frac{\partial q}{\partial V}_i + q_i\right)\nu_{k,i}
\end{aligned} \tag{329}$$

Converting to Jacobian Update form:

$$\mathcal{J}_{k+2,2} += \left(V \frac{\partial q}{\partial V}_i + q_i \right) \nu_{k,i} \tag{330}$$

$$\frac{\partial q}{\partial V}_k = \left(-\frac{[C]S''}{V} k_{r\,i} + \frac{[C]S'}{V} k_{f\,i} - \frac{R_{f\,i}}{V} \sum_{k=1} \nu'_{k,i} + \frac{R_{r\,i}}{V} \sum_{k=1} \nu''_{k,i} \right) c_i + R_i \frac{\partial c}{\partial V}_i \tag{331}$$

18.3.1 Pressure-dependent reactions

For PLOG:

$$\frac{\partial q}{\partial V}_k = \frac{1}{V} \left(-[C]S'' k_{r\,i} + [C]S' k_{f\,i} - R_{f\,i} \sum_{k=1} \nu'_{k,i} + R_{r\,i} \sum_{k=1} \nu''_{k,i} \right) \tag{332}$$

For Chebyshev:

$$\frac{\partial q}{\partial V}_k = -\frac{[C]S''}{V} k_{r\,i} + \frac{[C]S'}{V} k_{f\,i} - \frac{R_{f\,i}}{V} \sum_{k=1} \nu'_{k,i} + \frac{R_{r\,i}}{V} \sum_{k=1} \nu''_{k,i} \tag{333}$$

18.3.2 Pressure independent reactions

$$\frac{\partial q}{\partial V}_k = -\frac{[C]S''}{V} k_{r\,i} + \frac{[C]S'}{V} k_{f\,i} - \frac{R_{f\,i}}{V} \sum_{k=1} \nu'_{k,i} + \frac{R_{r\,i}}{V} \sum_{k=1} \nu''_{k,i} \tag{334}$$

18.3.3 Third-body enhanced reactions

For mixture as third-body:

$$\begin{aligned} \frac{\partial q}{\partial V}_k = [X]_i &\left(-\frac{[C]S''}{V} k_{r\,i} + \frac{[C]S'}{V} k_{f\,i} - \frac{R_{f\,i}}{V} \sum_{k=1} \nu'_{k,i} + \frac{R_{r\,i}}{V} \sum_{k=1} \nu''_{k,i} \right) \\ &+ \frac{R_i}{V} \left([C]\alpha_{,i} - [X]_i \right) \end{aligned} \tag{335}$$

For species m as third-body:

$$\begin{aligned} \frac{\partial q}{\partial V}_k = \left((-\delta_m + 1) [C]_m + \delta_m [C] \right) &\left(-\frac{[C]S''}{V} k_{r\,i} + \frac{[C]S'}{V} k_{f\,i} - \frac{R_{f\,i}}{V} \sum_{k=1} \nu'_{k,i} \right. \\ &\left. + \frac{R_{r\,i}}{V} \sum_{k=1} \nu''_{k,i} \right) + \left(\frac{\delta_m}{V} \left([C] - [C] \right) + \frac{[C]_m}{V} \left(\delta_m - 1 \right) \right) R_i \end{aligned} \tag{336}$$

If all $\alpha_{j,i} = 1$:

$$\frac{\partial q}{\partial V}_k = [C] \left(-\frac{[C]S''}{V} k_{r\,i} + \frac{[C]S'}{V} k_{f\,i} - \frac{R_{f\,i}}{V} \sum_{k=1} \nu'_{k,i} + \frac{R_{r\,i}}{V} \sum_{k=1} \nu''_{k,i} \right) \tag{337}$$

18.3.4 Unimolecular/recombination fall-off reactions

$$\frac{\partial q}{\partial V}_i = \left(\frac{F_i\bar{\theta}_{P_{r,i},\partial V}}{P_{r,i}+1} + \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial V}}{P_{r,i}+1} + \Theta_{F_i,\partial V} + \Theta_{P_{r,i},\partial V} - \frac{\bar{\theta}_{P_{r,i},\partial V}}{P_{r,i}+1}\right) c_i\right) R_i + \left(-\frac{[C]S''}{V}k_{r\,i} + \frac{[C]S'}{V}k_{f\,i} - \frac{R_{f\,i}}{V}\sum_{k=1}\nu'_{k,i} + \frac{R_{r\,i}}{V}\sum_{k=1}\nu''_{k,i}\right) c_i \tag{338}$$

18.3.5 Chemically-activated bimolecular reactions

$$\frac{\partial q}{\partial V}_i = \left(\left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial V}}{P_{r,i}+1} + \Theta_{F_i,\partial V} - \frac{\bar{\theta}_{P_{r,i},\partial V}}{P_{r,i}+1}\right) R_i - \frac{[C]S''}{V}k_{r\,i} + \frac{[C]S'}{V}k_{f\,i} - \frac{R_{f\,i}}{V}\sum_{k=1}\nu'_{k,i} + \frac{R_{r\,i}}{V}\sum_{k=1}\nu''_{k,i}\right) c_i \tag{339}$$

18.3.6 Reduced Pressure Derivatives

For mixture as third-body:

$$\Theta_{P_{r,i},\partial V} = -\frac{1}{V} \tag{340}$$

$$\bar{\theta}_{P_{r,i},\partial V} = \frac{[C]k_{0,i}\alpha_{,i}}{Vk_{\infty,i}} \tag{341}$$

For species m as third-body:

$$\Theta_{P_{r,i},\partial V} = -\frac{1}{V} \tag{342}$$

$$\bar{\theta}_{P_{r,i},\partial V} = \frac{[C]k_{0,i}\delta_m}{Vk_{\infty,i}} \tag{343}$$

If all $\alpha_{j,i} = 1$:

$$\Theta_{P_{r,i},\partial V} = 0 \tag{344}$$

$$\bar{\theta}_{P_{r,i},\partial V} = 0 \tag{345}$$

18.3.7 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i,\partial V} = 0 \tag{346}$$

For Troe

$$\Theta_{F_i,\partial V} = -\frac{2A_{Troe}B_{Troe}\log\left(F_{cent}\right)}{P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2\log\left(10\right)}\left(0.14A_{Troe} + B_{Troe}\right)\left(P_{r,i}\Theta_{P_{r,i},\partial V} + \bar{\theta}_{P_{r,i},\partial V}\right) \tag{347}$$

For SRI

$$\Theta_{F_i,\partial V} = -\frac{2X^2 \log\left(P_{r,i}\right)}{P_{r,i}\log^2\left(10\right)}\left(P_{r,i}\Theta_{P_{r,i},\partial V}\right.$$
$$\left. + \bar{\theta}_{P_{r,i},\partial V}\right)\log\left(\left(a\exp\left(\frac{T}{c}\right)+\exp\left(\frac{b}{T}\right)\right)\exp\left(-\frac{T}{c}-\frac{b}{T}\right)\right) \tag{348}$$