

CAPRAM 2.4 mechanism revision tables

Revised phase transfer data in CAPRAM 2.4 rev

Species	K_H 298, M atm ⁻¹	$-\Delta H / R$, K	reference	α	reference	D_g 10 ⁵ m ² s ⁻¹	reference	Date
Cl ₂	9.15·10 ⁻² 9.15·10⁻²	2490	Wilhelm et al., 1977 Wilhelm et al., 1977	0.08	estimated	1.28	Schwartz, 1986	08/2006 08/2006
Br ₂	0.758 0.760	3800 4100	Dean, 1992	0.08	estimated	1.00	Schwartz, 1986	08/2006
NO	1.9·10 ⁻³ 1.9·10⁻³	1400	Lide and Frederikse, 1995	0.001		2.24		08/2006

Remarks: revised values in bold

Revised reactions in CAPRAM 2.4 rev

Process in CAPRAM 2.4	Should be replaced by	Rate coefficients ^(a)	Reference	Comment	Date
FeO ²⁺ + HSO ₃ ⁻ → Fe ³⁺ + SO ₃ ⁻ + OH ⁻	FeO ²⁺ + HSO ₃ ⁻ → Fe ³⁺ + SO ₃ ⁻ + OH ⁻	k = 2.5·10⁵ M⁻¹ s⁻¹	Jacobsen <i>et al.</i> , 1998a	Correct charge balance	03/2003
FeO ²⁺ + HCOO ⁻ → Fe ³⁺ + COOH + OH ⁻	FeO ²⁺ + HCOO ⁻ + H ⁺ → Fe ³⁺ + COOH + OH ⁻	k = 3·10⁵ M⁻¹ s⁻¹	Jacobsen <i>et al.</i> , 1998a	Correct charge balance	03/2003
[Fe(OH) ₂ Fe] ⁴⁺ + 2 H ⁺ → 2 Fe ³⁺ + 2 H ₂ O	[Fe(OH) ₂ Fe] ⁴⁺ + H ⁺ → 2 Fe ³⁺ + OH ⁻ + H ₂ O	k = 1.95 M⁻¹ s⁻¹ E_a/R = 5653 K	Jacobsen <i>et al.</i> , 1997a	Modified for correct reaction order	03/2003
2 O ₂ CH ₂ COO ⁻ → 2 O ₂ ⁻ + (OH) ₂ CHCOO ⁻ + 2 H ₂ O	2 O ₂ CH ₂ COO ⁻ + O ₂ + 2 OH ⁻ → 2 (OH) ₂ CHCOO ⁻ + 2 O ₂ ⁻	k = 7.5·10⁶ M⁻¹ s⁻¹	Schuchmann <i>et al.</i> , 1985	Correct mass and charge balance	03/2003
CO ₂ + H ₂ O ⇌ H ₂ CO ₃		K = 7.7·10 ⁻⁷ M ⁻¹ ; E _a /R = 750 K k _{forw.} = 4.3·10 ⁻² M ⁻¹ s ⁻¹ ; k _{back.} = 5.6·10 ⁴ s ⁻¹ ; K = 2·10 ⁻⁴ M k _{forw.} = 1·10 ⁷ s ⁻¹ k _{back.} = 5·10 ¹⁰ M ⁻¹ s ⁻¹	Graedel and Weschler, 1981 Welch <i>et al.</i> , 1969 Graedel and Weschler, 1981 Graedel and Weschler, 1981 Graedel and Weschler, 1981 Graedel and Weschler, 1981	Use after Chameides (1984)	03/2003
H ₂ CO ₃ ⇌ H ⁺ + HCO ₃ ⁻	CO ₂ + H ₂ O ⇌ HCO ₃ ⁻ + H ⁺	K = 4.3·10⁻⁷ M; E_a/R = 913 K k_{back.} = 5.6·10⁴ M⁻¹ s⁻¹ K = 2·10 ⁸ M ⁻¹ K = 6.6·10⁹ M⁻¹	Chameides, 1984 Graedel and Weschler, 1981		03/2003
HCHO + HSO ₃ ⁻ ⇌ HMS ⁻		K = 6.6·10⁹ M⁻¹ k _{forw.} = 0.436 M ⁻¹ s ⁻¹ ; E _a /R = 2990 K k_{forw.} = 790 M⁻¹ s⁻¹ E_a/R = 3293 K k _{back.} = 2.2·10 ⁻⁹ s ⁻¹ ; E _a /R = 2990 K k_{back.} = 1.197·10⁻⁷ s⁻¹; E_a/R = 5831 K K = 33	Olson and Hoffmann, 1989 Boyce and Hoffmann, 1984 Olson and Hoffmann, 1989	Corrected K value Corrected k _{forw.} and E _a /R values	03/2003
CH ₂ (OH) ₂ + SO ₃ ²⁻ ⇌ HMS ⁻ + OH ⁻		k _{forw.} = 1.36·10 ⁵ M ⁻¹ s ⁻¹ ; E _a /R = 2450 K k _{back.} = 4.15·10 ³ M ⁻¹ s ⁻¹ ; E _a /R = 5530 K K = 6.6·10⁹ M⁻¹ k_{forw.} = 2.5·10⁷ M⁻¹ s⁻¹ E_a/R = 2752 K k_{back.} = 3.79·10⁻³ s⁻¹; E_a/R = 5290 K	Boyce and Hoffmann, 1984 Olson and Hoffmann, 1989 Olson and Hoffmann, 1989	k _{back.} calculated from K and k _{forw.} Replace 'CH ₂ (OH) ₂ ' by 'HCHO'	03/2003
HCHO + SO ₃ ²⁻ + H ₂ O ⇌ HMS ⁻ + OH ⁻		k = 3·10⁹ M⁻¹ s⁻¹ k = 2.3·10⁹ M⁻¹ s⁻¹ k = 6·10⁶ M⁻¹ s⁻¹ k = 1.0·10⁷ M⁻¹ s⁻¹ k = 1.8·10⁴ M⁻¹ s⁻¹ E_a/R = 5052 K k = 17 M⁻¹ s⁻¹	Kozlov and Berdnikov, 1973 Jacobsen <i>et al.</i> , 1997b Logager <i>et al.</i> , 1992 Jacobsen <i>et al.</i> , 1997a Buxton <i>et al.</i> , 1997	Corrected K value Corrected k _{forw.} and E _a /R values k _{back.} calculated from K and k _{forw.} Corrected k value Revised mass and charge balance Revised mass and charge balance Revised mass balance Revised reaction products	08/2006 08/2006 08/2006 08/2006 08/2006
HO ₂ + Cu ⁺ (+ H ⁺) → H ₂ O ₂ + Cu ²⁺	HO ₂ + Cu ⁺ (+ H ⁺) → H ₂ O ₂ + Cu ²⁺				
MnO ₂ ⁺ + MnO ₂ ⁺ → 2 Mn ²⁺ + H ₂ O ₂	MnO ₂ ⁺ + MnO ₂ ⁺ (+ 2 H ₂ O) → 2 Mn ²⁺ + H ₂ O ₂ + 2 OH ⁻				
FeO ²⁺ + OH ⁻ → Fe ³⁺ + H ₂ O ₂	FeO ²⁺ + OH ⁻ (+ H ⁺) → Fe ³⁺ + H ₂ O ₂				
FeO ²⁺ + Fe ²⁺ (+ 2H ₂ O) → FeOH ₂ Fe ⁴⁺ + 2 OH ⁻	FeO ²⁺ + Fe ²⁺ (+ H ₂ O) → FeOH ₂ Fe ⁴⁺				
Fe ²⁺ + S ₂ O ₈ ²⁻ (+ H ₂ O) → Fe(OH) ²⁺ + SO ₄ ²⁻ + SO ₄ ²⁻ + H ⁺	Fe ²⁺ + S ₂ O ₈ ²⁻ → Fe ³⁺ + SO ₄ ²⁻ + SO ₄ ²⁻				

Process in CAPRAM 2.4	Should be replaced by	Rate coefficients ^(a)	Reference	Comment	Date
$\text{SO}_5^- + \text{O}_2^- (+\text{H}^+) \rightarrow \text{HSO}_5^- + \text{OH}^- + \text{O}_2$	$\text{SO}_5^- + \text{O}_2^- (+\text{H}^+) \rightarrow \text{HSO}_5^- + \text{O}_2$	$k = 2.34 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$	Buxton et al., 1996a	Revised mass balance	08/2006
$\text{SO}_5^- + \text{C}_2\text{O}_4^{2-} \rightarrow \text{HSO}_5^- + \text{C}_2\text{O}_4^-$	$\text{SO}_5^- + \text{C}_2\text{O}_4^{2-} (+\text{H}^+) \rightarrow \text{HSO}_5^- + \text{C}_2\text{O}_4^-$	$k = 1 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Herrmann et al., 2000	Revised mass and charge balance	08/2006
$\text{O}_2\text{CH}_2\text{OH} + \text{O}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} + \text{O}_2 + \text{HCHO}$	$\text{O}_2\text{CH}_2\text{OH} + \text{O}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{OH} + 2 \text{O}_2 + \text{HCHO}$	$k = 1.05 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	von Sonntag, 1987	Revised mass balance	08/2006
$\text{CH}_3\text{CH}_2\text{OH} + \text{OH} (+\text{O}_2) \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHOH}$	$\text{CH}_3\text{CH}_2\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CHOH}$	$k = 1.9 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $k = 2.1 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 1200 \text{ K}$	Buxton et al., 1988a Ervens et al., 2003	Revised kinetic data and mass balance	08/2006
$\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{O}_2\text{CH}_3\text{CHOH}$	$\text{CH}_3\text{CHOH} + \text{O}_2 \rightarrow \text{O}_2\text{CH}_3\text{CHOH}$	$k = 2 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $k = 4.6 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	estimated Adams, 1969	Revised kinetic data	08/2006
$\text{CH}_3\text{CHO} + \text{OH} (+\text{O}_2 + \text{H}_2\text{O}) \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO}$	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CO}$	$k = 3.6 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Schuchmann and v. Sonntag, 1988	Revised mass balance in the table	08/2006
	$\text{CH}_3\text{CHO} + \text{NO}_3 \rightarrow \text{NO}_3^- + \text{H}^+ + \text{CH}_3\text{CO}$	$k = 1.9 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$	Zellner et al., 1996	Newly included reaction	08/2006
	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{Cl}_2^- \rightarrow 2 \text{Cl}^- + \text{H}^+ + \text{CH}_3\text{C}(\text{OH})_2$	$k = 4 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Jacobi, 1996	Newly included reaction	08/2006
$\text{CH}_3\text{CHO} + \text{Br}_2^- \rightarrow 2 \text{Br}^- + \text{H}^+ + \text{CH}_3\text{CO}$	$\text{CH}_3\text{CHO} + \text{Br}_2^- \rightarrow 2 \text{Br}^- + \text{H}^+ + \text{CH}_3\text{CO}$	$k = 2.15 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 2526 \text{ K}$	Measured value (IfT)	Revised kinetic data	08/2006
	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{Br}_2^- \rightarrow 2 \text{Br}^- + \text{H}^+ + \text{CH}_3\text{C}(\text{OH})_2$	$k = 2.15 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 2526 \text{ K}$	Measured value (IfT)	Newly included reaction	08/2006
	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{CO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+ + \text{CH}_3\text{C}(\text{OH})_2$	$k = 1 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$	estimated	Newly included reaction	08/2006
$\text{OH} + \text{HC}_2\text{O}_4^- \rightarrow \text{H}_2\text{O} + \text{C}_2\text{O}_4^-$	$\text{OH} + \text{HC}_2\text{O}_4^- \rightarrow \text{H}_2\text{O} + \text{C}_2\text{O}_4^-$	$k = 3.2 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ $k = 1.9 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 2800 \text{ K}$	Getoff et al., 1971 Ervens et al., 2003	Revised kinetic data	08/2006
$\text{OH} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{OH}^- + \text{C}_2\text{O}_4^-$	$\text{OH} + \text{C}_2\text{O}_4^{2-} \rightarrow \text{OH}^- + \text{C}_2\text{O}_4^-$	$k = 5.3 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$ $k = 1.6 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 4300 \text{ K}$	Getoff et al., 1971 Ervens et al., 2003	Revised kinetic data	08/2006
$\text{Cl}_2^- + \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{Cl}^- + \text{H}^+ + \text{C}_2\text{O}_4^-$	$\text{Cl}_2^- + \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{Cl}^- + \text{C}_2\text{O}_4^-$	$k = 4.0 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$	estimated (ETR)	Revised mass balance	08/2006
$\text{OH} + \text{CH}(\text{OH})_2\text{COOH} \rightarrow \text{H}_2\text{O} + \text{C}(\text{OH})_2\text{COOH}$	$\text{OH} + \text{CH}(\text{OH})_2\text{COOH} \rightarrow \text{H}_2\text{O} + \text{C}(\text{OH})_2\text{COOH}$	$k = 1.1 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 1516 \text{ K}$ $k = 3.6 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 1000 \text{ K}$	Estimate equal as $k(\text{CH}(\text{OH})_2)$ Ervens et al., 2003	Revised kinetic data	08/2006
$2 \text{O}_2\text{CH}_2\text{COO}^- (+\text{H}_2\text{O}) \rightarrow 2 \text{CH}(\text{OH})_2\text{COO}^- + \text{H}_2\text{O}_2$	$2 \text{O}_2\text{CH}_2\text{COO}^- (+2 \text{H}_2\text{O}) \rightarrow 2 \text{CH}(\text{OH})_2\text{COO}^- + \text{H}_2\text{O}_2$	$k = 2 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$	Schuchmann et al., 1985	Revised mass balance	08/2006
$\text{Cl}_2^- + \text{Fe}^{2+} \rightarrow \text{FeCl}^{2+}$	$\text{Cl}_2^- + \text{Fe}^{2+} \rightarrow \text{FeCl}^{2+} + \text{Cl}^-$	$k = 4 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 3490 \text{ K}$	Thornton and Laurence, 1973	Revised mass balance	08/2006
$\text{Cl}_2^- + \text{O}_2^- \rightarrow 2 \text{Cl}^- + \text{O}_2$	$\text{Cl}_2^- + \text{O}_2^- \rightarrow 2 \text{Cl}^- + \text{O}_2$	$k = 6.0 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$	Jacobi, 1996	Revised typo in the table (reaction considered also in CAPRAM 2.4)	08/2006
$\text{Cl}_2^- + \text{H}_2\text{O} \rightarrow \text{H}^+ + 2 \text{Cl}^- + \text{OH}$	$\text{Cl}_2^- + \text{H}_2\text{O} \rightarrow \text{H}^+ + 2 \text{Cl}^- + \text{OH}$	$k = 23.4 \text{ M}^{-1} \text{ s}^{-1}$	Jacobi, 1996	Revised kinetic data and reference	08/2006
$\text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{Br}^- + \text{H}^+ + \text{HOBr}$		$k = 1.7 \text{ M}^{-1} \text{ s}^{-1}$ $k = 1.7 \text{ M}^{-1} \text{ s}^{-1}$ $E_a/R = 7500 \text{ K}$	Buxton et al., 1998 Beckwith et al., 1996	Revised kinetic data	08/2006
$\text{HCO}_3^- + \text{Br}_2^- \rightarrow 2 \text{Cl}^- + \text{CO}_3^-$	$\text{HCO}_3^- + \text{Br}_2^- \rightarrow 2 \text{Br}^- + \text{CO}_3^- + \text{H}^+$	$k = 1.1 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$	estimated	Revised mass and charge balance	08/2006
$\text{CH}_3\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}(\text{OH})_2$	$\text{CH}_3\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}(\text{OH})_2$	$K = 367$; $k_{\text{forw.}} = 1.1 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{back.}} = 3 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$ $K = 1.2 \cdot 10^{-2}$; $k_{\text{forw.}} = 2 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{back.}} = 3 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$	Schuchmann and v. Sonntag, 1988	revised kinetic data and reference	08/2006

Remarks: ^(a) recommended values in bold

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