1 State Variables

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

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

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

2 Source Terms

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

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{N_s} U_k \dot{\omega}_k}{\sum_{k=1}^{N_s} [C]_k C_{v\,k}} \tag{5}$$

From conservation of mass:

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

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

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

$$n = \frac{PV}{TR_u} \tag{9}$$

Thus...

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

And...

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{1}{\sum_{k=1}^{N_s} [C]_k C_{v\,k}} \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \dot{\omega}_k \tag{11}$$

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

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

From the ideal gas law:

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

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

2.1 Other defns

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

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{P}{T}\frac{\mathrm{d}T}{\mathrm{d}t} + TR_u \sum_{k=1}^{-1+N_s}\left(1 - \frac{W_k}{W_{N_s}}\right)\dot{\omega}_k \tag{17}$$

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

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

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

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

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

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

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

3 Thermo Definitions

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

$$ {C_p}_k = R_u \left(T \left(T \left(T a_{k,4} + a_{k,3}\right) + a_{k,2}\right) + a_{k,1}\right) + a_{k,0}\right) \tag{26} $$

$$ {C_p}_k = T^4 R_u a_{k,4} + T^3 R_u a_{k,3} + T^2 R_u a_{k,2} + T R_u a_{k,1} + R_u a_{k,0} \tag{27} $$

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

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

$$ \bar{c_p} = \sum_{k=1}^{N_s} \frac{n_k {C_p}_k}{n} \tag{30} $$

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

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

$$ {C_v}_k = T^4 R_u a_{k,4} + T^3 R_u a_{k,3} + T^2 R_u a_{k,2} + T R_u a_{k,1} + R_u a_{k,0} - R_u \tag{33} $$

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

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

$$ \bar{c_v} = \sum_{k=1}^{N_s} \frac{n_k {C_v}_k}{n} \tag{36} $$

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

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

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

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

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

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

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

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

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

4 Definitions

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

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

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

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

5 Rate of Progress

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

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

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

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

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

8 Equilibrium Constants

$$K_{c\,i} = \left(\left(\frac{P_{atm}}{TR_u}\right)^{\sum_{k=1}^{N_s} \nu_{k,i}}\right) K_{p\,i} \tag{58}$$

$$K_{p\,i} = \exp(\frac{\Delta S_k^\circ}{R_u} - \frac{\Delta H_k^\circ}{R_u T}) \tag{59}$$

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

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

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

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

9 Reverse Reaction Rate

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

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

10 Third-Body Efficiencies

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

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

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

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

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

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

11 Falloff Reactions

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

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

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

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

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

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

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

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

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

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

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

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

12 Pressure-Dependent Reactions

For PLog reactions

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

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

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

For Chebyshev reactions

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

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

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

13 Derivatives

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

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

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

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

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

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

14 Rate of Progress Derivatives

14.1 Molar Derivatives

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

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

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

$$\frac{\partial [C_{Ns}]^{\nu'_{Ns,i}}}{\partial [n_j]} = -\frac{\left(\left(\frac{P}{TR_u} - \sum_{k=1}^{-1+N_s} \frac{n_k}{V}\right)^{\nu'_{N_s,i}}\right) \nu'_{N_s,i} \sum_{k=1}^{-1+N_s} \frac{\delta_{jk}}{V}}{\frac{P}{TR_u} - \sum_{k=1}^{-1+N_s} \frac{n_k}{V}} \tag{99}$$

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

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

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

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

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

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

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

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

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

For all reversible reactions

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

14.2 Temperature Derivative

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

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

$$R_f = \left(\left(\frac{P}{TR_u} - \sum_{k=1}^{-1+N_s} [C]_k \right)^{\nu'_{N_s,i}} \right) k_{f\,i} \prod_{k=1}^{-1+N_s} [C]_k^{\nu'_{k,i}} \tag{112}$$

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

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

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

For reactions with explicit reverse Arrhenius coefficients

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

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

For non-explicit reversible reactions

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

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

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

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

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

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

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

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

14.3 Pressure derivatives

$$\frac{\partial [C]_k}{\partial P} = 0 \tag{126}$$

$$\frac{\partial [C]_{N_s}}{\partial P} = \frac{1}{TR_u} \tag{127}$$

$$\frac{\partial [C_{Ns}]^{\nu'_{Ns,i}}}{\partial P} = \frac{\nu'_{k,i}[C]_{N_s}^{\nu'_{k,i}-1}}{TR_u} \tag{128}$$

$$\frac{\partial [C]}{\partial P} = \frac{1}{TR_u} \tag{129}$$

$$R_{f\,i} = \left(\left(\frac{P}{TR_u} - \sum_{k=1}^{-1+N_s} [C]_k\right)^{\nu'_{N_s,i}}\right) k_{f\,i} \prod_{k=1}^{-1+N_s} [C]_k^{\nu'_{k,i}} \tag{130}$$

$$\frac{\partial R_f}{\partial P}_i = \frac{\nu'_{N_s,i}[C]_{N_s}^{\nu'_{N_s,i}} k_{f\,i}}{TR_u [C]_{N_s}} \prod_{k=1}^{-1+N_s} [C]_k^{\nu'_{k,i}} \tag{131}$$

$$\frac{\partial R_f}{\partial P}_i = \frac{\nu'_{N_s,i}[C]_{N_s}^{\nu'_{N_s,i}} k_{f\,i}}{TR_u [C]_{N_s}} \prod_{k=1}^{-1+N_s} [C]_k^{\nu'_{k,i}} \tag{132}$$

$$\frac{\partial R_f}{\partial P}_i = \frac{\nu'_{N_s,i}[C]_{N_s}^{\nu'_{N_s,i}} k_{f\,i}}{TR_u[C]_{N_s}} \prod_{k=1}^{-1+N_s} [C]_k^{\nu'_{k,i}} \tag{133}$$

$$\frac{\partial R_f}{\partial P}_i = \frac{S'_{N_s} k_{f\,i}}{TR_u} \tag{134}$$

$$\frac{\partial R_f}{\partial P}_i = \frac{S'_{N_s} k_{f\,i}}{TR_u} \tag{135}$$

$$R_{r\,i} = \left(\left(\frac{P}{TR_u} - \sum_{k=1}^{-1+N_s} [C]_k\right)^{\nu''_{N_s,i}}\right) k_{r\,i} \prod_{k=1}^{-1+N_s} [C]_k^{\nu''_{k,i}} \tag{136}$$

$$\frac{\partial R_r}{\partial P}_i = \frac{\nu''_{N_s,i}[C]_{N_s}^{\nu''_{N_s,i}} k_{r\,i}}{TR_u[C]_{N_s}} \prod_{k=1}^{-1+N_s} [C]_k^{\nu''_{k,i}} \tag{137}$$

$$\frac{\partial R_r}{\partial P}_i = \frac{\nu''_{N_s,i}[C]_{N_s}^{\nu''_{N_s,i}} k_{r\,i}}{TR_u[C]_{N_s}} \prod_{k=1}^{-1+N_s} [C]_k^{\nu''_{k,i}} \tag{138}$$

$$\frac{\partial R_r}{\partial P}_i = \frac{\nu''_{N_s,i}[C]_{N_s}^{\nu''_{N_s,i}} k_{r\,i}}{TR_u[C]_{N_s}} \prod_{k=1}^{-1+N_s} [C]_k^{\nu''_{k,i}} \tag{139}$$

$$\frac{\partial R_r}{\partial P}_i = \frac{S''_{N_s} k_{r\,i}}{TR_u} \tag{140}$$

$$\frac{\partial R_r}{\partial P}_i = \frac{S''_{N_s} k_{r\,i}}{TR_u} \tag{141}$$

15 Third-Body/Falloff Derivatives

15.1 Elementary reactions

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

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

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

15.2 Third-body enhanced reactions

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

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

$$\frac{\partial [X]_i}{\partial P} = \frac{\alpha_{N_s,i}}{TR_u} \tag{147}$$

For species m as the third-body

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

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

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

$$\frac{\partial c}{\partial P}_i = \frac{\delta_{N_s m}}{TR_u} \tag{151}$$

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

$$\frac{\partial c}{\partial T}_i = -\frac{[C]}{T} \tag{152}$$

$$\frac{\partial c}{\partial n[j]}_i = 0 \tag{153}$$

$$\frac{\partial c}{\partial P}_i = \frac{1}{TR_u} \tag{154}$$

15.3 Unimolecular/recombination fall-off reactions

$$\frac{\partial c}{\partial T}_i = \frac{1}{P_{r,i}+1}\left(P_{r,i}\frac{\partial F_i}{\partial T} + \frac{\partial P_{r,i}}{\partial T}\left(F_i - c_i\right)\right) \tag{155}$$

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

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

15.4 Chemically-activated bimolecular reactions

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

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

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

15.5 Reduced Pressure derivatives

For the mixture as the third body

$$\frac{\partial P_{r,i}}{\partial T} = \frac{P_{r,i}}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) - \frac{[C]k_{0,i}\alpha_{N_s,i}}{Tk_{\infty,i}} \tag{161}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{k_{0,i}\left(-\alpha_{N_s,i} + \alpha_{j,i}\right)}{k_{\infty,i}V} \tag{162}$$

$$\frac{\partial P_{r,i}}{\partial P} = \frac{k_{0,i}\alpha_{N_s,i}}{Tk_{\infty,i}R_u} \tag{163}$$

Simplifying:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T,mix} + \bar{\theta}_{P_{r,i},\partial T,mix} \tag{164}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{\bar{\theta}_{P_{r,i},\partial n_j,mix}}{k_{\infty,i}V}k_{0,i} \tag{165}$$

$$\frac{\partial P_{r,i}}{\partial P} = \bar{\theta}_{P_{r,i},\partial P,mix} \tag{166}$$

$$\Theta_{P_{r,i},\partial T,mix} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \tag{167}$$

$$\bar{\theta}_{P_{r,i},\partial T,mix} = -\frac{[C]k_{0,i}\alpha_{N_s,i}}{Tk_{\infty,i}} \tag{168}$$

$$\bar{\theta}_{P_{r,i},\partial n_j,mix} = -\alpha_{N_s,i} + \alpha_{j,i} \tag{169}$$

$$\Theta_{P_{r,i},\partial P,mix} = 0 \tag{170}$$

$$\bar{\theta}_{P_{r,i},\partial P,mix} = \frac{k_{0,i}\alpha_{N_s,i}}{Tk_{\infty,i}R_u} \tag{171}$$

For species m as the third-body

$$\frac{\partial P_{r,i}}{\partial T} = \frac{P_{r,i}}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) - \frac{[C]k_{0,i}\delta_{N_s m}}{Tk_{\infty,i}} \tag{172}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{k_{0,i}}{k_{\infty,i}V}\left(-\delta_{N_s m} + \delta_{jm}\right) \tag{173}$$

$$\frac{\partial P_{r,i}}{\partial P} = \frac{k_{0,i}\delta_{N_s m}}{Tk_{\infty,i}R_u} \tag{174}$$

Simplifying:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T,spec} + \bar{\theta}_{P_{r,i},\partial T,spec} \tag{175}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{\bar{\theta}_{P_{r,i},\partial n_j,spec}}{k_{\infty,i}V}k_{0,i} \tag{176}$$

$$\frac{\partial P_{r,i}}{\partial P} = \bar{\theta}_{P_{r,i},\partial P,spec} \tag{177}$$

$$\Theta_{P_{r,i},\partial T,spec} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \tag{178}$$

$$\bar{\theta}_{P_{r,i},\partial T,spec} = -\frac{[C]k_{0,i}\delta_{N_s m}}{Tk_{\infty,i}} \tag{179}$$

$$\bar{\theta}_{P_{r,i},\partial n_j,spec} = -\delta_{N_s m} + \delta_{jm} \tag{180}$$

$$\Theta_{P_{r,i},\partial P,spec} = 0 \tag{181}$$

$$\bar{\theta}_{P_{r,i},\partial P,spec} = \frac{k_{0,i}\delta_{N_s m}}{Tk_{\infty,i}R_u} \tag{182}$$

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

$$\frac{\partial P_{r,i}}{\partial T} = \frac{P_{r,i}}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \tag{183}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = 0 \tag{184}$$

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

Simplifying:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T,unity} \tag{186}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \bar{\theta}_{P_{r,i},\partial n_j,unity} \tag{187}$$

$$\frac{\partial P_{r,i}}{\partial P} = \bar{\theta}_{P_{r,i},\partial P,unity} \tag{188}$$

$$\Theta_{P_{r,i},\partial T,unity} = \frac{1}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \tag{189}$$

$$\bar{\theta}_{P_{r,i},\partial T,unity} = 0 \tag{190}$$

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

$$\Theta_{P_{r,i},\partial P,unity} = 0 \tag{192}$$

$$\bar{\theta}_{P_{r,i},\partial P,unity} = \frac{k_{0,i}}{k_{\infty,i}}\frac{\partial [C]}{\partial P} \tag{193}$$

Thus we write:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i}\Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T} \tag{194}$$

$$\frac{\partial P_{r,i}}{\partial n[j]} = \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}}{k_{\infty,i}V} \tag{195}$$

$$\frac{\partial P_{r,i}}{\partial P} = \bar{\theta}_{P_{r,i},\partial P} \tag{196}$$

For

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \quad \text{if mix} \tag{197a}$$

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \quad \text{if species} \tag{197b}$$

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \quad \text{if unity} \tag{197c}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\alpha_{N_s,i}}{Tk_{\infty,i}} \quad \text{if mix} \tag{198a}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\delta_{N_s m}}{Tk_{\infty,i}} \quad \text{if species} \tag{198b}$$

$$\bar{\theta}_{P_{r,i},\partial T} = 0 \quad \text{if unity} \tag{198c}$$

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\alpha_{N_s,i} + \alpha_{j,i} \quad \text{if mix} \tag{199a}$$
$$\bar{\theta}_{P_{r,i},\partial n_j} = -\delta_{N_s m} + \delta_{jm} \quad \text{if species} \tag{199b}$$
$$\bar{\theta}_{P_{r,i},\partial n_j} = 0 \quad \text{if unity} \tag{199c}$$

$$\Theta_{P_{r,i},\partial P} = 0 \quad \text{if mix} \tag{200a}$$
$$\Theta_{P_{r,i},\partial P} = 0 \quad \text{if species} \tag{200b}$$
$$\Theta_{P_{r,i},\partial P} = 0 \quad \text{if unity} \tag{200c}$$

$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i}\alpha_{N_s,i}}{Tk_{\infty,i}R_u} \quad \text{if mix} \tag{201a}$$
$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i}\delta_{N_s m}}{Tk_{\infty,i}R_u} \quad \text{if species} \tag{201b}$$
$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i}}{k_{\infty,i}}\frac{\partial [C]}{\partial P} \quad \text{if unity} \tag{201c}$$

15.6 Falloff Blending Factor derivatives

For Lindemann reactions

$$\frac{\partial F_i}{\partial T} = 0 \tag{202}$$

$$\frac{\partial F_i}{\partial n[j]} = 0 \tag{203}$$

$$\frac{\partial F_i}{\partial P} = 0 \tag{204}$$

For Troe reactions

$$\frac{\partial F_i}{\partial T} = \frac{\partial F_i}{\partial F_{cent}}\frac{\mathrm{d}F_{cent}}{\mathrm{d}T} + \frac{\partial F_i}{\partial P_{r,i}}\frac{\partial P_{r,i}}{\partial T} \tag{205}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{\partial F_i}{\partial P_{r,i}}\frac{\partial P_{r,i}}{\partial n[j]} \tag{206}$$

$$\frac{\partial F_i}{\partial P} = \frac{\partial F_i}{\partial P_{r,i}}\frac{\partial P_{r,i}}{\partial P} \tag{207}$$

where

$$\frac{\partial F_i}{\partial F_{cent}} = \frac{F_i}{\frac{A_{Troe}^2}{B_{Troe}^2}+1}\left(\frac{2A_{Troe}\log\left(F_{cent}\right)}{B_{Troe}^2\left(\frac{A_{Troe}^2}{B_{Troe}^2}+1\right)}\left(\frac{A_{Troe}}{B_{Troe}}\frac{\partial B_{Troe}}{\partial F_{cent}} - \frac{\partial A_{Troe}}{\partial F_{cent}}\right) + \frac{1}{F_{cent}}\right) \tag{208}$$

$$\frac{\mathrm{d}F_{cent}}{\mathrm{d}T} = -\frac{a}{T^*}\exp\left(-\frac{T}{T^*}\right) - \frac{\exp\left(-\frac{T}{T^{***}}\right)}{T^{***}}\left(-a+1\right) + \frac{T^{**}}{T^2}\exp\left(-\frac{T^{**}}{T}\right) \tag{209}$$

$$\frac{\partial F_i}{\partial P_{r,i}} = \frac{2F_i A_{Troe} \log\left(F_{cent}\right)}{B_{Troe}^2 \left(\frac{A_{Troe}^2}{B_{Troe}^2} + 1\right)^2} \left(\frac{A_{Troe}}{B_{Troe}} \frac{\partial B_{Troe}}{\partial P_{r,i}} - \frac{\partial A_{Troe}}{\partial P_{r,i}}\right) \tag{210}$$

And

$$\frac{\partial A_{Troe}}{\partial F_{cent}} = -\frac{0.67}{F_{cent} \log\left(10\right)} \tag{211}$$

$$\frac{\partial B_{Troe}}{\partial F_{cent}} = -\frac{1.1762}{F_{cent} \log\left(10\right)} \tag{212}$$

$$\frac{\partial A_{Troe}}{\partial P_{r,i}} = \frac{1}{P_{r,i} \log\left(10\right)} \tag{213}$$

$$\frac{\partial B_{Troe}}{\partial P_{r,i}} = -\frac{0.14}{P_{r,i} \log\left(10\right)} \tag{214}$$

Thus

$$\begin{split}\frac{\partial F_i}{\partial F_{cent}} = -\frac{F_i B_{Troe}}{F_{cent} \left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log\left(10\right)} \Big(2A_{Troe} \left(1.1762A_{Troe}\right. \\ \left. - 0.67B_{Troe}\right) \log\left(F_{cent}\right) - B_{Troe} \left(A_{Troe}^2 + B_{Troe}^2\right) \log\left(10\right)\Big)\end{split} \tag{215}$$

$$\frac{\partial F_i}{\partial P_{r,i}} = -\frac{2F_i A_{Troe} \left(\frac{0.14A_{Troe}}{B_{Troe}} + 1\right) \log\left(F_{cent}\right)}{B_{Troe}^2 P_{r,i} \left(\frac{A_{Troe}^2}{B_{Troe}^2} + 1\right)^2 \log\left(10\right)} \tag{216}$$

And

$$\frac{\partial F_i}{\partial T} = F_i \Theta_{F_i, \partial T} \tag{217}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{F_i k_{0,i} \Theta_{F_i, \partial n_j}}{k_{\infty,i} V} \bar{\theta}_{P_{r,i}, \partial n_j} \tag{218}$$

$$\frac{\partial F_i}{\partial P} = F_i \Theta_{F_i, \partial P} \tag{219}$$

Where

$$\begin{split}\Theta_{F_i, \partial T} = -\frac{B_{Troe}}{F_{cent} P_{r,i} \left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log\left(10\right)} \Bigg(2A_{Troe} F_{cent} \left(0.14A_{Troe}\right. \\ \left. + B_{Troe}\right) \left(P_{r,i} \Theta_{P_{r,i}, \partial T} + \bar{\theta}_{P_{r,i}, \partial T}\right) \log\left(F_{cent}\right) \\ + P_{r,i} \frac{\mathrm{d}F_{cent}}{\mathrm{d}T} \Big(2A_{Troe} \left(1.1762A_{Troe} - 0.67B_{Troe}\right) \log\left(F_{cent}\right) \\ - B_{Troe} \left(A_{Troe}^2 + B_{Troe}^2\right) \log\left(10\right)\Big)\Bigg)\end{split} \tag{220}$$

$$\Theta_{F_i,\partial n_j} = -\frac{2A_{Troe}B_{Troe}\left(0.14A_{Troe}+B_{Troe}\right)\log\left(F_{cent}\right)}{P_{r,i}\left(A_{Troe}^2+B_{Troe}^2\right)^2\log\left(10\right)} \tag{221}$$

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

For SRI reactions

$$\begin{split}\frac{\partial F_i}{\partial T} = F_i\left(\frac{X\left(-\frac{\exp\left(-\frac{T}{c}\right)}{c}+\frac{ab}{T^2}\exp\left(-\frac{b}{T}\right)\right)}{a\exp\left(-\frac{b}{T}\right)+\exp\left(-\frac{T}{c}\right)}\right.\\ \left.+\frac{\partial P_{r,i}}{\partial T}\frac{\mathrm{d}X}{\mathrm{d}P_{r,i}}\log\left(a\exp\left(-\frac{b}{T}\right)+\exp\left(-\frac{T}{c}\right)\right)+\frac{e}{T}\right)\end{split} \tag{223}$$

$$\frac{\partial F_i}{\partial n[j]} = F_i\frac{\partial P_{r,i}}{\partial n[j]}\frac{\mathrm{d}X}{\mathrm{d}P_{r,i}}\log\left(a\exp\left(-\frac{b}{T}\right)+\exp\left(-\frac{T}{c}\right)\right) \tag{224}$$

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

Where

$$\frac{\mathrm{d}X}{\mathrm{d}P_{r,i}} = -\frac{2X^2\log\left(P_{r,i}\right)}{P_{r,i}\log^2\left(10\right)} \tag{226}$$

$$\frac{\partial X}{\partial n_j} = \frac{\partial P_{r,i}}{\partial n[j]}\frac{\mathrm{d}X}{\mathrm{d}P_{r,i}} \tag{227}$$

And

$$\frac{\partial F_i}{\partial T} = F_i\Theta_{F_i,\partial T} \tag{228}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{F_i k_{0,i}\Theta_{F_i,\partial n_j}}{k_{\infty,i}V}\bar{\theta}_{P_{r,i},\partial n_j} \tag{229}$$

$$\frac{\partial F_i}{\partial P} = F_i\Theta_{F_i,\partial P} \tag{230}$$

Where

$$\begin{split}\Theta_{F_i,\partial T} = -\frac{X\left(\frac{\exp\left(-\frac{T}{c}\right)}{c}-\frac{ab}{T^2}\exp\left(-\frac{b}{T}\right)\right)}{a\exp\left(-\frac{b}{T}\right)+\exp\left(-\frac{T}{c}\right)}+\frac{e}{T}\\ -\frac{2X^2\log\left(a\exp\left(-\frac{b}{T}\right)+\exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2\left(10\right)}\left(P_{r,i}\Theta_{P_{r,i},\partial T}+\bar{\theta}_{P_{r,i},\partial T}\right)\log\left(P_{r,i}\right)\end{split} \tag{231}$$

$$\Theta_{F_i,\partial n_j} = -\frac{2X^2 \log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2(10)}\log(P_{r,i}) \tag{232}$$

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

Simplifying:

$$\frac{\partial F_i}{\partial T} = F_i\Theta_{F_i,\partial T} \tag{234}$$

$$\frac{\partial F_i}{\partial n[j]} = \frac{F_i k_{0,i}\Theta_{F_i,\partial n_j}}{k_{\infty,i}V}\bar{\theta}_{P_{r,i},\partial n_j} \tag{235}$$

$$\frac{\partial F_i}{\partial P} = F_i\Theta_{F_i,\partial P} \tag{236}$$

Where:

$$\Theta_{F_i,\partial T} = 0 \quad \text{if Lindemann} \tag{237a}$$

$$\begin{aligned}\Theta_{F_i,\partial T} = -&\frac{B_{Troe}}{F_{cent}P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2\log(10)}\Big(2A_{Troe}F_{cent}\left(0.14A_{Troe}\right.\\ &\left.+ B_{Troe}\right)\left(P_{r,i}\Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right)\log(F_{cent})\\ &+ P_{r,i}\frac{\mathrm{d}F_{cent}}{\mathrm{d}T}\left(2A_{Troe}\left(1.1762A_{Troe} - 0.67B_{Troe}\right)\log(F_{cent})\right.\\ &\left.- B_{Troe}\left(A_{Troe}^2 + B_{Troe}^2\right)\log(10)\right)\Big) \quad \text{if Troe}\end{aligned} \tag{237b}$$

$$\begin{aligned}\Theta_{F_i,\partial T} = -&\frac{X\left(\frac{\exp\left(-\frac{T}{c}\right)}{c} - \frac{ab}{T^2}\exp\left(-\frac{b}{T}\right)\right)}{a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)} + \frac{e}{T}\\ &- \frac{2X^2\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2(10)}\left(P_{r,i}\Theta_{P_{r,i},\partial T}\right.\\ &\left.+ \bar{\theta}_{P_{r,i},\partial T}\right)\log(P_{r,i}) \quad \text{if SRI}\end{aligned} \tag{237c}$$

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

$$\Theta_{F_i,\partial n_j} = -\frac{2A_{Troe}B_{Troe}\left(0.14A_{Troe} + B_{Troe}\right)\log(F_{cent})}{P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2\log(10)} \quad \text{if Troe} \tag{238b}$$

$$\Theta_{F_i,\partial n_j} = -\frac{2X^2\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2(10)}\log(P_{r,i}) \quad \text{if SRI} \tag{238c}$$

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

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

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

15.7 Unimolecular/recombination fall-off reactions (complete)

$$\frac{\partial c}{\partial T}_i = \frac{F_i \bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1} + \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial T}}{P_{r,i}+1} + \Theta_{F_i,\partial T} + \Theta_{P_{r,i},\partial T} - \frac{\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1}\right) c_i \tag{240}$$

$$\frac{\partial c}{\partial n[j]}_i = \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}}{k_{\infty,i} V \left(P_{r,i}+1\right)} \left(F_i \left(P_{r,i}\Theta_{F_i,\partial n_j} + 1\right) - c_i\right) \tag{241}$$

$$\frac{\partial c}{\partial P}_i = \frac{F_i \bar{\theta}_{P_{r,i},\partial P}}{P_{r,i}+1} + \left(\Theta_{F_i,\partial P} - \frac{\bar{\theta}_{P_{r,i},\partial P}}{P_{r,i}+1}\right) c_i \tag{242}$$

15.8 Chemically-activated bimolecular reactions (complete)

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

$$\frac{\partial c}{\partial n[j]}_i = \frac{k_{0,i}\bar{\theta}_{P_{r,i},\partial n_j}\left(F_i \Theta_{F_i,\partial n_j} - c_i\right)}{k_{\infty,i} V \left(P_{r,i}+1\right)} \tag{244}$$

$$\frac{\partial c}{\partial P}_i = \left(\Theta_{F_i,\partial P} - \frac{\bar{\theta}_{P_{r,i},\partial P}}{P_{r,i}+1}\right) c_i \tag{245}$$

16 Pressure-dependent reaction derivatives

For PLog reactions

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \left(\frac{1}{k_1}\frac{\mathrm{d}k_1}{\mathrm{d}T} + \frac{1}{-\log\left(P_1\right) + \log\left(P_2\right)}\left(-\frac{1}{k_1}\frac{\mathrm{d}k_1}{\mathrm{d}T} + \frac{1}{k_2}\frac{\mathrm{d}k_2}{\mathrm{d}T}\right)\left(\log\left(P\right) - \log\left(P_1\right)\right)\right) k_{f\,i} \tag{246}$$

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \left(\frac{1}{-\log\left(P_1\right) + \log\left(P_2\right)}\left(-\frac{1}{T}\left(\beta_1 + \frac{E_{a_1}}{TR_u}\right) + \frac{1}{T}\left(\beta_2 + \frac{E_{a_2}}{TR_u}\right)\right)\left(\log\left(P\right) - \log\left(P_1\right)\right) + \frac{1}{T}\left(\beta_1 + \frac{E_{a_1}}{TR_u}\right)\right) k_{f\,i} \tag{247}$$

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \frac{k_{f\,i}}{T}\left(\beta_1 + \frac{\left(\log\left(P\right) - \log\left(P_1\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{TR_u} + \frac{E_{a_2}}{TR_u}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{TR_u}\right) \tag{248}$$

$$\frac{\partial R_f}{\partial T}_i = -\frac{[C]S'_{N_s}}{T}k_{f\,i} + \frac{R_{f\,i}}{T}\left(\beta_1 + \frac{\left(\log\left(P\right) - \log\left(P_1\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{TR_u} + \frac{E_{a_2}}{TR_u}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{TR_u}\right) \tag{249}$$

$$\frac{\mathrm{d}k_r}{\mathrm{d}T}_i = \left(-\sum_{k=1}^{N_s}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_1 + \frac{\left(\log\left(P\right) - \log\left(P_1\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{TR_u} + \frac{E_{a_2}}{TR_u}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{TR_u}\right)\right)k_{r\,i} \tag{250}$$

$$\frac{\partial R_r}{\partial T}_i = \left(-\sum_{k=1}^{N_s}\nu_{k,i}\frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_1 + \frac{\left(\log\left(P\right) - \log\left(P_1\right)\right)\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{TR_u} + \frac{E_{a_2}}{TR_u}\right)}{-\log\left(P_1\right) + \log\left(P_2\right)} + \frac{E_{a_1}}{TR_u}\right)\right)R_{r\,i} - \frac{[C]S''_{N_s}}{T}k_{r\,i} \tag{251}$$

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

$$\frac{\partial k_f}{\partial P}_i = \frac{\left(-\log\left(k_1\right) + \log\left(k_2\right)\right)k_{f\,i}}{P\left(-\log\left(P_1\right) + \log\left(P_2\right)\right)} \tag{253}$$

$$\frac{\partial R_f}{\partial P}_i = \frac{S'_{N_s}k_{f\,i}}{TR_u} + \frac{\left(-\log\left(k_1\right) + \log\left(k_2\right)\right)R_{f\,i}}{P\left(-\log\left(P_1\right) + \log\left(P_2\right)\right)} \tag{254}$$

$$\frac{\partial k_r}{\partial P}_i = \frac{1}{K_{ci}} \frac{\partial k_f}{\partial P}_i \tag{255}$$

$$\frac{\partial k_r}{\partial P}_i = \frac{\left(-\log\left(k_1\right) + \log\left(k_2\right)\right) k_{r\,i}}{P\left(-\log\left(P_1\right) + \log\left(P_2\right)\right)} \tag{256}$$

$$\frac{\partial R_r}{\partial P}_i = \frac{S''_{N_s} k_{r\,i}}{T R_u} + \frac{\left(-\log\left(k_1\right) + \log\left(k_2\right)\right) R_{r\,i}}{P\left(-\log\left(P_1\right) + \log\left(P_2\right)\right)} \tag{257}$$

$$\frac{\partial R}{\partial P}_i = \frac{1}{T R_u}\left(-S''_{N_s} k_{r\,i} + S'_{N_s} k_{f\,i}\right) + \frac{\left(-\log\left(k_1\right) + \log\left(k_2\right)\right)\left(R_{f\,i} - R_{r\,i}\right)}{P\left(-\log\left(P_1\right) + \log\left(P_2\right)\right)} \tag{258}$$

For Chebyshev reactions

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \log(10) k_{f\,i} \sum_{\substack{1 \le l \le N_P \\ 1 \le j \le N_T}} \frac{\mathrm{d}\tilde{T}}{\mathrm{d}T}\left(j-1\right) T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j} \tag{259}$$

$$\frac{\mathrm{d}k_f}{\mathrm{d}T}_i = \log(10) k_{f\,i} \sum_{\substack{1 \le l \le N_P \\ 1 \le j \le N_T}} -\frac{2 T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)}\left(j-1\right) \tag{260}$$

$$\frac{\partial R_f}{\partial T}_i = \log(10) R_{f\,i} \sum_{\substack{1 \le l \le N_P \\ 1 \le j \le N_T}} -\frac{2 T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)}\left(j-1\right) - \frac{[C] S'_{N_s}}{T} k_{f\,i} \tag{261}$$

$$\begin{multline}\frac{\mathrm{d}k_r}{\mathrm{d}T}_i = -\left(\sum_{k=1}^{N_s} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} \sum_{\substack{1 \le l \le N_P \\ 1 \le j \le N_T}} (j \right. \\ \left. -1) T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}\right) k_{r\,i}\end{multline} \tag{262}$$

$$\begin{multline}\frac{\partial R_r}{\partial T}_i = -\left(\sum_{k=1}^{N_s} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} \sum_{\substack{1 \le l \le N_P \\ 1 \le j \le N_T}} (j \right. \\ \left. -1) T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j}\right) R_{r\,i} - \frac{[C] S''_{N_s}}{T} k_{r\,i}\end{multline} \tag{263}$$

$$\frac{\partial R}{\partial T}_i = \left(\sum_{k=1}^{N_s} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}}+\frac{1}{T_{max}}\right)} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} (j-1)\, T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j} \right) R_{r\,i} + \log(10) R_{f\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} -\frac{2T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right)\eta_{l,j}}{T^2\left(-\frac{1}{T_{min}}+\frac{1}{T_{max}}\right)}(j-1) + \frac{[C]}{T}\left(S''_{N_s} k_{r\,i} - S'_{N_s} k_{f\,i}\right) \tag{264}$$

$$\frac{\partial k_f}{\partial P}_i = \log(10) k_{f\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} \frac{\mathrm{d}\tilde{P}}{\mathrm{d}P} (l-1)\, T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right) \eta_{l,j} \tag{265}$$

$$\frac{\partial k_f}{\partial P}_i = \log(10) k_{f\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} \frac{2(l-1)\, T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right)\eta_{l,j}}{P\left(\log(P_{max}) - \log(P_{min})\right)} \tag{266}$$

$$\frac{\partial R_f}{\partial P}_i = \log(10) R_{f\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} \frac{2(l-1)\, T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right)\eta_{l,j}}{P\left(\log(P_{max}) - \log(P_{min})\right)} + \frac{S'_{N_s} k_{f\,i}}{TR_u} \tag{267}$$

$$\frac{\partial k_r}{\partial P}_i = \log(10) k_{r\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} \frac{2(l-1)\, T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right)\eta_{l,j}}{P\left(\log(P_{max}) - \log(P_{min})\right)} \tag{268}$$

$$\frac{\partial R_r}{\partial P}_i = \log(10) R_{r\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} \frac{2(l-1)\, T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right)\eta_{l,j}}{P\left(\log(P_{max}) - \log(P_{min})\right)} + \frac{S''_{N_s} k_{r\,i}}{TR_u} \tag{269}$$

$$\frac{\partial R}{\partial P}_i = \log(10) R_{f\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} \frac{2(l-1)\, T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right)\eta_{l,j}}{P\left(\log(P_{max}) - \log(P_{min})\right)} - \log(10) R_{r\,i} \sum_{\substack{1\leq l\leq N_P\\1\leq j\leq N_T}} \frac{2(l-1)\, T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right)\eta_{l,j}}{P\left(\log(P_{max}) - \log(P_{min})\right)} + \frac{1}{TR_u}\left(-S''_{N_s} k_{r\,i} + S'_{N_s} k_{f\,i}\right) \tag{270}$$

17 Jacobian entries

17.1 Energy Equation

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \dot{\omega}_k \tag{271}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \dot{\omega}_k}{\left(\frac{P}{T R_u} - \sum_{k=1}^{-1+N_s}[C]_k \right) C_{v\,N_s} + \sum_{k=1}^{-1+N_s}[C]_k C_{v\,k}} \tag{272}$$

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \dot{\omega}_k}{[C] C_{v\,N_s} + \sum_{k=1}^{-1+N_s} \left(-C_{v\,N_s} + C_{v\,k} \right) [C]_k} \tag{273}$$

17.2 $\dot{T}$ Derivatives

Molar derivative

$$\begin{aligned} \frac{\partial \dot{T}}{\partial n_j} = &-\frac{\sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial n[j]}_k}{[C] C_{v\,N_s} + \sum_{k=1}^{-1+N_s} - \left(C_{v\,N_s} - C_{v\,k} \right) [C]_k} \\ &+ \frac{\left(\sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \dot{\omega}_k \right) \sum_{k=1}^{-1+N_s} - \frac{\delta_{jk}}{V} \left(C_{v\,N_s} - C_{v\,k} \right)}{\left([C] C_{v\,N_s} + \sum_{k=1}^{-1+N_s} - \left(C_{v\,N_s} - C_{v\,k} \right) [C]_k \right)^2} \end{aligned} \tag{274}$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial n_j} = &\frac{1}{\left(\sum_{k=1}^{N_s}[C]_k C_{v\,k} \right)^2} \left(\sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \dot{\omega}_k \right) \sum_{k=1}^{-1+N_s} \\ &- \frac{\delta_{jk}}{V} \left(C_{v\,N_s} - C_{v\,k} \right) - \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial n[j]}_k \end{aligned} \tag{275}$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial n_j} = &\frac{1}{V \left(\sum_{k=1}^{N_s}[C]_k C_{v\,k} \right)^2} \left(-C_{v\,N_s} + C_{v\,j} \right) \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \dot{\omega}_k \\ &- \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial n[j]}_k \end{aligned} \tag{276}$$

$$\begin{aligned} &\frac{\partial \dot{T}}{\partial n_j} \\ &= \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(-\frac{1}{V} \frac{\mathrm{d}T}{\mathrm{d}t} \left(-C_{v\,N_s} + C_{v\,j} \right) - \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial n[j]}_k \right) \end{aligned} \tag{277}$$

Temperature derivative

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{\sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \dot{\omega}_k}{\frac{P C_{v\,N_s}}{T R_u} + \sum_{k=1}^{-1+N_s} \left(-C_{v\,N_s} + C_{v\,k}\right) [C]_k} \tag{278}$$

$$\begin{split}\frac{\partial \dot{T}}{\partial T} = &-\frac{1}{\frac{P C_{v\,N_s}}{T R_u} + \sum_{k=1}^{-1+N_s} \left(-C_{v\,N_s} + C_{v\,k}\right) [C]_k} \sum_{k=1}^{-1+N_s} \left(\left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \frac{\partial \dot{\omega}}{\partial T}_k \right.\\ &\left. + \left(\frac{\mathrm{d}U}{\mathrm{d}T}_k - \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s}\right) \dot{\omega}_k\right)\\ &- \frac{1}{\left(\frac{P C_{v\,N_s}}{T R_u} + \sum_{k=1}^{-1+N_s} \left(-C_{v\,N_s} + C_{v\,k}\right) [C]_k\right)^2} \left(-\frac{P}{T R_u} \frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} + \frac{P C_{v\,N_s}}{T^2 R_u}\right.\\ &\left. - \sum_{k=1}^{-1+N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} + \frac{\mathrm{d}C_v}{\mathrm{d}T}_k\right) [C]_k\right) \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \dot{\omega}_k\end{split} \tag{279}$$

$$\begin{split}\frac{\partial \dot{T}}{\partial T} = &-\frac{1}{[C] C_{v\,N_s} + \sum_{k=1}^{-1+N_s} \left(-C_{v\,N_s} + C_{v\,k}\right) [C]_k} \sum_{k=1}^{-1+N_s} \left(\left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \frac{\partial \dot{\omega}}{\partial T}_k \right.\\ &\left. + \left(\frac{\mathrm{d}U}{\mathrm{d}T}_k - \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s}\right) \dot{\omega}_k\right)\\ &- \frac{1}{\left([C] C_{v\,N_s} + \sum_{k=1}^{-1+N_s} \left(-C_{v\,N_s} + C_{v\,k}\right) [C]_k\right)^2} \left(-[C] \frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s}\right.\\ &\left. - \sum_{k=1}^{-1+N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} + \frac{\mathrm{d}C_v}{\mathrm{d}T}_k\right) [C]_k + \frac{[C] C_{v\,N_s}}{T}\right) \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \dot{\omega}_k\end{split} \tag{280}$$

$$\begin{split}\frac{\partial \dot{T}}{\partial T} = &-\frac{1}{\left(\sum_{k=1}^{N_s} [C]_k C_{v\,k}\right)^2} \left(-[C] \frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} - \sum_{k=1}^{-1+N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} + \frac{\mathrm{d}C_v}{\mathrm{d}T}_k\right) [C]_k \right.\\ &\left. + \frac{[C] C_{v\,N_s}}{T}\right) \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \dot{\omega}_k\\ &- \frac{1}{\sum_{k=1}^{N_s} [C]_k C_{v\,k}} \sum_{k=1}^{-1+N_s} \left(\left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \frac{\partial \dot{\omega}}{\partial T}_k \right.\\ &\left. + \left(\frac{\mathrm{d}U}{\mathrm{d}T}_k - \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s}\right) \dot{\omega}_k\right)\end{split} \tag{281}$$

$$\frac{\partial \dot{T}}{\partial T} = -\frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(\frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(-[C]\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} - \sum_{k=1}^{-1+N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} + \frac{\mathrm{d}C_v}{\mathrm{d}T}_{k} \right)[C]_k + \frac{[C]C_{v\,N_s}}{T} \right) \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right)\dot{\omega}_k + \sum_{k=1}^{-1+N_s} \left(\left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(\frac{\mathrm{d}U}{\mathrm{d}T}_k - \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s} \right)\dot{\omega}_k \right) \right) \tag{282}$$

$$\frac{\partial \dot{T}}{\partial T} = \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(\frac{\mathrm{d}T}{\mathrm{d}t} \left(-[C]\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} - \sum_{k=1}^{-1+N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} + \frac{\mathrm{d}C_v}{\mathrm{d}T}_{k} \right)[C]_k + \frac{[C]C_{v\,N_s}}{T} \right) - \sum_{k=1}^{-1+N_s} \left(\left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(\frac{\mathrm{d}U}{\mathrm{d}T}_k - \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s} \right)\dot{\omega}_k \right) \right) \tag{283}$$

$$\frac{\partial \dot{T}}{\partial T} = \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(\frac{\mathrm{d}T}{\mathrm{d}t} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} \sum_{k=1}^{N_s}[C]_k - \sum_{k=1}^{-1+N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{N_s} + \frac{\mathrm{d}C_v}{\mathrm{d}T}_{k} \right)[C]_k + \frac{C_{v\,N_s}}{T} \sum_{k=1}^{N_s}[C]_k \right) - \sum_{k=1}^{-1+N_s} \left(\left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(\frac{\mathrm{d}U}{\mathrm{d}T}_k - \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s} \right)\dot{\omega}_k \right) \right) \tag{284}$$

$$\frac{\partial \dot{T}}{\partial T} = \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(\frac{\mathrm{d}T}{\mathrm{d}t} \sum_{k=1}^{N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{k} + \frac{C_{v\,N_s}}{T} \right)[C]_k + \sum_{k=1}^{-1+N_s} \left(\left(-U_k + \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(-\frac{\mathrm{d}U}{\mathrm{d}T}_k + \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s} \right)\dot{\omega}_k \right) \right) \tag{285}$$

$$\frac{\partial \dot{T}}{\partial T} = \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(\frac{\mathrm{d}T}{\mathrm{d}t} \sum_{k=1}^{N_s} \left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_{k} + \frac{C_{v\,N_s}}{T} \right)[C]_k + \sum_{k=1}^{-1+N_s} \left(\left(-U_k + \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(-C_{v\,k} + \frac{W_k}{W_{N_s}} \frac{\mathrm{d}U}{\mathrm{d}T}_{N_s} \right)\dot{\omega}_k \right) \right) \tag{286}$$

Pressure Derivative

$$\frac{\partial \dot{T}}{\partial P} = \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(- \sum_{k=1}^{-1+N_s} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{\omega}}{\partial P}_k - \frac{C_{v\,N_s}}{T R_u} \frac{\mathrm{d}T}{\mathrm{d}t} \right) \tag{287}$$

17.3 $\dot{P}$ Derivatives

Temperature Derivative

$$\frac{\partial \dot{P}}{\partial T} = \frac{P}{T}\left(\frac{\mathrm{d}\dot{T}}{\mathrm{d}T} - \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t}\right) + R_u \sum_{k=1}^{-1+N_s} \left(1 - \frac{W_k}{W_{N_s}}\right)\left(T\frac{\partial \dot{\omega}}{\partial T}_k + \dot{\omega}_k\right) \tag{288}$$

Molar Derivative

$$\frac{\partial \dot{P}}{\partial n[j]} = \frac{P}{T}\frac{\mathrm{d}\dot{T}}{\mathrm{d}n[j]} + TR_u \sum_{k=1}^{-1+N_s} \left(1 - \frac{W_k}{W_{N_s}}\right)\frac{\partial \dot{\omega}}{\partial n[j]}_k \tag{289}$$

Pressure Derivative

$$\frac{\partial \dot{P}}{\partial P} = TR_u \sum_{k=1}^{-1+N_s} \left(1 - \frac{W_k}{W_{N_s}}\right)\frac{\partial \dot{\omega}}{\partial P}_k + \frac{1}{T}\left(P\frac{\mathrm{d}\dot{T}}{\mathrm{d}P} + \dot{T}\right) \tag{290}$$

17.4 $\dot{n_k}$ Derivatives

$$\frac{\partial \dot{n}}{\partial n[j]}_k = V\frac{\partial \dot{\omega}}{\partial n[j]}_k \tag{291}$$

$$\frac{\partial \dot{n}}{\partial T}_k = V\frac{\partial \dot{\omega}}{\partial T}_k \tag{292}$$

$$\frac{\partial \dot{n}}{\partial P}_k = V\frac{\partial \dot{\omega}}{\partial P}_k \tag{293}$$

18 Jacobian Update Form

18.1 Temperature Derivatives

$$\begin{aligned}\mathcal{J}_{1,1} = \frac{1}{\sum_{k=1}^{N_s}[C]_k {C_v}_k}\Bigg(&\frac{\mathrm{d}T}{\mathrm{d}t}\sum_{k=1}^{N_s}\left(-\frac{\mathrm{d}C_v}{\mathrm{d}T}_k + \frac{{C_v}_{N_s}}{T}\right)[C]_k \\ &+ \sum_{k=1}^{-1+N_s}\left(\frac{1}{V}\left(-U_k + \frac{W_k U_{N_s}}{W_{N_s}}\right)\frac{\partial \dot{n}}{\partial T}_k + \left(-{C_v}_k + \frac{W_k}{W_{N_s}}\frac{\mathrm{d}U}{\mathrm{d}T}_{N_s}\right)\dot{\omega}_k\right)\Bigg)\end{aligned} \tag{294}$$

$$\mathcal{J}_{2,1} = \frac{P}{T}\left(\frac{\mathrm{d}\dot{T}}{\mathrm{d}T} - \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}t}\right) + R_u \sum_{k=1}^{-1+N_s}\left(1 - \frac{W_k}{W_{N_s}}\right)\left(\frac{T}{V}\frac{\partial \dot{n}}{\partial T}_k + \dot{\omega}_k\right) \tag{295}$$

$$\mathcal{J}_{k+2,1} = V\sum_{i=1}^{N_r}\nu_{k,i}\frac{\partial q}{\partial T}_i \tag{296}$$

Converting to update form:

$$\mathcal{J}_{k+2,1} \mathrel{+}= V\nu_{k,i}\frac{\partial q}{\partial T}_i \quad k = 1, \ldots, N_{sp} - 1 \tag{297}$$

18.1.1 Explicit reversible reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} c_i + R_i \frac{\partial c}{\partial T}_i \tag{298}$$

$$\Theta_{\partial T,i} = \frac{[C] S''_{N_s}}{T} k_{r\,i} - \frac{[C] S'_{N_s}}{T} k_{f\,i} + \frac{R_{f\,i}}{T}\left(\beta_i + \frac{E_{a\,i}}{T R_u}\right) - \frac{R_{r\,i}}{T}\left(\beta_{r\,i} + \frac{E_{a,r\,i}}{T R_u}\right) \tag{299}$$

18.1.2 Non-explicit reversible reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} c_i + R_i \frac{\partial c}{\partial T}_i \tag{300}$$

$$\begin{aligned}\Theta_{\partial T,i} = &- \left(-\sum_{k=1}^{N_s} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_i + \frac{E_{a\,i}}{T R_u}\right)\right) R_{r\,i} \\ &+ \frac{[C] S''_{N_s}}{T} k_{r\,i} - \frac{[C] S'_{N_s}}{T} k_{f\,i} + \frac{R_{f\,i}}{T}\left(\beta_i + \frac{E_{a\,i}}{T R_u}\right)\end{aligned} \tag{301}$$

18.1.3 Pressure-dependent reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} \tag{302}$$

For PLog reactions:

$$\begin{aligned}\Theta_{\partial T,i} = &- \left(-\sum_{k=1}^{N_s} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k + \frac{1}{T}\left(\beta_1 \right.\right. \\ &\left.\left. + \frac{(\log(P) - \log(P_1))\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T R_u} + \frac{E_{a_2}}{T R_u}\right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a_1}}{T R_u}\right)\right) R_{r\,i} \\ &+ \frac{[C]}{T}\left(S''_{N_s} k_{r\,i} - S'_{N_s} k_{f\,i}\right) \\ &+ \frac{R_{f\,i}}{T}\left(\beta_1 + \frac{(\log(P) - \log(P_1))\left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T R_u} + \frac{E_{a_2}}{T R_u}\right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a_1}}{T R_u}\right)\end{aligned} \tag{303}$$

For Chebyshev reactions:

$$
\begin{aligned}
\Theta_{\partial T,i} = &\left(\sum_{k=1}^{N_s} \nu_{k,i} \frac{\mathrm{d}B}{\mathrm{d}T}_k \right.\\
&\left. + \frac{2\log(10)}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} \sum_{\substack{1\leq l\leq N_P\\ 1\leq j\leq N_T}} (j-1)\, T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right) \eta_{l,j} \right) R_{r\,i}\\
&+ \log(10) R_{f\,i} \sum_{\substack{1\leq l\leq N_P\\ 1\leq j\leq N_T}} -\frac{2T_{l-1}\left(\tilde{P}\right) U_{j-2}\left(\tilde{T}\right)\eta_{l,j}}{T^2\left(-\frac{1}{T_{min}} + \frac{1}{T_{max}}\right)} (j-1)\\
&+ \frac{[C]}{T}\left(S''_{N_s} k_{r\,i} - S'_{N_s} k_{f\,i}\right)
\end{aligned}
\tag{304}
$$

18.1.4 Pressure independent reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} \tag{305}$$

18.1.5 Third-body enhanced reactions

For mixture as third-body:

$$\frac{\partial q}{\partial T}_i = [X]_i \Theta_{\partial T,i} - \frac{[C]\alpha_{N_s,i}}{T} R_i \tag{306}$$

For species m as third-body:

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i}\left(\left(-\delta_{N_s m} + 1\right)[C]_m + \delta_{N_s m}[C]_{N_s}\right) - \frac{\delta_{N_s m}}{T}[C] R_i \tag{307}$$

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

$$\frac{\partial q}{\partial T}_i = [C]\left(\Theta_{\partial T,i} - \frac{R_i}{T}\right) \tag{308}$$

18.1.6 Unimolecular/recombination fall-off reactions

$$
\begin{aligned}
\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} c_i + &\left(\frac{F_i \bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1} \right.\\
&\left. + \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial T}}{P_{r,i}+1} + \Theta_{F_i,\partial T} + \Theta_{P_{r,i},\partial T} - \frac{\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1} \right) c_i \right) R_i
\end{aligned}
\tag{309}
$$

18.1.7 Chemically-activated bimolecular reactions

$$\frac{\partial q}{\partial T}_i = \left(\Theta_{\partial T,i} + \left(-\frac{P_{r,i}\Theta_{P_{r,i},\partial T}}{P_{r,i}+1} + \Theta_{F_i,\partial T} - \frac{\bar{\theta}_{P_{r,i},\partial T}}{P_{r,i}+1} \right) R_i \right) c_i \tag{310}$$

18.1.8 Reduced Pressure Derivatives

For mixture as third-body:

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \tag{311}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\alpha_{N_s,i}}{Tk_{\infty,i}} \tag{312}$$

For species m as third-body:

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \tag{313}$$

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\delta_{N_s m}}{Tk_{\infty,i}} \tag{314}$$

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

$$\Theta_{P_{r,i},\partial T} = \frac{1}{T}\left(\beta_0 - \beta_\infty - 1 + \frac{E_{a,0}}{TR_u} - \frac{E_{a,\infty}}{TR_u}\right) \tag{315}$$

$$\bar{\theta}_{P_{r,i},\partial T} = 0 \tag{316}$$

18.1.9 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i,\partial T} = 0 \tag{317}$$

For Troe

$$\begin{aligned}\Theta_{F_i,\partial T} = -\frac{B_{Troe}}{F_{cent}P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log(10)} \Bigg(& 2A_{Troe}F_{cent}\left(0.14A_{Troe}\right. \\ & \left. + B_{Troe}\right)\left(P_{r,i}\Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right)\log\left(F_{cent}\right) \\ & + P_{r,i}\frac{\mathrm{d}F_{cent}}{\mathrm{d}T}\left(2A_{Troe}\left(1.1762A_{Troe} - 0.67B_{Troe}\right)\log\left(F_{cent}\right)\right. \\ & \left. - B_{Troe}\left(A_{Troe}^2 + B_{Troe}^2\right)\log(10)\right)\Bigg)\end{aligned} \tag{318}$$

For SRI

$$\begin{aligned}\Theta_{F_i,\partial T} = & -\frac{X\left(\frac{\exp\left(-\frac{T}{c}\right)}{c} - \frac{ab}{T^2}\exp\left(-\frac{b}{T}\right)\right)}{a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)} + \frac{e}{T} \\ & - \frac{2X^2\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2(10)}\left(P_{r,i}\Theta_{P_{r,i},\partial T} + \bar{\theta}_{P_{r,i},\partial T}\right)\log\left(P_{r,i}\right)\end{aligned} \tag{319}$$

18.2 Molar Derivatives

$$
\begin{aligned}
\mathcal{J}_{1,j+2} &= \frac{\partial \dot{T}}{\partial n_j} \\
&= \frac{1}{\sum_{k=1}^{N_s}[C]_k C_{v\,k}} \left(-\frac{1}{V}\frac{\mathrm{d}T}{\mathrm{d}t}\left(-C_{v\,N_s} + C_{v\,j}\right) \right. \\
&\qquad \left. - \sum_{k=1}^{-1+N_s} \frac{1}{V}\left(U_k - \frac{W_k U_{N_s}}{W_{N_s}}\right) \frac{\partial \dot{n}}{\partial n[j]}_k \right)
\end{aligned} \tag{320}
$$

$$
\begin{aligned}
\mathcal{J}_{2,j+2} &= \frac{\partial \dot{P}}{\partial n[j]} \\
&= \frac{P}{T}\frac{\mathrm{d}\dot{T}}{\mathrm{d}n[j]} + T R_u \sum_{k=1}^{-1+N_s} \frac{1}{V}\left(1 - \frac{W_k}{W_{N_s}}\right) \frac{\partial \dot{n}}{\partial n[j]}_k
\end{aligned} \tag{321}
$$

$$
\begin{aligned}
\mathcal{J}_{k+2,j+2} &= \frac{\partial \dot{n_k}}{\partial n_j} \\
&= V \sum_{i=1}^{N_r} \nu_{k,i} \frac{\partial q}{\partial n[j]}_i
\end{aligned} \tag{322}
$$

Converting to Jacobian Update form:

$$
\mathcal{J}_{k+2,j+2} \mathrel{+}= V \nu_{k,i} \frac{\partial q}{\partial n[j]}_i \tag{323}
$$

$$
V\frac{\partial q}{\partial n[j]}_k = \left(\left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i}\right) c_i + V R_i \frac{\partial c}{\partial n[j]}_i \tag{324}
$$

18.2.1 Pressure-dependent reactions

$$
V\frac{\partial q}{\partial n[j]}_k = \left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i} \tag{325}
$$

18.2.2 Pressure independent reactions

$$
V\frac{\partial q}{\partial n[j]}_k = \left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i} \tag{326}
$$

18.2.3 Third-body enhanced reactions

For mixture as third-body:

$$
V\frac{\partial q}{\partial n[j]}_k = [X]_i \left(\left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i}\right) + \left(-\alpha_{N_s,i} + \alpha_{j,i}\right) R_i \tag{327}
$$

For species m as third-body:

$$V \frac{\partial q}{\partial n[j]}_k = \left(\left(-\delta_{N_s m} + 1\right)[C]_m + \delta_{N_s m}[C]_{N_s}\right)\left(\left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i}\right) + \left(-\delta_{N_s m} + \delta_{jm}\right) R_i \tag{328}$$

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

$$V \frac{\partial q}{\partial n[j]}_k = [C]\left(\left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i}\right) \tag{329}$$

18.2.4 Falloff Reactions

Unimolecular/recombination fall-off reactions:

$$V \frac{\partial q}{\partial n[j]}_i = \frac{k_{0,i} \bar{\theta}_{P_{r,i},\partial n_j} R_i}{k_{\infty,i}\left(P_{r,i} + 1\right)}\left(F_i P_{r,i} \Theta_{F_i,\partial n_j} + F_i - c_i\right) + \left(\left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i}\right) c_i \tag{330}$$

18.2.5 Chemically-activated bimolecular reactions

$$V \frac{\partial q}{\partial n[j]}_i = \frac{k_{0,i} \bar{\theta}_{P_{r,i},\partial n_j} R_i}{k_{\infty,i}\left(P_{r,i} + 1\right)}\left(F_i \Theta_{F_i,\partial n_j} - c_i\right) + \left(\left(S''_{N_s} - S''_j\right) k_{r\,i} - \left(S'_{N_s} - S'_j\right) k_{f\,i}\right) c_i \tag{331}$$

18.2.6 Reduced Pressure Derivatives

For mixture as third-body:

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\alpha_{N_s,i} + \alpha_{j,i} \tag{332}$$

For species m as third-body:

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\delta_{N_s m} + \delta_{jm} \tag{333}$$

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

$$\bar{\theta}_{P_{r,i},\partial n_j} = 0 \tag{334}$$

18.2.7 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i,\partial n_j} = 0 \tag{335}$$

For Troe

$$\Theta_{F_i,\partial n_j} = -\frac{2 A_{Troe} B_{Troe}\left(0.14 A_{Troe} + B_{Troe}\right)\log\left(F_{cent}\right)}{P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2 \log\left(10\right)} \tag{336}$$

For SRI

$$\Theta_{F_i,\partial n_j} = -\frac{2X^2 \log\left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right)}{P_{r,i}\log^2\left(10\right)}\log\left(P_{r,i}\right) \tag{337}$$

18.3 Pressure Derivatives

$$\begin{aligned}\mathcal{J}_{1,2} &= \frac{\partial \dot{T}}{\partial P} \\ &= \frac{1}{\sum_{k=1}^{N_s} [C]_k C_{v\,k}} \left(- \sum_{k=1}^{-1+N_s} \frac{1}{V} \left(U_k - \frac{W_k U_{N_s}}{W_{N_s}} \right) \frac{\partial \dot{n}}{\partial P}_k - \frac{C_{v\,N_s}}{T R_u} \frac{\mathrm{d}T}{\mathrm{d}t} \right)\end{aligned} \tag{338}$$

$$\begin{aligned}\mathcal{J}_{2,2} &= \frac{\partial \dot{P}}{\partial P} \\ &= T R_u \sum_{k=1}^{-1+N_s} \frac{1}{V} \left(1 - \frac{W_k}{W_{N_s}} \right) \frac{\partial \dot{n}}{\partial P}_k + \frac{1}{T} \left(P \frac{\mathrm{d}\dot{T}}{\mathrm{d}P} + \dot{T} \right)\end{aligned} \tag{339}$$

$$\begin{aligned}\mathcal{J}_{k+2,2} &= \frac{\partial \dot{n}_k}{\partial P} \\ &= V \sum_{i=1}^{N_r} \nu_{k,i} \frac{\partial q}{\partial P}_i\end{aligned} \tag{340}$$

Converting to Jacobian Update form:

$$\mathcal{J}_{k+2,2} += V \nu_{k,i} \frac{\partial q}{\partial P}_i \tag{341}$$

$$\frac{\partial q}{\partial P}_k = \left(- \frac{S''_{N_s} k_{r\,i}}{T R_u} + \frac{S'_{N_s} k_{f\,i}}{T R_u} \right) c_i + R_i \frac{\partial c}{\partial P}_i \tag{342}$$

18.3.1 Pressure-dependent reactions

For PLOG:

$$\frac{\partial q}{\partial P}_k = \frac{1}{T R_u} \left(- S''_{N_s} k_{r\,i} + S'_{N_s} k_{f\,i} \right) + \frac{\left(- \log\left(k_1\right) + \log\left(k_2\right) \right) \left(R_{f\,i} - R_{r\,i} \right)}{P \left(- \log\left(P_1\right) + \log\left(P_2\right) \right)} \tag{343}$$

For Chebyshev:

$$\begin{aligned}\frac{\partial q}{\partial P}_k = \log(10) R_{f\,i} &\sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2\left(l-1\right) T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right) \eta_{l,j}}{P\left(\log\left(P_{max}\right) - \log\left(P_{min}\right)\right)} \\ - \log(10) R_{r\,i} &\sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2\left(l-1\right) T_{j-1}\left(\tilde{T}\right) U_{l-2}\left(\tilde{P}\right) \eta_{l,j}}{P\left(\log\left(P_{max}\right) - \log\left(P_{min}\right)\right)} \\ + \frac{1}{T R_u} &\left(- S''_{N_s} k_{r\,i} + S'_{N_s} k_{f\,i} \right)\end{aligned} \tag{344}$$

18.3.2 Pressure independent reactions

$$\frac{\partial q}{\partial P}_k = - \frac{S''_{N_s} k_{r\,i}}{T R_u} + \frac{S'_{N_s} k_{f\,i}}{T R_u} \tag{345}$$

18.3.3 Third-body enhanced reactions

For mixture as third-body:

$$\frac{\partial q}{\partial P}_k = [X]_i \left(-\frac{S''_{N_s} k_{ri}}{TR_u} + \frac{S'_{N_s} k_{fi}}{TR_u} \right) + \frac{\alpha_{N_s,i} R_i}{TR_u} \tag{346}$$

For species m as third-body:

$$\frac{\partial q}{\partial P}_k = \left(\left(-\delta_{N_s m} + 1 \right) [C]_m + \delta_{N_s m} [C]_{N_s} \right) \left(-\frac{S''_{N_s} k_{ri}}{TR_u} + \frac{S'_{N_s} k_{fi}}{TR_u} \right) + \frac{\delta_{N_s m} R_i}{TR_u} \tag{347}$$

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

$$\frac{\partial q}{\partial P}_k = [C] \left(-\frac{S''_{N_s} k_{ri}}{TR_u} + \frac{S'_{N_s} k_{fi}}{TR_u} \right) + \frac{R_i}{TR_u} \tag{348}$$

18.3.4 Unimolecular/recombination fall-off reactions

$$\frac{\partial q}{\partial P}_i = \left(\frac{F_i \bar{\theta}_{P_{r,i},\partial P}}{P_{r,i} + 1} + \left(\Theta_{F_i,\partial P} - \frac{\bar{\theta}_{P_{r,i},\partial P}}{P_{r,i} + 1} \right) c_i \right) R_i + \left(-\frac{S''_{N_s} k_{ri}}{TR_u} + \frac{S'_{N_s} k_{fi}}{TR_u} \right) c_i \tag{349}$$

18.3.5 Chemically-activated bimolecular reactions

$$\frac{\partial q}{\partial P}_i = \left(\left(\Theta_{F_i,\partial P} - \frac{\bar{\theta}_{P_{r,i},\partial P}}{P_{r,i} + 1} \right) R_i - \frac{S''_{N_s} k_{ri}}{TR_u} + \frac{S'_{N_s} k_{fi}}{TR_u} \right) c_i \tag{350}$$

18.3.6 Reduced Pressure Derivatives

For mixture as third-body:

$$\Theta_{P_{r,i},\partial P} = 0 \tag{351}$$

$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i} \alpha_{N_s,i}}{T k_{\infty,i} R_u} \tag{352}$$

For species m as third-body:

$$\Theta_{P_{r,i},\partial P} = 0 \tag{353}$$

$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i} \delta_{N_s m}}{T k_{\infty,i} R_u} \tag{354}$$

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

$$\Theta_{P_{r,i},\partial P} = 0 \tag{355}$$

$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i}}{k_{\infty,i}} \frac{\partial [C]}{\partial P} \tag{356}$$

18.3.7 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i,\partial P} = 0 \tag{357}$$

For Troe

$$\Theta_{F_i,\partial P} = -\frac{2A_{Troe}B_{Troe}\bar{\theta}_{P_{r,i},\partial P}\left(0.14A_{Troe} + B_{Troe}\right)\log\left(F_{cent}\right)}{P_{r,i}\left(A_{Troe}^2 + B_{Troe}^2\right)^2\log\left(10\right)} \tag{358}$$

For SRI

$$\Theta_{F_i,\partial P} = -\frac{2X^2\bar{\theta}_{P_{r,i},\partial P}\log\left(P_{r,i}\right)}{P_{r,i}\log^2\left(10\right)}\log\left(a\exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right)\right) \tag{359}$$