

1 State Variables

$$[C]_k = \frac{n_k}{V} \quad (1)$$

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

$$\frac{d\Phi}{dt} = \left\{ \frac{dT}{dt}, \frac{dP}{dt}, \frac{dn}{dt}[1], \frac{dn}{dt}[2] \dots \frac{dn}{dt}[-1 + Ns()] \right\} \quad (3)$$

2 Source Terms

$$\frac{dn}{dt}_k = V\dot{\omega}_k \quad (4)$$

$$\frac{dT}{dt} = - \frac{\sum_{k=1}^{N_{sp}} U_k \dot{\omega}_k}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \quad (5)$$

From conservation of mass:

$$m = \sum_{k=1}^{N_{sp}} W_k n_k \quad (6)$$

$$0 = \sum_{k=1}^{N_{sp}} W_k \frac{dn}{dt}_k \quad (7)$$

$$\frac{dn}{dt}_{N_{sp}} = - \frac{1}{W_{N_{sp}}} \sum_{k=1}^{-1+N_{sp}} W_k \frac{dn}{dt}_k \quad (8)$$

$$n = \frac{PV}{T\mathcal{R}} \quad (9)$$

Thus...

$$\dot{\omega}_{N_{sp}} = - \frac{1}{W_{N_{sp}}} \sum_{k=1}^{-1+N_{sp}} W_k \dot{\omega}_k \quad (10)$$

And...

$$\frac{dT}{dt} = - \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \quad (11)$$

$$\frac{dn}{dt} = \sum_{k=1}^{N_{sp}} \frac{dn}{dt}_k \quad (12)$$

$$\frac{dn}{dt} = \sum_{k=1}^{-1+N_{sp}} \left(1 - \frac{W_k}{W_{N_{sp}}}\right) \frac{dn}{dt}_k \quad (13)$$

From the ideal gas law:

$$\frac{dP}{dt} = \frac{\mathcal{R}}{V} \left(T \frac{dn}{dt} + \frac{dT}{dt} n \right) \quad (14)$$

$$\frac{dP}{dt} = \frac{P}{T} \frac{dT}{dt} + T \mathcal{R} \sum_{k=1}^{-1+N_{sp}} \left(1 - \frac{W_k}{W_{N_{sp}}}\right) \dot{\omega}_k \quad (15)$$

2.1 Other defs

$$[C] = \frac{P}{T \mathcal{R}} \quad (16)$$

$$\frac{dP}{dt} = \frac{P}{T} \frac{dT}{dt} + T \mathcal{R} \sum_{k=1}^{-1+N_{sp}} \left(1 - \frac{W_k}{W_{N_{sp}}}\right) \dot{\omega}_k \quad (17)$$

$$[C]_{N_{sp}} = [C] - \sum_{k=1}^{-1+N_{sp}} [C]_k \quad (18)$$

$$[C]_{N_{sp}} = \frac{P}{T \mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \quad (19)$$

$$W = \sum_{k=1}^{N_{sp}} W_k X_k \quad (20)$$

$$W = \frac{1}{[C]} \sum_{k=1}^{N_{sp}} W_k [C]_k \quad (21)$$

$$[C]_{N_{sp}} = \frac{P}{T \mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \quad (22)$$

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

$$W = W_{N_{sp}} + \frac{1}{[C]} \sum_{k=1}^{-1+N_{sp}} (-W_{N_{sp}} + W_k) [C]_k \quad (24)$$

3 Thermo Definitions

$$C_{p,k}^{\circ} = C_{p_k} \quad (25)$$

$$C_{p_k} = \mathcal{R} (T (T (T (T a_{k,4} + a_{k,3}) + a_{k,2}) + a_{k,1}) + a_{k,0}) \quad (26)$$

$$C_{p_k} = T^4 \mathcal{R} a_{k,4} + T^3 \mathcal{R} a_{k,3} + T^2 \mathcal{R} a_{k,2} + T \mathcal{R} a_{k,1} + \mathcal{R} a_{k,0} \quad (27)$$

$$\frac{dC_p}{dT}_k = \mathcal{R} (4T^3 a_{k,4} + 3T^2 a_{k,3} + 2T a_{k,2} + a_{k,1}) \quad (28)$$

$$\frac{dC_p}{dT}_k = \mathcal{R} (T (T (4T a_{k,4} + 3a_{k,3}) + 2a_{k,2}) + a_{k,1}) \quad (29)$$

$$\bar{c}_p = \sum_{k=1}^{N_{sp}} \frac{n_k C_{p_k}}{n} \quad (30)$$

$$C_{v,k}^{\circ} = C_{v_k} \quad (31)$$

$$C_{v_k} = \mathcal{R} (T (T (T (T a_{k,4} + a_{k,3}) + a_{k,2}) + a_{k,1}) + a_{k,0} - 1) \quad (32)$$

$$C_{v_k} = T^4 \mathcal{R} a_{k,4} + T^3 \mathcal{R} a_{k,3} + T^2 \mathcal{R} a_{k,2} + T \mathcal{R} a_{k,1} + \mathcal{R} a_{k,0} - \mathcal{R} \quad (33)$$

$$\frac{dC_v}{dT}_k = \mathcal{R} (4T^3 a_{k,4} + 3T^2 a_{k,3} + 2T a_{k,2} + a_{k,1}) \quad (34)$$

$$\frac{dC_v}{dT}_k = \mathcal{R} (T (T (4T a_{k,4} + 3a_{k,3}) + 2a_{k,2}) + a_{k,1}) \quad (35)$$

$$\bar{c}_v = \sum_{k=1}^{N_{sp}} \frac{n_k C_{v_k}}{n} \quad (36)$$

$$H_k^{\circ} = H_k \quad (37)$$

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

$$H_k = \frac{T^5 a_{k,4}}{5} \mathcal{R} + \frac{T^4 a_{k,3}}{4} \mathcal{R} + \frac{T^3 a_{k,2}}{3} \mathcal{R} + \frac{T^2 a_{k,1}}{2} \mathcal{R} + T \mathcal{R} a_{k,0} + \mathcal{R} a_{k,5} \quad (39)$$

$$\frac{dH}{dT}_k = \mathcal{R} (T (T (T (T a_{k,4} + a_{k,3}) + a_{k,2}) + a_{k,1}) + a_{k,0}) \quad (40)$$

$$H_k = U_k + \frac{PV}{n} \quad (41)$$

$$U_k = -T\mathcal{R} + H_k \quad (42)$$

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

$$\frac{dU}{dT_k} = \mathcal{R} (T (T (T (Ta_{k,4} + a_{k,3}) + a_{k,2}) + a_{k,1}) + a_{k,0} - 1) \quad (44)$$

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

4 Definitions

$$\nu_{k,i} = \nu''_{k,i} - \nu'_{k,i} \quad (46)$$

$$\dot{\omega}_k = \sum_{i=1}^{N_{reac}} \nu_{k,i} q_i \quad (47)$$

$$q_i = R_i c_i \quad (48)$$

$$\dot{\omega}_k = \sum_{i=1}^{N_{reac}} \nu_{k,i} R_i c_i \quad (49)$$

5 Rate of Progress

$$R_i = R_{f_i} - R_{r_i} \quad (50)$$

$$R_{f_i} = k_{f_i} \prod_{k=1}^{N_{sp}} [C]_k^{\nu'_{k,i}} \quad (51)$$

$$R_{r_i} = k_{r_i} \prod_{k=1}^{N_{sp}} [C]_k^{\nu''_{k,i}} \quad (52)$$

6 Third-body effect

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

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

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

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

7 Forward Reaction Rate

$$k_{fi} = T^{\beta_i} \exp\left(-\frac{E_{ai}}{T\mathcal{R}}\right) A_i \quad (57)$$

8 Equilibrium Constants

$$K_{ci} = \left(\left(\frac{P_{atm}}{T\mathcal{R}} \right)^{\sum_{k=1}^{N_{sp}} \nu_{k,i}} \right) K_{pi} \quad (58)$$

$$K_{pi} = \exp\left(\frac{\Delta S_k^\circ}{\mathcal{R}} - \frac{\Delta H_k^\circ}{\mathcal{R}T}\right) \quad (59)$$

$$K_{pi} = \exp\left(\sum_{k=1}^{N_{sp}} \nu_{ki} \left(\frac{S_k^\circ}{\mathcal{R}} - \frac{H_k^\circ}{\mathcal{R}T} \right)\right) \quad (60)$$

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

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

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

9 Reverse Reaction Rate

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

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

10 Third-Body Efficiencies

$$[X]_i = \sum_{k=1}^{N_{sp}} \alpha_{k,i} [C]_k \quad (66)$$

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

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

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

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

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

11 Falloff Reactions

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

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

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

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

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

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

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

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

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

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

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

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

12 Pressure-Dependent Reactions

For PLog reactions

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

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

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

For Chebyshev reactions

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

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

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

13 Derivatives

$$\frac{\partial q}{\partial T_i} = R_i \frac{\partial c}{\partial T_i} + \frac{\partial R}{\partial T_i} c_i \quad (90)$$

$$\frac{\partial \dot{\omega}}{\partial T_k} = \sum_{i=1}^{N_{reac}} \left(\nu_{k,i} R_i \frac{\partial c}{\partial T_i} + \nu_{k,i} \frac{\partial R}{\partial T_i} c_i \right) \quad (91)$$

$$\frac{\partial q}{\partial n[k]_i} = R_i \frac{\partial c}{\partial n_{j_i}} + \frac{\partial R}{\partial n_{j_i}} c_i \quad (92)$$

$$\frac{\partial \dot{\omega}}{\partial n_{j_k}} = \sum_{i=1}^{N_{reac}} \left(\nu_{k,i} R_i \frac{\partial c}{\partial n_{j_i}} + \nu_{k,i} \frac{\partial R}{\partial n_{j_i}} c_i \right) \quad (93)$$

$$\frac{\partial q}{\partial P_i} = R_i \frac{\partial c}{\partial P_i} + \frac{\partial R}{\partial P_i} c_i \quad (94)$$

$$\frac{\partial \dot{\omega}}{\partial P_k} = \sum_{i=1}^{N_{reac}} \left(\nu_{k,i} R_i \frac{\partial c}{\partial P_i} + \nu_{k,i} \frac{\partial R}{\partial P_i} c_i \right) \quad (95)$$

14 Rate of Progress Derivatives

14.1 Molar Derivatives

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

$$\frac{\partial [C_k]}{\partial n_j} = \frac{\delta_{jk}}{V} \quad (97)$$

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

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

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

$$\frac{\partial R_f}{\partial n_{j_i}} = k_{fi} \sum_{k=1}^{N_{sp}} \left(-\frac{\delta_{N_{sp}k}}{V} + \frac{\delta_{jk}}{V} \right) \nu'_{k,i} [C]_k^{\nu'_{k,i}-1} \prod_{\substack{1 \leq l \leq k-1 \\ k+1 \leq l \leq N_{sp}}} [C]_l^{\nu'_{l,i}} \quad (101)$$

$$\frac{\partial R_f}{\partial n_{j_i}} = \frac{k_{fi}}{V} \left(-\nu'_{Ns,i} [C]_{Ns}^{\nu'_{Ns,i}-1} \prod_{l=1}^{-1+N_{sp}} [C]_l^{\nu'_{l,i}} + \nu'_{j,i} [C]_j^{\nu'_{j,i}-1} \prod_{\substack{1 \leq l \leq j-1 \\ j+1 \leq l \leq N_{sp}}} [C]_l^{\nu'_{l,i}} \right) \quad (102)$$

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

$$\frac{\partial R_f}{\partial n_{j_i}} = \frac{k_{fi}}{V} \left(-S'_{N_{sp}} + S'_j \right) \quad (104)$$

$$\frac{\partial R_r}{\partial n_{j_i}} = k_{ri} \sum_{k=1}^{N_{sp}} \left(-\frac{\delta_{N_{sp}k}}{V} + \frac{\delta_{jk}}{V} \right) \nu''_{k,i} [C]_k^{\nu''_{k,i}-1} \prod_{\substack{1 \leq l \leq k-1 \\ k+1 \leq l \leq N_{sp}}} [C]_l^{\nu''_{l,i}} \quad (105)$$

$$\frac{\partial R_r}{\partial n_{j_i}} = \frac{k_{ri}}{V} \left(-\nu''_{Ns,i} [C]_{Ns}^{\nu''_{Ns,i}-1} \prod_{l=1}^{-1+N_{sp}} [C]_l^{\nu''_{l,i}} + \nu''_{j,i} [C]_j^{\nu''_{j,i}-1} \prod_{\substack{1 \leq l \leq j-1 \\ j+1 \leq l \leq N_{sp}}} [C]_l^{\nu''_{l,i}} \right) \quad (106)$$

$$S''_l = \nu''_{l,i} [C]_l^{\nu''_{l,i}-1} \prod_{\substack{1 \leq l \leq l-1 \\ l+1 \leq l \leq N_{sp}}} [C]_l^{\nu''_{l,i}} \quad (107)$$

$$\frac{\partial R_r}{\partial n_{j_i}} = \frac{k_{ri}}{V} \left(-S''_{N_{sp}} + S''_j \right) \quad (108)$$

For all reversible reactions

$$\frac{\partial R}{\partial n_{j_i}} = -\frac{k_{ri}}{V} \left(-S''_{N_{sp}} + S''_j \right) + \frac{k_{fi}}{V} \left(-S'_{N_{sp}} + S'_j \right) \quad (109)$$

14.2 Temperature Derivative

$$R_f = k_{fi} \prod_{k=1}^{N_{sp}} [C]_k^{\nu'_{k,i}} \quad (110)$$

$$\frac{dk_f}{dT}_i = \frac{k_{fi}}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \quad (111)$$

$$R_f = \left(\left(\frac{P}{T\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \right)^{\nu'_{N_{sp},i}} \right) k_{fi} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}} \quad (112)$$

$$\begin{aligned} \frac{\partial R_f}{\partial T}_i = & - \frac{P \left(\left(\frac{P}{T\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \right)^{\nu'_{N_{sp},i}} \right) \nu'_{N_{sp},i} k_{fi} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}}}{T^2 \mathcal{R} \left(\frac{P}{T\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \right)} \\ & + \left(\left(\frac{P}{T\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \right)^{\nu'_{N_{sp},i}} \right) \frac{dk_f}{dT}_i \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}} \end{aligned} \quad (113)$$

$$\frac{\partial R_f}{\partial T}_i = \frac{dk_f}{dT}_i \prod_{k=1}^{N_{sp}} [C]_k^{\nu'_{k,i}} - \frac{[C] \nu'_{N_{sp},i}}{T} [C]_{N_{sp}}^{\nu'_{N_{sp},i}-1} k_{fi} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}} \quad (114)$$

$$\frac{\partial R_f}{\partial T}_i = - \frac{[C] S'_{N_{sp}}}{T} k_{fi} + \frac{R_{fi}}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \quad (115)$$

For reactions with explicit reverse Arrhenius coefficients

$$\frac{\partial R_r}{\partial T}_i = - \frac{[C] S''_{N_{sp}}}{T} k_{ri} + \frac{R_{ri}}{T} \left(\beta_{ri} + \frac{E_{a,ri}}{T\mathcal{R}} \right) \quad (116)$$

$$\frac{\partial R}{\partial T}_i = \frac{[C] S''_{N_{sp}}}{T} k_{ri} - \frac{[C] S'_{N_{sp}}}{T} k_{fi} + \frac{R_{fi}}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) - \frac{R_{ri}}{T} \left(\beta_{ri} + \frac{E_{a,ri}}{T\mathcal{R}} \right) \quad (117)$$

For non-explicit reversible reactions

$$\frac{dk_r}{dT}_i = - \frac{k_{fi}}{K_{ci}^2} \frac{dK_c}{dT}_i + \frac{1}{K_{ci}} \frac{dk_f}{dT}_i \quad (118)$$

$$\frac{dk_r}{dT}_i = \left(- \frac{1}{K_{ci}} \frac{dK_c}{dT}_i + \frac{1}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \right) k_{ri} \quad (119)$$

$$\frac{dK_c}{dT}_i = K_{ci} \sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT}_k \quad (120)$$

$$\frac{dk_r}{dT}_i = \left(-\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT}_k + \frac{1}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \right) k_{ri} \quad (121)$$

$$\frac{\partial R_r}{\partial T}_i = \left(-\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT}_k + \frac{1}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \right) R_{ri} - \frac{[C]S''_{N_{sp}}}{T} k_{ri} \quad (122)$$

$$\frac{\partial R_r}{\partial T}_i = \left(-\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT}_k + \frac{1}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \right) R_{ri} - \frac{[C]S''_{N_{sp}}}{T} k_{ri} \quad (123)$$

$$\begin{aligned} \frac{\partial R}{\partial T}_i = & - \left(-\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT}_k + \frac{1}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \right) R_{ri} \\ & + \frac{[C]S''_{N_{sp}}}{T} k_{ri} - \frac{[C]S'_{N_{sp}}}{T} k_{fi} + \frac{R_{fi}}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \end{aligned} \quad (124)$$

$$\frac{dB}{dT}_k = T \left(T \left(\frac{Ta_{k,4}}{5} + \frac{a_{k,3}}{4} \right) + \frac{a_{k,2}}{3} \right) + \frac{a_{k,1}}{2} + \frac{1}{T} \left(a_{k,0} - 1 + \frac{a_{k,5}}{T} \right) \quad (125)$$

14.3 Pressure derivatives

$$\frac{\partial [C]_k}{\partial P} = 0 \quad (126)$$

$$\frac{\partial [C]_{N_{sp}}}{\partial P} = \frac{1}{T\mathcal{R}} \quad (127)$$

$$\frac{\partial [C_{Ns}]^{\nu'_{Ns,i}}}{\partial P} = \frac{\nu'_{k,i} [C]_{N_{sp}}^{\nu'_{k,i}-1}}{T\mathcal{R}} \quad (128)$$

$$\frac{\partial [C]}{\partial P} = \frac{1}{T\mathcal{R}} \quad (129)$$

$$R_{fi} = \left(\left(\frac{P}{T\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \right)^{\nu'_{N_{sp},i}} \right) k_{fi} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}} \quad (130)$$

$$\frac{\partial R_f}{\partial P}_i = \frac{\nu'_{N_{sp},i} [C]_{N_{sp}}^{\nu'_{N_{sp},i}} k_{fi}}{T\mathcal{R}[C]_{N_{sp}}} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}} \quad (131)$$

$$\frac{\partial R_f}{\partial P_i} = \frac{\nu'_{N_{sp},i}[C]_{N_{sp}}^{\nu'_{N_{sp},i}} k_{fi}}{T\mathcal{R}[C]_{N_{sp}}} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}} \quad (132)$$

$$\frac{\partial R_f}{\partial P_i} = \frac{\nu'_{N_{sp},i}[C]_{N_{sp}}^{\nu'_{N_{sp},i}} k_{fi}}{T\mathcal{R}[C]_{N_{sp}}} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu'_{k,i}} \quad (133)$$

$$\frac{\partial R_f}{\partial P_i} = \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \quad (134)$$

$$\frac{\partial R_f}{\partial P_i} = \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \quad (135)$$

$$R_{ri} = \left(\left(\frac{P}{T\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \right)^{\nu''_{N_{sp},i}} \right) k_{ri} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu''_{k,i}} \quad (136)$$

$$\frac{\partial R_r}{\partial P_i} = \frac{\nu''_{N_{sp},i}[C]_{N_{sp}}^{\nu''_{N_{sp},i}} k_{ri}}{T\mathcal{R}[C]_{N_{sp}}} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu''_{k,i}} \quad (137)$$

$$\frac{\partial R_r}{\partial P_i} = \frac{\nu''_{N_{sp},i}[C]_{N_{sp}}^{\nu''_{N_{sp},i}} k_{ri}}{T\mathcal{R}[C]_{N_{sp}}} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu''_{k,i}} \quad (138)$$

$$\frac{\partial R_r}{\partial P_i} = \frac{\nu''_{N_{sp},i}[C]_{N_{sp}}^{\nu''_{N_{sp},i}} k_{ri}}{T\mathcal{R}[C]_{N_{sp}}} \prod_{k=1}^{-1+N_{sp}} [C]_k^{\nu''_{k,i}} \quad (139)$$

$$\frac{\partial R_r}{\partial P_i} = \frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} \quad (140)$$

$$\frac{\partial R_r}{\partial P_i} = \frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} \quad (141)$$

15 Third-Body/Falloff Derivatives

15.1 Elementary reactions

$$\frac{\partial c}{\partial T_i} = 0 \quad (142)$$

$$\frac{\partial c}{\partial n_{j_i}} = 0 \quad (143)$$

$$\frac{\partial c}{\partial P_i} = 0 \quad (144)$$

15.2 Third-body enhanced reactions

$$\frac{\partial[X]_i}{\partial T} = -\frac{[C]\alpha_{N_{sp},i}}{T} \quad (145)$$

$$\frac{\partial[X]_i}{\partial n_j} = \frac{1}{V} (-\alpha_{N_{sp},i} + \alpha_{j,i}) \quad (146)$$

$$\frac{\partial[X]_i}{\partial P} = \frac{\alpha_{N_{sp},i}}{T\mathcal{R}} \quad (147)$$

For species m as the third-body

$$\frac{\partial c}{\partial T_i} = -\frac{\delta_{N_{sp}m}}{T}[C] \quad (148)$$

$$\frac{\partial c}{\partial n_{j_i}} = \frac{1}{V} (-\delta_{N_{sp}m}\delta_{jm} - \delta_{N_{sp}m} + \delta_{jm}) \quad (149)$$

$$\frac{\partial c}{\partial n_{j_i}} = \frac{1}{V} (-\delta_{N_{sp}m} + \delta_{jm}) \quad (150)$$

$$\frac{\partial c}{\partial P_i} = \frac{\delta_{N_{sp}m}}{T\mathcal{R}} \quad (151)$$

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

$$\frac{\partial c}{\partial T_i} = -\frac{[C]}{T} \quad (152)$$

$$\frac{\partial c}{\partial n_{j_i}} = 0 \quad (153)$$

$$\frac{\partial c}{\partial P_i} = \frac{1}{T\mathcal{R}} \quad (154)$$

15.3 Unimolecular/recombination fall-off reactions

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

$$\frac{\partial c}{\partial n_{j_i}} = \frac{1}{P_{r,i} + 1} \left(P_{r,i} \frac{\partial F_i}{\partial n_j} + \frac{\partial P_{r,i}}{\partial n_j} (F_i - c_i) \right) \quad (156)$$

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

15.4 Chemically-activated bimolecular reactions

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

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

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

15.5 Reduced Pressure derivatives

For the mixture as the third body

$$\frac{\partial P_{r,i}}{\partial T} = \frac{P_{r,i}}{T} \left(\beta_0 - \beta_\infty + \frac{E_{a,0}}{T\mathcal{R}} - \frac{E_{a,\infty}}{T\mathcal{R}} \right) - \frac{[C]k_{0,i}\alpha_{N_{sp},i}}{Tk_{\infty,i}} \quad (161)$$

$$\frac{\partial P_{r,i}}{\partial n_j} = \frac{k_{0,i}(-\alpha_{N_{sp},i} + \alpha_{j,i})}{k_{\infty,i}V} \quad (162)$$

$$\frac{\partial P_{r,i}}{\partial P} = \frac{k_{0,i}\alpha_{N_{sp},i}}{Tk_{\infty,i}\mathcal{R}} \quad (163)$$

Simplifying:

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

$$\frac{\partial P_{r,i}}{\partial n_j} = \frac{\bar{\theta}_{P_{r,i},\partial n_j,mix}}{k_{\infty,i}V} k_{0,i} \quad (165)$$

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

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

$$\bar{\theta}_{P_{r,i},\partial T,mix} = -\frac{[C]k_{0,i}\alpha_{N_{sp},i}}{Tk_{\infty,i}} \quad (168)$$

$$\bar{\theta}_{P_{r,i},\partial n_j,mix} = -\alpha_{N_{sp},i} + \alpha_{j,i} \quad (169)$$

$$\Theta_{P_{r,i},\partial P,mix} = 0 \quad (170)$$

$$\bar{\theta}_{P_{r,i},\partial P,mix} = \frac{k_{0,i}\alpha_{N_{sp},i}}{Tk_{\infty,i}\mathcal{R}} \quad (171)$$

For species m as the third-body

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

$$\frac{\partial P_{r,i}}{\partial n_j} = \frac{k_{0,i}}{k_{\infty,i}V} (-\delta_{N_{sp}m} + \delta_{jm}) \quad (173)$$

$$\frac{\partial P_{r,i}}{\partial P} = \frac{k_{0,i}\delta_{N_{sp}m}}{Tk_{\infty,i}\mathcal{R}} \quad (174)$$

Simplifying:

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

$$\frac{\partial P_{r,i}}{\partial n_j} = \frac{\bar{\theta}_{P_{r,i},\partial n_j,spec}}{k_{\infty,i}V} k_{0,i} \quad (176)$$

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

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

$$\bar{\theta}_{P_{r,i},\partial T,spec} = -\frac{[C]k_{0,i}\delta_{N_{sp}m}}{Tk_{\infty,i}} \quad (179)$$

$$\bar{\theta}_{P_{r,i},\partial n_j,spec} = -\delta_{N_{sp}m} + \delta_{jm} \quad (180)$$

$$\Theta_{P_{r,i},\partial P,spec} = 0 \quad (181)$$

$$\bar{\theta}_{P_{r,i},\partial P,spec} = \frac{k_{0,i}\delta_{N_{sp}m}}{Tk_{\infty,i}\mathcal{R}} \quad (182)$$

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

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

$$\frac{\partial P_{r,i}}{\partial n_j} = 0 \quad (184)$$

$$\frac{\partial P_{r,i}}{\partial n_j} = \frac{k_{0,i}}{k_{\infty,i}} \frac{\partial[C]}{\partial P} \quad (185)$$

Simplifying:

$$\frac{\partial P_{r,i}}{\partial T} = P_{r,i} \Theta_{P_{r,i}, \partial T, \text{unity}} \quad (186)$$

$$\frac{\partial P_{r,i}}{\partial n_j} = \bar{\theta}_{P_{r,i}, \partial n_j, \text{unity}} \quad (187)$$

$$\frac{\partial P_{r,i}}{\partial P} = \bar{\theta}_{P_{r,i}, \partial P, \text{unity}} \quad (188)$$

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

$$\bar{\theta}_{P_{r,i}, \partial T, \text{unity}} = 0 \quad (190)$$

$$\bar{\theta}_{P_{r,i}, \partial n_j, \text{unity}} = 0 \quad (191)$$

$$\Theta_{P_{r,i}, \partial P, \text{unity}} = 0 \quad (192)$$

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

Thus we write:

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

$$\frac{\partial P_{r,i}}{\partial n_j} = \frac{k_{0,i} \bar{\theta}_{P_{r,i}, \partial n_j}}{k_{\infty,i} V} \quad (195)$$

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

For

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

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

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

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

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

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

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\alpha_{N_{sp},i} + \alpha_{j,i} \quad \text{if mix} \quad (199a)$$

$$\bar{\theta}_{P_{r,i},\partial n_j} = -\delta_{N_{sp}m} + \delta_{jm} \quad \text{if species} \quad (199b)$$

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

$$\Theta_{P_{r,i},\partial P} = 0 \quad \text{if mix} \quad (200a)$$

$$\Theta_{P_{r,i},\partial P} = 0 \quad \text{if species} \quad (200b)$$

$$\Theta_{P_{r,i},\partial P} = 0 \quad \text{if unity} \quad (200c)$$

$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i}\alpha_{N_{sp},i}}{Tk_{\infty,i}\mathcal{R}} \quad \text{if mix} \quad (201a)$$

$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i}\delta_{N_{sp}m}}{Tk_{\infty,i}\mathcal{R}} \quad \text{if species} \quad (201b)$$

$$\bar{\theta}_{P_{r,i},\partial P} = \frac{k_{0,i}}{k_{\infty,i}} \frac{\partial[C]}{\partial P} \quad \text{if unity} \quad (201c)$$

15.6 Falloff Blending Factor derivatives

For Lindemann reactions

$$\frac{\partial F_i}{\partial T} = 0 \quad (202)$$

$$\frac{\partial F_i}{\partial n_j} = 0 \quad (203)$$

$$\frac{\partial F_i}{\partial P} = 0 \quad (204)$$

For Troe reactions

$$\frac{\partial F_i}{\partial T} = \frac{\partial F_i}{\partial F_{cent}} \frac{dF_{cent}}{dT} + \frac{\partial F_i}{\partial P_{r,i}} \frac{\partial P_{r,i}}{\partial T} \quad (205)$$

$$\frac{\partial F_i}{\partial n_j} = \frac{\partial F_i}{\partial P_{r,i}} \frac{\partial P_{r,i}}{\partial n_j} \quad (206)$$

$$\frac{\partial F_i}{\partial P} = \frac{\partial F_i}{\partial P_{r,i}} \frac{\partial P_{r,i}}{\partial P} \quad (207)$$

where

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

$$\frac{dF_{cent}}{dT} = -\frac{a}{T^*} \exp\left(-\frac{T}{T^*}\right) - \frac{\exp\left(-\frac{T}{T^{***}}\right)}{T^{***}} (-a+1) + \frac{T^{**}}{T^2} \exp\left(-\frac{T^{**}}{T}\right) \quad (209)$$

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

And

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

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

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

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

Thus

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

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

And

$$\frac{\partial F_i}{\partial T} = F_i \Theta_{F_i, \partial T} \quad (217)$$

$$\frac{\partial F_i}{\partial n_j} = \frac{F_i k_{0,i} \Theta_{F_i, \partial n_j}}{k_{\infty,i} V} \bar{\theta}_{P_{r,i}, \partial n_j} \quad (218)$$

$$\frac{\partial F_i}{\partial P} = F_i \Theta_{F_i, \partial P} \quad (219)$$

Where

$$\begin{aligned} \Theta_{F_i, \partial T} = & -\frac{B_{Troe}}{F_{cent} P_{r,i} (A_{Troe}^2 + B_{Troe}^2)^2 \log(10)} \left(2A_{Troe} F_{cent} (0.14 A_{Troe} \right. \\ & \left. + B_{Troe}) (P_{r,i} \Theta_{P_{r,i}, \partial T} + \bar{\theta}_{P_{r,i}, \partial T}) \log(F_{cent}) \right. \\ & \left. + P_{r,i} \frac{dF_{cent}}{dT} (2A_{Troe} (1.1762 A_{Troe} - 0.67 B_{Troe}) \log(F_{cent}) \right. \\ & \left. - B_{Troe} (A_{Troe}^2 + B_{Troe}^2) \log(10)) \right) \end{aligned} \quad (220)$$

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

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

For SRI reactions

$$\begin{aligned} \frac{\partial F_i}{\partial T} = F_i & \left(\frac{X \left(-\frac{\exp(-\frac{T}{c})}{c} + \frac{ab}{T^2} \exp(-\frac{b}{T}) \right)}{a \exp(-\frac{b}{T}) + \exp(-\frac{T}{c})} \right. \\ & \left. + \frac{\partial P_{r,i}}{\partial T} \frac{dX}{dP_{r,i}} \log \left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right) \right) + \frac{e}{T} \right) \end{aligned} \quad (223)$$

$$\frac{\partial F_i}{\partial n_j} = F_i \frac{\partial P_{r,i}}{\partial n_j} \frac{dX}{dP_{r,i}} \log \left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right) \right) \quad (224)$$

$$\frac{\partial F_i}{\partial P} = F_i \frac{\partial P_{r,i}}{\partial P} \frac{dX}{dP_{r,i}} \log \left(a \exp\left(-\frac{b}{T}\right) + \exp\left(-\frac{T}{c}\right) \right) \quad (225)$$

Where

$$\frac{dX}{dP_{r,i}} = -\frac{2X^2 \log(P_{r,i})}{P_{r,i} \log^2(10)} \quad (226)$$

$$\frac{\partial X}{\partial n_j} = \frac{\partial P_{r,i}}{\partial n_j} \frac{dX}{dP_{r,i}} \quad (227)$$

And

$$\frac{\partial F_i}{\partial T} = F_i \Theta_{F_i, \partial T} \quad (228)$$

$$\frac{\partial F_i}{\partial n_j} = \frac{F_i k_{0,i} \Theta_{F_i, \partial n_j} \bar{\theta}_{P_{r,i}, \partial n_j}}{k_{\infty,i} V} \quad (229)$$

$$\frac{\partial F_i}{\partial P} = F_i \Theta_{F_i, \partial P} \quad (230)$$

Where

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

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

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

Simplifying:

$$\frac{\partial F_i}{\partial T} = F_i \Theta_{F_i, \partial T} \quad (234)$$

$$\frac{\partial F_i}{\partial n_j} = \frac{F_i k_{0,i} \Theta_{F_i, \partial n_j}}{k_{\infty,i} V} \bar{\theta}_{P_{r,i}, \partial n_j} \quad (235)$$

$$\frac{\partial F_i}{\partial P} = F_i \Theta_{F_i, \partial P} \quad (236)$$

Where:

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

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

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

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

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

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

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

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

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

15.7 Unimolecular/recombination fall-off reactions (complete)

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

$$\frac{\partial c}{\partial n_{j_i}} = \frac{k_{0,i} \bar{\theta}_{P_{r,i}, \partial n_j}}{k_{\infty,i} V (P_{r,i} + 1)} (F_i (P_{r,i} \Theta_{F_i, \partial n_j} + 1) - c_i) \quad (241)$$

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

15.8 Chemically-activated bimolecular reactions (complete)

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

$$\frac{\partial c}{\partial n_{j_i}} = \frac{k_{0,i} \bar{\theta}_{P_{r,i}, \partial n_j} (F_i \Theta_{F_i, \partial n_j} - c_i)}{k_{\infty,i} V (P_{r,i} + 1)} \quad (244)$$

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

16 Pressure-dependent reaction derivatives

For PLog reactions

$$\frac{dk_f}{dT_i} = \left(\frac{1}{k_1} \frac{dk_1}{dT} + \frac{1}{-\log(P_1) + \log(P_2)} \left(-\frac{1}{k_1} \frac{dk_1}{dT} + \frac{1}{k_2} \frac{dk_2}{dT} \right) (\log(P) - \log(P_1)) \right) k_{f_i} \quad (246)$$

$$\begin{aligned} \frac{dk_f}{dT_i} = & \left(\frac{1}{-\log(P_1) + \log(P_2)} \left(-\frac{1}{T} \left(\beta_1 + \frac{E_{a_1}}{T\mathcal{R}} \right) \right. \right. \\ & \left. \left. + \frac{1}{T} \left(\beta_2 + \frac{E_{a_2}}{T\mathcal{R}} \right) \right) (\log(P) - \log(P_1)) + \frac{1}{T} \left(\beta_1 + \frac{E_{a_1}}{T\mathcal{R}} \right) \right) k_{f_i} \end{aligned} \quad (247)$$

$$\frac{dk_f}{dT_i} = \frac{k_{f_i}}{T} \left(\beta_1 + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a_1}}{T\mathcal{R}} + \frac{E_{a_2}}{T\mathcal{R}} \right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a_1}}{T\mathcal{R}} \right) \quad (248)$$

$$\begin{aligned} \frac{\partial R_f}{\partial T_i} = & -\frac{[C]S'_{N_{sp}}}{T}k_{fi} + \frac{R_{fi}}{T} \left(\beta_1 \right. \\ & \left. + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a1}}{T\mathcal{R}} + \frac{E_{a2}}{T\mathcal{R}} \right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a1}}{T\mathcal{R}} \right) \end{aligned} \quad (249)$$

$$\begin{aligned} \frac{dk_r}{dT_i} = & \left(-\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT_k} + \frac{1}{T} \left(\beta_1 \right. \right. \\ & \left. \left. + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a1}}{T\mathcal{R}} + \frac{E_{a2}}{T\mathcal{R}} \right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a1}}{T\mathcal{R}} \right) \right) k_{ri} \end{aligned} \quad (250)$$

$$\begin{aligned} \frac{\partial R_r}{\partial T_i} = & \left(-\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT_k} \right. \\ & \left. + \frac{1}{T} \left(\beta_1 + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a1}}{T\mathcal{R}} + \frac{E_{a2}}{T\mathcal{R}} \right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a1}}{T\mathcal{R}} \right) \right) R_{ri} \\ & - \frac{[C]S''_{N_{sp}}}{T}k_{ri} \end{aligned} \quad (251)$$

$$\begin{aligned} \frac{\partial R}{\partial T_i} = & - \left(-\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT_k} \right. \\ & + \frac{1}{T} \left(\beta_1 + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a1}}{T\mathcal{R}} + \frac{E_{a2}}{T\mathcal{R}} \right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a1}}{T\mathcal{R}} \right) \right) R_{ri} \\ & + \frac{[C]}{T} \left(S''_{N_{sp}}k_{ri} - S'_{N_{sp}}k_{fi} \right) \\ & + \frac{R_{fi}}{T} \left(\beta_1 + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a1}}{T\mathcal{R}} + \frac{E_{a2}}{T\mathcal{R}} \right)}{-\log(P_1) + \log(P_2)} + \frac{E_{a1}}{T\mathcal{R}} \right) \end{aligned} \quad (252)$$

$$\frac{\partial k_f}{\partial P_i} = \frac{(-\log(k_1) + \log(k_2))k_{fi}}{P(-\log(P_1) + \log(P_2))} \quad (253)$$

$$\frac{\partial R_f}{\partial P_i} = \frac{S'_{N_{sp}}k_{fi}}{T\mathcal{R}} + \frac{(-\log(k_1) + \log(k_2))R_{fi}}{P(-\log(P_1) + \log(P_2))} \quad (254)$$

$$\frac{\partial k_r}{\partial P_i} = \frac{1}{K_{c_i}} \frac{\partial k_f}{\partial P_i} \quad (255)$$

$$\frac{\partial k_r}{\partial P_i} = \frac{(-\log(k_1) + \log(k_2)) k_{ri}}{P(-\log(P_1) + \log(P_2))} \quad (256)$$

$$\frac{\partial R_r}{\partial P_i} = \frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{(-\log(k_1) + \log(k_2)) R_{ri}}{P(-\log(P_1) + \log(P_2))} \quad (257)$$

$$\frac{\partial R}{\partial P_i} = \frac{1}{T\mathcal{R}} \left(-S''_{N_{sp}} k_{ri} + S'_{N_{sp}} k_{fi} \right) + \frac{(-\log(k_1) + \log(k_2)) (R_{fi} - R_{ri})}{P(-\log(P_1) + \log(P_2))} \quad (258)$$

For Chebyshev reactions

$$\frac{dk_f}{dT_i} = \log(10) k_{fi} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{d\tilde{T}}{dT} (j-1) T_{l-1}(\tilde{P}) U_{j-2}(\tilde{T}) \eta_{l,j} \quad (259)$$

$$\frac{dk_f}{dT_i} = \log(10) k_{fi} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} -\frac{2T_{l-1}(\tilde{P}) U_{j-2}(\tilde{T}) \eta_{l,j}}{T^2 \left(-\frac{1}{T_{min}} + \frac{1}{T_{max}} \right)} (j-1) \quad (260)$$

$$\frac{\partial R_f}{\partial T_i} = \log(10) R_{fi} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} -\frac{2T_{l-1}(\tilde{P}) U_{j-2}(\tilde{T}) \eta_{l,j}}{T^2 \left(-\frac{1}{T_{min}} + \frac{1}{T_{max}} \right)} (j-1) - \frac{[C] S'_{N_{sp}} k_{fi}}{T} \quad (261)$$

$$\frac{dk_r}{dT_i} = - \left(\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT_k} + \frac{2 \log(10)}{T^2 \left(-\frac{1}{T_{min}} + \frac{1}{T_{max}} \right)} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} (j-1) T_{l-1}(\tilde{P}) U_{j-2}(\tilde{T}) \eta_{l,j} \right) k_{ri} \quad (262)$$

$$\frac{\partial R_r}{\partial T_i} = - \left(\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT_k} + \frac{2 \log(10)}{T^2 \left(-\frac{1}{T_{min}} + \frac{1}{T_{max}} \right)} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} (j-1) T_{l-1}(\tilde{P}) U_{j-2}(\tilde{T}) \eta_{l,j} \right) R_{ri} - \frac{[C] S''_{N_{sp}} k_{ri}}{T} \quad (263)$$

$$\begin{aligned}
\frac{\partial R}{\partial T_i} = & \left(\sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT_k} \right. \\
& + \frac{2 \log(10)}{T^2 \left(-\frac{1}{T_{min}} + \frac{1}{T_{max}} \right)} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} (j-1) T_{l-1} \left(\tilde{P} \right) U_{j-2} \left(\tilde{T} \right) \eta_{l,j} \left. R_{ri} \right. \\
& + \log(10) R_{fi} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} - \frac{2 T_{l-1} \left(\tilde{P} \right) U_{j-2} \left(\tilde{T} \right) \eta_{l,j}}{T^2 \left(-\frac{1}{T_{min}} + \frac{1}{T_{max}} \right)} (j-1) \\
& + \frac{[C]}{T} \left(S''_{N_{sp}} k_{ri} - S'_{N_{sp}} k_{fi} \right)
\end{aligned} \tag{264}$$

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

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

$$\frac{\partial R_f}{\partial P_i} = \log(10) R_{fi} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2(l-1) T_{j-1} \left(\tilde{T} \right) U_{l-2} \left(\tilde{P} \right) \eta_{l,j}}{P (\log(P_{max}) - \log(P_{min}))} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \tag{267}$$

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

$$\frac{\partial R_r}{\partial P_i} = \log(10) R_{ri} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2(l-1) T_{j-1} \left(\tilde{T} \right) U_{l-2} \left(\tilde{P} \right) \eta_{l,j}}{P (\log(P_{max}) - \log(P_{min}))} + \frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} \tag{269}$$

$$\begin{aligned}
\frac{\partial R}{\partial P_i} = & \log(10) R_{fi} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2(l-1) T_{j-1} \left(\tilde{T} \right) U_{l-2} \left(\tilde{P} \right) \eta_{l,j}}{P (\log(P_{max}) - \log(P_{min}))} \\
& - \log(10) R_{ri} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2(l-1) T_{j-1} \left(\tilde{T} \right) U_{l-2} \left(\tilde{P} \right) \eta_{l,j}}{P (\log(P_{max}) - \log(P_{min}))} \\
& + \frac{1}{T\mathcal{R}} \left(-S''_{N_{sp}} k_{ri} + S'_{N_{sp}} k_{fi} \right)
\end{aligned} \tag{270}$$

17 Jacobian entries

17.1 Energy Equation

$$\frac{dT}{dt} = -\frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \quad (271)$$

$$\frac{dT}{dt} = -\frac{\sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k}{\left(\frac{P}{T\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} [C]_k \right) C_{vN_{sp}} + \sum_{k=1}^{-1+N_{sp}} [C]_k C_{vk}} \quad (272)$$

$$\frac{dT}{dt} = -\frac{\sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k}{[C] C_{vN_{sp}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k} \quad (273)$$

17.2 \dot{T} Derivatives

Molar derivative

$$\begin{aligned} \frac{\partial \dot{T}}{\partial n_j} = & -\frac{\sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial n_j k}}{[C] C_{vN_{sp}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k} \\ & + \frac{\left(\sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \right) \sum_{k=1}^{-1+N_{sp}} -\frac{\delta_{jk}}{V} (C_{vN_{sp}} - C_{vk})}{\left([C] C_{vN_{sp}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k \right)^2} \end{aligned} \quad (274)$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial n_j} = & \frac{1}{\left(\sum_{k=1}^{N_{sp}} [C]_k C_{vk} \right)^2} \left(\sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \right) \sum_{k=1}^{-1+N_{sp}} \\ & - \frac{\delta_{jk}}{V} (C_{vN_{sp}} - C_{vk}) - \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial n_j k} \end{aligned} \quad (275)$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial n_j} = & \frac{1}{V \left(\sum_{k=1}^{N_{sp}} [C]_k C_{vk} \right)^2} (-C_{vN_{sp}} + C_{vj}) \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \\ & - \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial n_j k} \end{aligned} \quad (276)$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial n_j} = & \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \left(-\frac{1}{V} \frac{dT}{dt} (-C_{vN_{sp}} + C_{vj}) \right. \\ & \left. - \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial n_j k} \right) \end{aligned} \quad (277)$$

Temperature derivative

$$\frac{dT}{dt} = - \frac{\sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k}{\frac{PC_{vN_{sp}}}{T\mathcal{R}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k} \quad (278)$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial T} = & - \frac{1}{\frac{PC_{vN_{sp}}}{T\mathcal{R}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k} \sum_{k=1}^{-1+N_{sp}} \left(\left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T_k} + \left(\frac{dU}{dT_k} - \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT_{N_{sp}}} \right) \dot{\omega}_k \right) \\ & - \frac{1}{\left(\frac{PC_{vN_{sp}}}{T\mathcal{R}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k \right)^2} \left(-\frac{P}{T\mathcal{R}} \frac{dC_v}{dT_{N_{sp}}} \right. \\ & \left. + \frac{PC_{vN_{sp}}}{T^2\mathcal{R}} - \sum_{k=1}^{-1+N_{sp}} \left(-\frac{dC_v}{dT_{N_{sp}}} + \frac{dC_v}{dT_k} \right) [C]_k \right) \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \end{aligned} \quad (279)$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial T} = & - \frac{1}{[C]C_{vN_{sp}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k} \sum_{k=1}^{-1+N_{sp}} \left(\left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T_k} + \left(\frac{dU}{dT_k} - \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT_{N_{sp}}} \right) \dot{\omega}_k \right) \\ & - \frac{1}{\left([C]C_{vN_{sp}} + \sum_{k=1}^{-1+N_{sp}} (-C_{vN_{sp}} + C_{vk}) [C]_k \right)^2} \left(-[C] \frac{dC_v}{dT_{N_{sp}}} \right. \\ & \left. - \sum_{k=1}^{-1+N_{sp}} \left(-\frac{dC_v}{dT_{N_{sp}}} + \frac{dC_v}{dT_k} \right) [C]_k + \frac{[C]C_{vN_{sp}}}{T} \right) \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \end{aligned} \quad (280)$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial T} = & - \frac{1}{\left(\sum_{k=1}^{N_{sp}} [C]_k C_{vk} \right)^2} \left(-[C] \frac{dC_v}{dT_{N_{sp}}} - \sum_{k=1}^{-1+N_{sp}} \left(-\frac{dC_v}{dT_{N_{sp}}} + \frac{dC_v}{dT_k} \right) [C]_k \right. \\ & \left. + \frac{[C]C_{vN_{sp}}}{T} \right) \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \\ & - \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \sum_{k=1}^{-1+N_{sp}} \left(\left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T_k} + \left(\frac{dU}{dT_k} - \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT_{N_{sp}}} \right) \dot{\omega}_k \right) \end{aligned} \quad (281)$$

$$\begin{aligned}
\frac{\partial \dot{T}}{\partial T} = & -\frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \left(\frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \left(-[C] \frac{dC_v}{dT}_{N_{sp}} \right. \right. \\
& - \sum_{k=1}^{-1+N_{sp}} \left(-\frac{dC_v}{dT}_{N_{sp}} + \frac{dC_v}{dT}_k \right) [C]_k + \frac{[C] C_{vN_{sp}}}{T} \left. \right) \sum_{k=1}^{-1+N_{sp}} \left(U_k \right. \\
& \left. \left. - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \dot{\omega}_k \right. \\
& + \sum_{k=1}^{-1+N_{sp}} \left(\left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(\frac{dU}{dT}_k - \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT}_{N_{sp}} \right) \dot{\omega}_k \right) \Bigg) \\
& (282)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \dot{T}}{\partial T} = & \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \left(\frac{dT}{dt} \left(-[C] \frac{dC_v}{dT}_{N_{sp}} - \sum_{k=1}^{-1+N_{sp}} \left(-\frac{dC_v}{dT}_{N_{sp}} + \frac{dC_v}{dT}_k \right) [C]_k \right. \right. \\
& \left. \left. + \frac{[C] C_{vN_{sp}}}{T} \right) \right. \\
& - \sum_{k=1}^{-1+N_{sp}} \left(\left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(\frac{dU}{dT}_k - \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT}_{N_{sp}} \right) \dot{\omega}_k \right) \Bigg) \\
& (283)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \dot{T}}{\partial T} = & \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \left(\frac{dT}{dt} \left(-\frac{dC_v}{dT}_{N_{sp}} \sum_{k=1}^{N_{sp}} [C]_k \right. \right. \\
& - \sum_{k=1}^{-1+N_{sp}} \left(-\frac{dC_v}{dT}_{N_{sp}} + \frac{dC_v}{dT}_k \right) [C]_k + \frac{C_{vN_{sp}}}{T} \sum_{k=1}^{N_{sp}} [C]_k \left. \right) \\
& - \sum_{k=1}^{-1+N_{sp}} \left(\left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(\frac{dU}{dT}_k - \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT}_{N_{sp}} \right) \dot{\omega}_k \right) \Bigg) \\
& (284)
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \dot{T}}{\partial T} = & \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \left(\frac{dT}{dt} \sum_{k=1}^{N_{sp}} \left(-\frac{dC_v}{dT}_k + \frac{C_{vN_{sp}}}{T} \right) [C]_k \right. \\
& + \sum_{k=1}^{-1+N_{sp}} \left(\left(-U_k + \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(-\frac{dU}{dT}_k + \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT}_{N_{sp}} \right) \dot{\omega}_k \right) \Bigg) \\
& (285)
\end{aligned}$$

$$\begin{aligned} \frac{\partial \dot{T}}{\partial T} = & \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{v_k}} \left(\frac{dT}{dt} \sum_{k=1}^{N_{sp}} \left(-\frac{dC_v}{dT}_k + \frac{C_{v_{N_{sp}}}}{T} \right) [C]_k \right. \\ & \left. + \sum_{k=1}^{-1+N_{sp}} \left(\left(-U_k + \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial T}_k + \left(-C_{v_k} + \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT}_{N_{sp}} \right) \dot{\omega}_k \right) \right) \end{aligned} \quad (286)$$

Pressure Derivative

$$\frac{\partial \dot{T}}{\partial P} = \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{v_k}} \left(- \sum_{k=1}^{-1+N_{sp}} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial P}_k - \frac{C_{v_{N_{sp}}}}{T \mathcal{R}} \frac{dT}{dt} \right) \quad (287)$$

17.3 \dot{P} Derivatives

Temperature Derivative

$$\frac{\partial \dot{P}}{\partial T} = \frac{P}{T} \left(\frac{d\dot{T}}{dT} - \frac{1}{T} \frac{dT}{dt} \right) + \mathcal{R} \sum_{k=1}^{-1+N_{sp}} \left(1 - \frac{W_k}{W_{N_{sp}}} \right) \left(T \frac{\partial \dot{\omega}}{\partial T}_k + \dot{\omega}_k \right) \quad (288)$$

Molar Derivative

$$\frac{\partial \dot{P}}{\partial n_j} = \frac{P}{T} \frac{d\dot{T}}{dn_j} + T \mathcal{R} \sum_{k=1}^{-1+N_{sp}} \left(1 - \frac{W_k}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial n_j}_k \quad (289)$$

Pressure Derivative

$$\frac{\partial \dot{P}}{\partial P} = T \mathcal{R} \sum_{k=1}^{-1+N_{sp}} \left(1 - \frac{W_k}{W_{N_{sp}}} \right) \frac{\partial \dot{\omega}}{\partial P}_k + \frac{1}{T} \left(P \frac{d\dot{T}}{dP} + \dot{T} \right) \quad (290)$$

17.4 \dot{n}_k Derivatives

$$\frac{\partial \dot{n}}{\partial n_j}_k = V \frac{\partial \dot{\omega}}{\partial n_j}_k \quad (291)$$

$$\frac{\partial \dot{n}}{\partial T}_k = V \frac{\partial \dot{\omega}}{\partial T}_k \quad (292)$$

$$\frac{\partial \dot{n}}{\partial P}_k = V \frac{\partial \dot{\omega}}{\partial P}_k \quad (293)$$

18 Jacobian Update Form

18.1 Temperature Derivatives

$$\begin{aligned} \mathcal{J}_{1,1} = & \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{v_k}} \left(\frac{dT}{dt} \sum_{k=1}^{N_{sp}} \left(-\frac{dC_v}{dT}_k + \frac{C_{v_{N_{sp}}}}{T} \right) [C]_k \right. \\ & \left. + \sum_{k=1}^{-1+N_{sp}} \left(\frac{1}{V} \left(-U_k + \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{n}}{\partial T}_k + \left(-C_{v_k} + \frac{W_k}{W_{N_{sp}}} \frac{dU}{dT}_{N_{sp}} \right) \dot{\omega}_k \right) \right) \end{aligned} \quad (294)$$

$$\mathcal{J}_{2,1} = \frac{P}{T} \left(\frac{d\dot{T}}{dT} - \frac{1}{T} \frac{dT}{dt} \right) + \mathcal{R} \sum_{k=1}^{-1+N_{sp}} \left(1 - \frac{W_k}{W_{N_{sp}}} \right) \left(\frac{T}{V} \frac{\partial \dot{n}}{\partial T}_k + \dot{\omega}_k \right) \quad (295)$$

$$\mathcal{J}_{k+2,1} = V \sum_{i=1}^{N_{reac}} \nu_{k,i} \frac{\partial q}{\partial T}_i \quad (296)$$

Converting to update form:

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

18.1.1 Explicit reversible reactions

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

$$\Theta_{\partial T,i} = \frac{[C] S''_{N_{sp}} k_{ri} - [C] S'_{N_{sp}} k_{fi} + \frac{R_{fi}}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) - \frac{R_{ri}}{T} \left(\beta_{ri} + \frac{E_{a,ri}}{T\mathcal{R}} \right)}{T} \quad (299)$$

18.1.2 Non-explicit reversible reactions

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

$$\begin{aligned} \Theta_{\partial T,i} = & - \left(- \sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT}_k + \frac{1}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right) \right) R_{ri} \\ & + \frac{[C] S''_{N_{sp}} k_{ri} - [C] S'_{N_{sp}} k_{fi} + \frac{R_{fi}}{T} \left(\beta_i + \frac{E_{ai}}{T\mathcal{R}} \right)}{T} \end{aligned} \quad (301)$$

18.1.3 Pressure-dependent reactions

$$\frac{\partial q}{\partial T}_i = \Theta_{\partial T,i} \quad (302)$$

For PLog reactions:

$$\begin{aligned} \Theta_{\partial T,i} = & - \left(- \sum_{k=1}^{N_{sp}} \nu_{k,i} \frac{dB}{dT}_k \right. \\ & + \frac{1}{T} \left(\beta_1 + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a1}}{T\mathcal{R}} + \frac{E_{a2}}{T\mathcal{R}} \right) + \frac{E_{a1}}{T\mathcal{R}}}{-\log(P_1) + \log(P_2)} + \frac{E_{a1}}{T\mathcal{R}} \right) \Bigg) R_{ri} \\ & + \frac{[C]}{T} \left(S''_{N_{sp}} k_{ri} - S'_{N_{sp}} k_{fi} \right) \\ & + \frac{R_{fi}}{T} \left(\beta_1 + \frac{(\log(P) - \log(P_1)) \left(-\beta_1 + \beta_2 - \frac{E_{a1}}{T\mathcal{R}} + \frac{E_{a2}}{T\mathcal{R}} \right) + \frac{E_{a1}}{T\mathcal{R}}}{-\log(P_1) + \log(P_2)} + \frac{E_{a1}}{T\mathcal{R}} \right) \end{aligned} \quad (303)$$

For Chebyshev reactions:

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

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:

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

For species m as third-body:

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

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

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

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:

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

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\alpha_{N_{sp},i}}{Tk_{\infty,i}} \quad (312)$$

For species m as third-body:

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

$$\bar{\theta}_{P_{r,i},\partial T} = -\frac{[C]k_{0,i}\delta_{N_{sp}m}}{Tk_{\infty,i}} \quad (314)$$

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

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

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

18.1.9 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i,\partial T} = 0 \quad (317)$$

For Troe

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

For SRI

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

18.2 Molar Derivatives

$$\begin{aligned}
\mathcal{J}_{1,j+2} &= \frac{\partial \dot{T}}{\partial n_j} \\
&= \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{vk}} \left(-\frac{1}{V} \frac{dT}{dt} (-C_{vN_{sp}} + C_{vj}) \right. \\
&\quad \left. - \sum_{k=1}^{-1+N_{sp}} \frac{1}{V} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{n}}{\partial n_{j\ k}} \right)
\end{aligned} \tag{320}$$

$$\begin{aligned}
\mathcal{J}_{2,j+2} &= \frac{\partial \dot{P}}{\partial n_j} \\
&= \frac{P}{T} \frac{dT}{dn_j} + T \mathcal{R} \sum_{k=1}^{-1+N_{sp}} \frac{1}{V} \left(1 - \frac{W_k}{W_{N_{sp}}} \right) \frac{\partial \dot{n}}{\partial n_{j\ k}}
\end{aligned} \tag{321}$$

$$\begin{aligned}
\mathcal{J}_{k+2,j+2} &= \frac{\partial \dot{n}_k}{\partial n_j} \\
&= V \sum_{i=1}^{N_{reac}} \nu_{k,i} \frac{\partial q}{\partial n_{j\ i}}
\end{aligned} \tag{322}$$

Converting to Jacobian Update form:

$$\mathcal{J}_{k+2,j+2} + = V \nu_{k,i} \frac{\partial q}{\partial n_{j\ i}} \tag{323}$$

$$V \frac{\partial q}{\partial n_{j\ k}} = \left((S''_{N_{sp}} - S''_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \right) c_i + V R_i \frac{\partial c}{\partial n_{j\ i}} \tag{324}$$

18.2.1 Pressure-dependent reactions

$$V \frac{\partial q}{\partial n_{j\ k}} = (S''_{N_{sp}} - S''_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \tag{325}$$

18.2.2 Pressure independent reactions

$$V \frac{\partial q}{\partial n_{j\ k}} = (S''_{N_{sp}} - S''_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \tag{326}$$

18.2.3 Third-body enhanced reactions

For mixture as third-body:

$$V \frac{\partial q}{\partial n_{j_k}} = [X]_i \left((S''_{N_{sp}} - S'_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \right) + (-\alpha_{N_{sp},i} + \alpha_{j,i}) R_i \quad (327)$$

For species m as third-body:

$$V \frac{\partial q}{\partial n_{j_k}} = ((-\delta_{N_{sp}m} + 1) [C]_m + \delta_{N_{sp}m} [C]_{N_{sp}}) \left((S''_{N_{sp}} - S'_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \right) + (-\delta_{N_{sp}m} + \delta_{jm}) R_i \quad (328)$$

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

$$V \frac{\partial q}{\partial n_{j_k}} = [C] \left((S''_{N_{sp}} - S'_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \right) \quad (329)$$

18.2.4 Falloff Reactions

Unimolecular/recombination fall-off reactions:

$$V \frac{\partial q}{\partial n_{j_i}} = \frac{k_{0,i} \bar{\theta}_{P_{r,i}, \partial n_j} R_i}{k_{\infty,i} (P_{r,i} + 1)} (F_i P_{r,i} \Theta_{F_i, \partial n_j} + F_i - c_i) + \left((S''_{N_{sp}} - S'_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \right) c_i \quad (330)$$

18.2.5 Chemically-activated bimolecular reactions

$$V \frac{\partial q}{\partial n_{j_i}} = \frac{k_{0,i} \bar{\theta}_{P_{r,i}, \partial n_j} R_i}{k_{\infty,i} (P_{r,i} + 1)} (F_i \Theta_{F_i, \partial n_j} - c_i) + \left((S''_{N_{sp}} - S'_j) k_{ri} - (S'_{N_{sp}} - S'_j) k_{fi} \right) c_i \quad (331)$$

18.2.6 Reduced Pressure Derivatives

For mixture as third-body:

$$\bar{\theta}_{P_{r,i}, \partial n_j} = -\alpha_{N_{sp},i} + \alpha_{j,i} \quad (332)$$

For species m as third-body:

$$\bar{\theta}_{P_{r,i}, \partial n_j} = -\delta_{N_{sp}m} + \delta_{jm} \quad (333)$$

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

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

18.2.7 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i, \partial n_j} = 0 \quad (335)$$

For Troe

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

For SRI

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

18.3 Pressure Derivatives

$$\begin{aligned} \mathcal{J}_{1,2} &= \frac{\partial \dot{T}}{\partial P} \\ &= \frac{1}{\sum_{k=1}^{N_{sp}} [C]_k C_{v,k}} \left(-\sum_{k=1}^{-1+N_{sp}} \frac{1}{V} \left(U_k - \frac{W_k U_{N_{sp}}}{W_{N_{sp}}} \right) \frac{\partial \dot{n}}{\partial P_k} - \frac{C_{v,N_{sp}}}{T\mathcal{R}} \frac{dT}{dt} \right) \end{aligned} \quad (338)$$

$$\begin{aligned} \mathcal{J}_{2,2} &= \frac{\partial \dot{P}}{\partial P} \\ &= T\mathcal{R} \sum_{k=1}^{-1+N_{sp}} \frac{1}{V} \left(1 - \frac{W_k}{W_{N_{sp}}} \right) \frac{\partial \dot{n}}{\partial P_k} + \frac{1}{T} \left(P \frac{d\dot{T}}{dP} + \dot{T} \right) \end{aligned} \quad (339)$$

$$\begin{aligned} \mathcal{J}_{k+2,2} &= \frac{\partial \dot{n}_k}{\partial P} \\ &= V \sum_{i=1}^{N_{reac}} \nu_{k,i} \frac{\partial q}{\partial P_i} \end{aligned} \quad (340)$$

Converting to Jacobian Update form:

$$\mathcal{J}_{k+2,2} + = V \nu_{k,i} \frac{\partial q}{\partial P_i} \quad (341)$$

$$\frac{\partial q}{\partial P_k} = \left(-\frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \right) c_i + R_i \frac{\partial c}{\partial P_i} \quad (342)$$

18.3.1 Pressure-dependent reactions

For PLOG:

$$\frac{\partial q}{\partial P_k} = \frac{1}{T\mathcal{R}} \left(-S''_{N_{sp}} k_{ri} + S'_{N_{sp}} k_{fi} \right) + \frac{(-\log(k_1) + \log(k_2)) (R_{fi} - R_{ri})}{P (-\log(P_1) + \log(P_2))} \quad (343)$$

For Chebyshev:

$$\begin{aligned} \frac{\partial q}{\partial P_k} = & \log(10) R_{fi} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2(l-1) T_{j-1}(\tilde{T}) U_{l-2}(\tilde{P}) \eta_{l,j}}{P (\log(P_{max}) - \log(P_{min}))} \\ & - \log(10) R_{ri} \sum_{\substack{1 \leq l \leq N_P \\ 1 \leq j \leq N_T}} \frac{2(l-1) T_{j-1}(\tilde{T}) U_{l-2}(\tilde{P}) \eta_{l,j}}{P (\log(P_{max}) - \log(P_{min}))} \\ & + \frac{1}{T\mathcal{R}} \left(-S''_{N_{sp}} k_{ri} + S'_{N_{sp}} k_{fi} \right) \end{aligned} \quad (344)$$

18.3.2 Pressure independent reactions

$$\frac{\partial q}{\partial P_k} = -\frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \quad (345)$$

18.3.3 Third-body enhanced reactions

For mixture as third-body:

$$\frac{\partial q}{\partial P_k} = [X]_i \left(-\frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \right) + \frac{\alpha_{N_{sp},i} R_i}{T\mathcal{R}} \quad (346)$$

For species m as third-body:

$$\frac{\partial q}{\partial P_k} = ((-\delta_{N_{sp}m} + 1) [C]_m + \delta_{N_{sp}m} [C]_{N_{sp}}) \left(-\frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \right) + \frac{\delta_{N_{sp}m} R_i}{T\mathcal{R}} \quad (347)$$

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

$$\frac{\partial q}{\partial P_k} = [C] \left(-\frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \right) + \frac{R_i}{T\mathcal{R}} \quad (348)$$

18.3.4 Unimolecular/recombination fall-off reactions

$$\frac{\partial q}{\partial P_i} = \left(\frac{F_i \bar{\theta}_{P_{r,i}, \partial P}}{P_{r,i} + 1} + \left(\Theta_{F_i, \partial P} - \frac{\bar{\theta}_{P_{r,i}, \partial P}}{P_{r,i} + 1} \right) c_i \right) R_i + \left(-\frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \right) c_i \quad (349)$$

18.3.5 Chemically-activated bimolecular reactions

$$\frac{\partial q}{\partial P_i} = \left(\left(\Theta_{F_i, \partial P} - \frac{\bar{\theta}_{P_{r,i}, \partial P}}{P_{r,i} + 1} \right) R_i - \frac{S''_{N_{sp}} k_{ri}}{T\mathcal{R}} + \frac{S'_{N_{sp}} k_{fi}}{T\mathcal{R}} \right) c_i \quad (350)$$

18.3.6 Reduced Pressure Derivatives

For mixture as third-body:

$$\Theta_{P_{r,i}, \partial P} = 0 \quad (351)$$

$$\bar{\theta}_{P_{r,i}, \partial P} = \frac{k_{0,i} \alpha_{N_{sp},i}}{T k_{\infty,i} \mathcal{R}} \quad (352)$$

For species m as third-body:

$$\Theta_{P_{r,i}, \partial P} = 0 \quad (353)$$

$$\bar{\theta}_{P_{r,i}, \partial P} = \frac{k_{0,i} \delta_{N_{sp}m}}{T k_{\infty,i} \mathcal{R}} \quad (354)$$

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

$$\Theta_{P_{r,i}, \partial P} = 0 \quad (355)$$

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

18.3.7 Falloff Blending Function Forms

For Lindemann

$$\Theta_{F_i, \partial P} = 0 \quad (357)$$

For Troe

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

For SRI

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