

Revised reactions in CAPRAM 2.3 rev

Process in CAPRAM 2.3	Should be replaced by	Rate coefficients ^(a)	Reference	Remarks	Date
$\text{NO}_3^- + \text{h}\nu \rightarrow \text{NO}_2^- + \text{OH} + \text{OH}^-$	$\text{NO}_3^- + \text{H}^+ + \text{h}\nu \rightarrow \text{NO}_2 + \text{OH}$	$\mathbf{J = 4.28 \cdot 10^{-7} \text{ s}^{-1}; \Phi = 0.017 \pm 0.003}$	Zellner <i>et al.</i> , 1990	Include 'H ⁺ ', erase OH ⁻	03/2003
$\text{SO}_2 + \text{O}_3 \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{O}_2$	$\text{SO}_2 + \text{O}_3 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}^+ + \text{O}_2$	$\mathbf{k = 2.4 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}}$	Hoffmann, 1986	Replace 'SO ₄ ²⁻ ' by 'HSO ₄ ⁻ ', include 'H ₂ O'	03/2003
$\text{SO}_3^{2-} + \text{O}_3 \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{O}_2$	$\text{SO}_3^{2-} + \text{O}_3 \rightarrow \text{SO}_4^{2-} + \text{O}_2$	$\mathbf{k = 1.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}; E_a/R = 5280 \text{ K}}$	Hoffmann, 1986	Erase 'H ⁺ '	03/2003
$\text{SO}_5^- + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HSO}_5^- + \text{O}_2$	$\text{SO}_5^- + \text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HSO}_5^- + \text{O}_2 + \text{OH}^-$	$k = 1.7 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $\mathbf{k = 2.34 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}}$	Buxton <i>et al.</i> , 1996	Include 'OH ⁻ ', corrected k value	03/2003
$\text{SO}_4^- + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_3^- + \text{H}^+$	$\text{SO}_4^- + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{SO}_3^-$	$\mathbf{k = 3.2 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}; E_a/R = 1200 \text{ K}}$	Reese, 1997	Erase 'H ⁺ '	03/2003
$\text{HCOO}^- + \text{SO}_4^- + \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{HO}_2 + \text{CO}_2$	$\text{HCOO}^- + \text{SO}_4^- + \text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{HO}_2 + \text{CO}_2$	$\mathbf{k = 2.1 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}}$	Reese, 1997	Erase 'H ⁺ '	03/2003
$\text{HCOO}^- + \text{CO}_3^- + \text{O}_2 \rightarrow 2 \text{CO}_3^{2-} + \text{CO}_2 + \text{HO}_2$	$\text{HCOO}^- + \text{CO}_3^- + \text{O}_2 \rightarrow \text{CO}_3^{2-} + \text{HO}_2 + \text{CO}_2$	$\mathbf{k = 1.4 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}; E_a/R = 3300 \text{ K}}$	Zellner <i>et al.</i> , 1996	Correct mass and charge balance	03/2003
$\text{CH}_3\text{COO}^- + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2\text{CH}_2\text{COO}^-$	$\text{CH}_3\text{COO}^- + \text{OH} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2\text{CH}_2\text{COO}^-$	$\mathbf{k = 1.0 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}; E_a/R = 1800 \text{ K}}$	Fisher and Hamill, 1973	Include 'O ₂ '	03/2003
$\text{aORA2}^{(b)} + \text{NO}_3 + \text{O}_2 \rightarrow \text{aACO}_3^{(c)} + \text{CO}_2 + \text{NO}_3^-$	$\text{aORA2} + \text{NO}_3 + \text{O}_2 \rightarrow \text{aACO}_3 + \text{NO}_3^- + \text{H}^+$	$\mathbf{k = 1.4 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}; E_a/R = 3800 \text{ K}}$	Exner <i>et al.</i> , 1994	Erase 'CO ₂ ', include 'H ⁺ '	03/2003
$\text{CH}_3\text{COO}^- + \text{NO}_3 + \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}^+ + \text{CH}_3\text{OO} + \text{CO}_2$	$\text{CH}_3\text{COO}^- + \text{NO}_3 + \text{O}_2 \rightarrow \text{NO}_3^- + \text{CH}_3\text{OO} + \text{CO}_2$	$\mathbf{k = 2.9 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}; E_a/R = 3800 \text{ K}}$	Exner <i>et al.</i> , 1994	Erase 'H ⁺ '	03/2003
$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$		$K = 7.7 \cdot 10^{-7} \text{ M}^{-1}; E_a/R = 750 \text{ K}$ $k_{\text{forw.}} = 4.3 \cdot 10^{-2} \text{ M}^{-1} \text{ s}^{-1}; k_{\text{back.}} = 5.6 \cdot 10^4 \text{ s}^{-1};$ $K = 2 \cdot 10^{-4} \text{ M}$	Graedel and Weschler, 1981 Welch <i>et al.</i> , 1969	Use after Chameides (1984)	03/2003
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$		$k_{\text{forw.}} = 1 \cdot 10^7 \text{ s}^{-1}; k_{\text{back.}} = 5 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $\mathbf{K = 4.3 \cdot 10^{-7} \text{ M}; E_a/R = 913 \text{ K}}$ $\mathbf{k_{\text{back.}} = 5.6 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}}$	Graedel and Weschler, 1981 Graedel and Weschler, 1981 Chameides, 1984		
	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$\mathbf{K_H = 3 \cdot 10^3 \text{ M atm}^{-1};}$ $\mathbf{K_H = 2.5 \text{ M atm}^{-1}; \Delta H/R = -7216 \text{ K}}$	Graedel and Weschler, 1981 Betterson and Hoffmann, 1988	Hydration should not be included in the Henry's Law constant	02/2002
$\text{HCHO}_{(g)} \rightleftharpoons \text{HCHO}_{(aq)}$		$K_H = 11.4 \text{ M atm}^{-1};$ $\mathbf{K_H = 4.8 \text{ M atm}^{-1}; \Delta H/R = -6254 \text{ K}}$	Betterson and Hoffmann, 1988	Hydration should not be included in the Henry's Law constant	02/2002
$\text{NO}_3 + \text{SO}_4^{2-} \rightarrow \text{NO}_3^- + \text{SO}_4^-$		$k = 5.6 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1};$ $\mathbf{k = 1 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1};}$	Logager <i>et al.</i> , 1993	Corrected value	02/2002
$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$		$\mathbf{K = 1.72 \cdot 10^6 \text{ M}; E_a/R = -6890 \text{ K}}$ $k_{\text{forw.}} = 8.6 \cdot 10^{16} \text{ s}^{-1}; k_{\text{back.}} = 5 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $\mathbf{k_{\text{forw.}} = 5 \cdot 10^{11} \text{ s}^{-1}; k_{\text{back.}} = 2.9 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}}$	Marsh and McElroy, 1985 Graedel and Weschler, 1981	K >> Diffusion limit	02/2002
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$		$K = 1.77 \cdot 10^{-5}; E_a/R = 560 \text{ K}$ $\mathbf{K = 3.17 \cdot 10^{-7}}$ $k_{\text{forw.}} = 6.02 \cdot 10^5 \text{ s}^{-1}; k_{\text{back.}} = 3.4 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ $\mathbf{k_{\text{forw.}} = 1.08 \cdot 10^4 \text{ s}^{-1}}$	Harned and Owen, 1958 Graedel and Weschler, 1981	Water included in K	02/2002

Process	Should be replaced by	Rate coefficients	Referenc	Remark	Date
HCHO + HSO ₃ ⁻ ⇌ HMS ⁻		K = 2·10 ⁸ M ⁻¹ K = 6.6·10⁹ M⁻¹ k _{forw.} = 790 M ⁻¹ s ⁻¹ ; E _a /R = 2990 K E_a/R = 3293 K k _{back.} = 3.95·10 ⁻⁶ s ⁻¹ ; E _a /R = 2990 K k_{back.} = 1.197·10⁻⁷ s⁻¹; E_a/R = 5831 K	Olson and Hoffmann, 1989	Corrected K value Corrected E _a /R values k _{back.} calculated from K and k _{forw.}	03/2003 (after 02/2002)
CH ₂ (OH) ₂ + SO ₃ ²⁻ ⇌ HMS ⁻ + OH ⁻	HCHO + SO ₃ ²⁻ + H ₂ O ⇌ HMS ⁻ + OH ⁻	K = 3.6·10 ⁶ K = 6.6·10⁹ M⁻¹ k _{forw.} = 2.5·10 ⁷ M ⁻¹ s ⁻¹ ; E _a /R = 2450 K E_a/R = 2752 K k _{back.} = 3.95·10 ⁻⁶ M ⁻¹ s ⁻¹ ; E _a /R = 5530 K k_{back.} = 3.79·10⁻³ s⁻¹; E_a/R = 5290 K	Olson and Hoffmann, 1989	Replace 'CH ₂ (OH) ₂ ' by 'HCHO' Corrected K value Corrected E _a /R values k _{back.} calculated from K and k _{forw.}	03/2003 (after 02/2002)
	O _{2(g)} ⇌ O _{2(aq)}	K_H = 1.3·10⁻³ M atm⁻¹; ΔH/R = -1700 K α = 0.1; D_g = 1.12·10⁻⁵ m² s⁻¹	Loomis, 1928 Fuller, 1986	Added reaction, α and D _g estimated	02/2002
	ACO ₃ + ACO ₃ → 2 CH ₃ O ₂ + 2 CO ₂ + O ₂	k = 1.5·10⁸ M⁻¹ s⁻¹		Added reaction, k estimated. Only sink reaction of ACO ₃ should be included to avoid accumulation of ACO _{3(aq)} .	02/2002
	H ₂ SO ₄ ⇌ HSO ₄ ⁻ + H ⁺	K_A = 1000 M k_{forw.} = 5·10¹³ s⁻¹; k_{back.} = 5·10¹⁰ M⁻¹ s⁻¹	Graedel and Weschler, 1981	Added reaction	02/2002

Remarks:

^(a): Recommended values in bold

^(b): Subsystem group including acetic acid and higher acids

^(c): Subsystem group including peroxy radicals containing a carbonyl group i.e. ACO₃ ≡ O₂CH₂COOH + O₂CH₂COO⁻ + CH₃C(O)OO

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