

Differential Equations for the Chemical Mechanism

$$O_2 \quad r_1 \quad r_2 \quad r_3 \quad r_4 \quad r_5 \quad r_8 \quad r_9 \quad r_{10} \quad 2r_{11} \quad r_{12} \quad r_{13}$$

$$O_3 \quad r_2 \quad r_3 \quad r_4 \quad r_9 \quad r_{11} \quad r_{12}$$

$$ClO_2 \quad r_6 \quad r_7$$

$$ClOO \quad r_7 \quad r_8$$

$$NO \quad r_9 \quad r_{10} \quad r_{11}$$

$$NO_2 \quad r_9 \quad r_{10} \quad r_{11}$$

$$BrCl \quad r_{13} \quad r_{14}$$

$$O \quad 2r_1 \quad r_2 \quad r_3 \quad r_5 \quad r_{10}$$

$$Cl \quad r_4 \quad r_5 \quad r_7 \quad r_8 \quad r_{14}$$

$$ClO \quad r_4 \quad r_5 \quad 2r_6 \quad r_{13}$$

$$Br \quad r_{12} \quad r_{14}$$

$$BrO \quad r_{12} \quad r_{13}$$

Reaction Expressions

$$r_1 \quad k_1 O_2$$

$$r_2 \quad k_2 O_2 O$$

$$r_3 \quad k_3 O_3$$

$$r_4 \quad k_4 O_3 Cl$$

$$r_5 \quad k_5 O ClO$$

$$r_6 \quad k_6 ClO^2$$

$$r_7 \quad k_7 ClO_2$$

$$r_8 \quad k_8 ClOO$$

$$r_9 \quad k_9 O_3 NO$$

$$r_{10} \quad k_{10} NO_2 O$$

$$r_{11} \quad k_{11} NO_2 O_3$$

$$r_{12} \quad k_{12} Br O_3$$

$$r_{13} \quad k_{13} BrO ClO$$

$$r_{14} \quad k_{14} BrCl$$

Applying a Pseudo-Steady-State Hypothesis

$$Br \quad r_{12} \quad r_{14} \quad 0$$

$$BrO \quad r_{12} \quad r_{13} \quad 0$$

$$r_{12} \quad r_{13} \quad \text{and } r_{12} \quad r_{14}, \text{ therefore } r_{12} \quad r_{13} \quad r_{14}$$

$$Br \quad r_{12} \quad r_{14}$$

$$k_{12} Br O_3 \quad k_{14} BrCl$$

$$\text{Br} \quad \frac{k_{14} \text{BrCl}}{k_{12} \text{O}_3}$$

$$\begin{array}{l} \text{BrO} \quad r_{12} \quad r_{13} \\ k_{12} \text{Br} \quad \text{O}_3 \quad k_{13} \text{BrO} \quad \text{ClO} \quad k_{14} \text{BrCl} \\ \text{BrO} \quad \frac{k_{14} \text{BrCl}}{k_{13} \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} \\ \text{Cl} \quad r_4 \quad r_5 \quad r_7 \quad r_8 \quad r_{14} \quad 0 \\ r_7 \quad r_8 \quad r_{14} \quad r_4 \quad r_5 \\ r_4 \quad r_5 \quad k_7 \text{ClO}_2 \quad k_8 \text{ClOO} \quad k_{14} \text{BrCl} \end{array}$$

$$\begin{array}{l} \text{ClO} \quad r_4 \quad r_5 \quad 2r_6 \quad r_{13} \quad 0 \\ 2r_6 \quad r_{13} \quad r_4 \quad r_5 \\ 2k_6 \text{ClO}_2 \quad k_{14} \text{BrCl} \quad k_7 \text{ClO}_2 \quad k_8 \text{ClOO} \quad k_{14} \text{BrCl} \\ 2k_6 x^2 \quad k_7 \text{ClO}_2 \quad k_8 \text{ClOO} \\ x \quad \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \\ \text{ClO} \quad \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \end{array}$$

$$\begin{array}{l} \text{O} \quad 2r_1 \quad r_2 \quad r_3 \quad r_5 \quad r_{10} \\ \text{O} \quad 2k_1 \text{O}_2 \quad k_2 \text{O}_2 \quad \text{O} \quad k_3 \text{O}_3 \quad k_5 \text{O} \quad \text{ClO} \quad k_{10} \text{NO}_2 \quad \text{O} \\ \text{O} \quad 2k_1 \text{O}_2 \quad k_2 \text{O}_2 \quad \text{O} \quad k_3 \text{O}_3 \quad k_5 \text{O} \quad \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \quad k_{10} \text{NO}_2 \quad \text{O} \\ 2k_1 \text{O}_2 \quad k_2 \text{O}_2 \quad \text{O} \quad k_3 \text{O}_3 \quad k_5 \text{O} \quad \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \quad k_{10} \text{NO}_2 \quad \text{O} \quad 0 \\ 2k_1 \text{O}_2 \quad k_2 \text{O}_2 \quad x \quad k_3 \text{O}_3 \quad k_5 x \quad \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \quad k_{10} \text{NO}_2 \quad x \quad 0 \\ 2k_1 \text{O}_2 \quad k_3 \text{O}_3 \quad k_2 \text{O}_2 \quad x \quad k_5 x \quad \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \quad k_{10} \text{NO}_2 \quad x \\ 2k_1 \text{O}_2 \quad k_3 \text{O}_3 \quad x \left[k_2 \text{O}_2 \quad k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \quad k_{10} \text{NO}_2 \right] \\ x \quad \frac{2k_1 \text{O}_2 \quad k_3 \text{O}_3}{\left[k_2 \text{O}_2 \quad k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \quad k_{10} \text{NO}_2 \right]} \\ \text{O} \quad \frac{2k_1 \text{O}_2 \quad k_3 \text{O}_3}{\left[k_2 \text{O}_2 \quad k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \quad k_{10} \text{NO}_2 \right]} \end{array}$$

$$\begin{array}{l} \text{Cl} \quad r_4 \quad r_5 \quad r_7 \quad r_8 \quad r_{14} \\ \text{Cl} \quad k_4 \text{O}_3 \quad \text{Cl} \quad k_5 \text{O} \quad \text{ClO} \quad k_7 \text{ClO}_2 \quad k_8 \text{ClOO} \quad k_{14} \text{BrCl} \quad 0 \\ k_4 \text{O}_3 \quad \text{Cl} \quad k_5 \text{O} \quad \text{ClO} \quad k_7 \text{ClO}_2 \quad k_8 \text{ClOO} \quad k_{14} \text{BrCl} \quad 0 \\ k_4 \text{O}_3 \quad \text{Cl} \quad k_5 \text{O} \quad \text{ClO} \quad k_7 \text{ClO}_2 \quad k_8 \text{ClOO} \quad k_{14} \text{BrCl} \\ \text{Cl} \quad \frac{k_5 \text{O} \quad \text{ClO} \quad k_7 \text{ClO}_2 \quad k_8 \text{ClOO} \quad k_{14} \text{BrCl}}{k_4 \text{O}_3} \end{array}$$

$$\text{Cl} \frac{k_5 \left[\frac{2k_1 O_2 k_3 O_3}{k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right] \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} k_7 \text{ClO}_2 k_8 \text{ClOO} k_{14} \text{BrCl}}{k_4 O_3}$$

$$\begin{aligned} & O_2 \quad r_1 \quad r_2 \quad r_3 \quad r_4 \quad r_5 \quad r_8 \quad r_9 \quad r_{10} \quad 2r_{11} \quad r_{12} \quad r_{13} \\ & O_2 \quad k_1 O_2 \quad k_2 O_2 \quad O \quad k_3 O_3 \quad k_4 O_3 \quad \text{Cl} \quad k_5 O \quad \text{ClO} \quad k_8 \text{ClOO} \\ & k_9 O_3 \quad \text{NO} \quad k_{10} \text{NO}_2 \quad O \quad 2k_{11} \text{NO}_2 \quad O_3 \quad k_{12} \text{Br} \quad O_3 \quad k_{13} \text{BrO} \quad \text{ClO} \\ & O_2 \quad -k_1(O_2) - k_2(O_2) \left(\frac{2k_1 O_2 k_3 O_3}{\left[k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right]} \right) k_3(O_3) \end{aligned}$$

$$k_4(O_3) \left(\frac{k_5 \left[\frac{2k_1 O_2 k_3 O_3}{k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right] \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} k_7 \text{ClO}_2 k_8 \text{ClOO} k_{14} \text{BrCl}}{k_4 O_3} \right)$$

$$k_5 \left(\frac{2k_1 O_2 k_3 O_3}{\left[k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right]} \right) \left(\sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \right) k_8(\text{ClOO}) k_9(O_3)(\text{NO})$$

$$k_{10}(\text{NO}_2) \left(\frac{2k_1 O_2 k_3 O_3}{\left[k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right]} \right) 2k_{11}(\text{NO}_2)(O_3) k_{12} \left(\frac{k_{14} \text{BrCl}}{k_{12} O_3} \right) (O_3)$$

$$k_{13} \left(\frac{k_{14} \text{BrCl}}{k_{13} \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} \right) \left(\sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \right)$$

$$\begin{aligned} & O_3 \quad r_2 \quad r_3 \quad r_4 \quad r_9 \quad r_{11} \quad r_{12} \\ & O_3 \quad k_2(O_2) \left(\frac{2k_1 O_2 k_3 O_3}{\left[k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right]} \right) - k_3(O_3) \end{aligned}$$

$$-k_4(O_3) \left(\frac{k_5 \left[\frac{2k_1 O_2 k_3 O_3}{k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right] \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} k_7 \text{ClO}_2 k_8 \text{ClOO} k_{14} \text{BrCl}}{k_4 O_3} \right)$$

$$-k_9(O_3)(\text{NO}) - k_{11}(\text{NO}_2)(O_3) - k_{12} \left(\frac{k_{14} \text{BrCl}}{k_{12} O_3} \right) (O_3)$$

$$\begin{aligned} & \text{ClO}_2 \quad r_6 \quad r_7 \\ & \text{ClO}_2 \quad k_6 \left(\sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}} \right)^2 - k_7(\text{ClO}_2) \end{aligned}$$

$$\begin{aligned} & \text{ClOO} \quad r_7 \quad r_8 \\ & \text{ClOO} \quad k_7(\text{ClO}_2) - k_8(\text{ClOO}) \end{aligned}$$

$$\begin{aligned} & \text{NO} \quad r_9 \quad r_{10} \quad r_{11} \\ & \text{NO} \quad -k_9(O_3)(\text{NO}) k_{10}(\text{NO}_2) \left(\frac{2k_1 O_2 k_3 O_3}{\left[k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right]} \right) k_{11}(\text{NO}_2)(O_3) \end{aligned}$$

$$\begin{aligned} & \text{NO}_2 \quad r_9 \quad r_{10} \quad r_{11} \\ & \text{NO}_2 \quad k_9(O_3)(\text{NO}) - k_{10}(\text{NO}_2) \left(\frac{2k_1 O_2 k_3 O_3}{\left[k_2 O_2 k_5 \sqrt{\frac{k_7 \text{ClO}_2 k_8 \text{ClOO}}{2k_6}}} k_{10} \text{NO}_2 \right]} \right) - k_{11}(\text{NO}_2)(O_3) \end{aligned}$$

$$\begin{array}{l}
BrCl \quad r_{13} \quad r_{14} \\
BrCl \quad k_{13} BrO \quad ClO \quad k_{14} BrCl \\
BrCl \quad k_{13} \frac{k_{14} BrCl}{k_{13} \sqrt{\frac{k_7 ClO_2 k_8 ClOO}{2k_6}}} \sqrt{\frac{k_7 ClO_2 k_8 ClOO}{2k_6}} \quad k_{14} BrCl \\
BrCl \quad k_{14} BrCl \quad k_{14} BrCl \quad 0 \\
BrCl \quad 0
\end{array}$$