

Chapter 15

Mercury Chemical Transformation in the Gas, Aqueous and Heterogeneous Phases: State-of-the-art Science and Uncertainties

Parisa A. Ariya, Kirk Peterson, Graydon Snider, and Marc Amyot

Summary Mercury is a persistent, toxic and bio-accumulative pollutant of global interest. This element is assumed to exist predominantly in the atmosphere, as elemental mercury, undergoing chemical reactions in the presence of atmospheric oxidants. The oxidized mercury can further deposit on the Earth's surface and may potentially be bioaccumulative in the aquatic food chain, through complex, but not yet well understood, mechanisms. Since the atmosphere plays a significant role as a medium for chemical and physical transformation, it is imperative to understand the fundamentals of the kinetics and thermodynamics of the elementary and complex reactions of $\text{Hg}^0_{(\text{g})}$ and oxidized mercury not only in the atmosphere as gas phase, but also the reactions in the aqueous and heterogeneous phases at atmospheric interfaces such as aerosols, fogs, clouds, and snow-water-air interfaces. In this chapter, we compile a comprehensive set of theoretical, laboratory and field observations involving mercury species in the course of homogeneous and heterogeneous reactions. We herein describe the state-of-the-knowledge in this domain and put forward the open questions and future direction of research.

15.1 Introduction

Atmospheric chemical processes of mercury promoted by interfaces have been largely overlooked until recently, although heterogeneously-catalyzed chemical reactions in the stratosphere have been well established for several decades. As a fluid metal, mercury is a liquid at room temperature and has the lowest known critical temperature of any metal (*c.a.*, 1478 °C) Although the dominant form of atmospheric mercury is gaseous elemental mercury ($\text{Hg}^0_{(\text{g})}$), traces of oxidized mercury in aquatic and heterogeneous systems are expected (Seiler et al., 1980; Slemr et al., 1985; Lindqvist et al., 1985). Figure 15.1 illustrates a simplified schematic of mercury transformation in the atmosphere and at atmospheric interfaces.

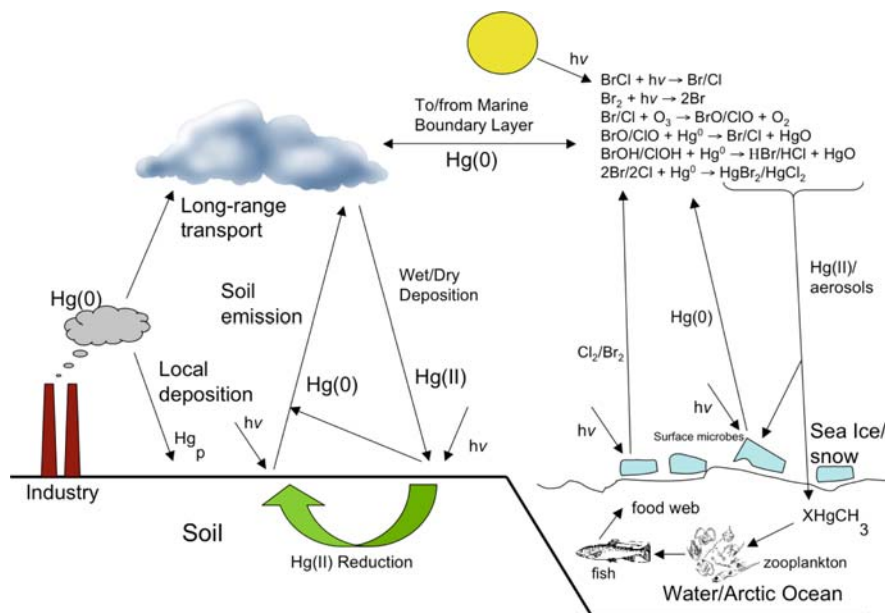


Figure 15.1 A simplified schematic of mercury transformation in the Earth's environment (inspired by Ariya, et al., 2004; Macdonald et al., 2005; Lindberg et al., 2007)

Elemental mercury (Hg^0) exists in ambient air, both in the vapour and particle phase associated with aerosols. As pointed out in the earlier chapters, mercury in the atmosphere is predominantly anthropogenic in origin, such as fuel and coal combustion and waste incineration. Natural emissions, including those from volcanic eruptions, soils, lakes, open water and forest fires, contribute less significantly than anthropogenic sources (c.a. 40%). However, there are significant uncertainties on natural emission inventories (Mason et al., 1994; Gardfeldt and Jonsson, 2003). Atmospheric chemical transformations of mercury can indeed play an important role in the global cycling of this toxic element, as the atmosphere is the fastest moving fluid in the Earth's ecosystem. A major interest in the understanding of atmospheric transformation stems from its potential impact on mercury bioaccumulation. Mercury speciation in the atmosphere has a significant influence on its deposition on environmental surfaces. Solubility and deposition of elemental mercury is quite distinct from $\text{Hg}(\text{II})$ (Ariya and Peterson, 2005), and thus deposition rates on the Earth's surface vary substantially. Amongst all mercury species, methyl mercury has been considered to be bio-magnified in fish. The extent of methylation depends on a constant supply of inorganic mercury from the atmosphere (Mason and Sheu, 2002). Indeed, atmospheric deposition is considered to be a major source of mercury in most remote aquatic systems (Mason et al., 1994; Nriagu, 1994). It is noteworthy that the chemical-biological processes that dictate the bioaccumulation of mercury in the food chain have yet to be fully characterized (Morel, 1998). Consequently, the extent of incorporation of oxidized mercury produced via

atmospheric chemical reactions into the food chain has yet to be evaluated. Figure 15.1 depicts a simplified schematic of mercury cycling in the Earth's ecosystem in atmosphere and at environmental interfaces.

Hg species are removed from atmosphere through dry and wet deposition processes (Lindqvist and Rodhe, 1985). Interestingly, in the high-Arctic region (Schroeder et al., 2002), Arctic (Lindberg et al., 1998), and sub-Arctic, the rapid depletion of mercury has been observed. Nearly complete depletions of ozone in the boundary layer occurred over large areas, and evidence of reactive halogens have been observed during most mercury depletion events (MDEs) (Ariya et al., 1998; 1999). Upon reaction with atmospheric oxidants, elemental mercury can be transformed to its oxidized forms, which are also more bio-accumulative than elemental mercury (Gardfeldt et al., 2001). Observed ozone depletion events at the ground are suggested to be driven by sunlight and bromine atoms derived from reactions of atmospheric reactive halogens with marine sea salt in surface snow and ice (Ariya et al., 1998; 1999; Gardfeldt et al., 2001). Soon after, mercury depletion was found to be wide spread. Such depletion events have also been observed in the Antarctic (Ebinghaus et al., 2002), where they are influenced by the photochemical oxidation of elemental mercury in the troposphere involving sea salt on snow/icepack or aerosols (Schroeder and Munthe, 1998).

The mechanism of the volatilization of gaseous elemental mercury from surfaces, chemical transformation in gas and condensed phases (liquid/solid/ heterogeneous), and deposition mechanisms are not well-defined processes. For instance, not much is known about chemical reactions occurring in the snow, especially catalytic and heterogeneous reactions occurring at the surface of snow grains and removal of $\text{Hg}_{(g)}^0$ over fly ash, but field observations support the importance of such surfaces in mercury cycling (Dommergue et al., 2007; Pavlish et al., 2003). Pure gaseous oxidation of mercury is mechanistically difficult to explain as well, and in some cases can be explained via heterogeneous phase chemistry (Raofie and Ariya, 2003). Inconsistencies between kinetic and thermodynamic data describing the homogeneous gas phase oxidation of mercury such as in case of one of the most predominant atmospheric oxidant, ozone or its well reactions (Calvert and Lindberg, 2005, Hall et al., 1995). Attempts to more clearly understand reduction of $\text{Hg}_{(s, aq)}^{(II)}$ to $\text{Hg}_{(g)}^0$ (or the reverse oxidation) are motivated by uncertainties in the Hg chemistry of the Arctic and in finding suitable surface catalysts for $\text{Hg}_{(g)}^0$ emission reduction in coal fire combustion. Noting the lack of detailed *mechanistic* understanding of mercury redox reactions, we herein strive to examine what changes alter surface reactivity, including the presence of water, various trace surface impurities, photochemistry, temperature, or other competing reactions. Surfaces can act as reactive sites for chemical reactions, active sites for catalysis, and as a platform for exchange between different planetary ecosystem compartments such as air-snow, air-water (lake/ocean), vegetation-air, water-soil and air-soil. However, due to the complexity of the nature of surfaces, its variability, its sensitivity towards environmental variables, its temporal and spatial heterogeneity, environmental surfaces studies are one of the major scientific domain of uncertainty that will face environmental scientists in this new century.

A significant part of the deposited mercury is photo-reduced and re-emitted as GEM (Ferrari et al., 2003; 2004; Brooks et al., 2006; Aspmo et al., 2006). There have been several excellent review articles on mercury transformation in atmosphere (Schroeder, 1991; Lin and Pehkonen, 1999; Steffen, et al., 2007), particularly on its properties, sources, sinks, and fluxes of mercury. As such, in the light of recent laboratory and computational studies, we will attempt to focus instead on a comprehensive review of the kinetic, product studies and thermochemical calculations of mercury redox reactions in the homogeneous and heterogeneous phases. We will discuss the importance of environmental interfaces and environmentally relevant (or potentially relevant) carbon surfaces (such as fly ash, charcoal). We will outline major gaps and some future research directions.

15.2 Atmospheric Oxidation and Reductions

Most atmospheric oxidation reactions are likely to react via multi-step reaction mechanisms. Tables 15.1-15.3 illustrate the detailed kinetic and theoretical studies, as well as estimation from field studies on various atmospheric reactions in gaseous and aqueous phases as well as reactions on surfaces i.e., heterogeneous phases. To be concise, we only focus on a few reactions of significant atmospheric relevance in the text, as the Tables are very detailed and full of information on conditions where these data were taken. Please note that in calculation of atmospheric lifetime for mercury, in contrast with many other chemical in the atmosphere that they can be irreversibly transformed to products, mercury can be oxidized, and oxidized mercury can be reduced by various atmospheric reductants in aerosols, fog, clouds and interfaces (see Tables 15.1 and 15.2). Hence, the oxidation alone represents merely one aspect of its transformation, can not yield to proper calculation of the lifetime.

15.2.1 Kinetic and Product Studies

The rate of the atmospheric chemical transformation of elemental mercury towards a given oxidant is dependent on two factors. The first factor is the reactivity of mercury toward a given oxidant at environmentally relevant conditions, such as temperature, pressure, oxygen concentration, and relative humidity. Since in our previous book chapter in 2004 edition (Ariya and Peterson, 2005), we have described in detail, the techniques used, as well as the importance of environmental condition, we will herein not describe them again. The second factor is the concentration (or mixing ratio) of the oxidant. The existing laboratory studies of mercury kinetic reactions have been obtained using steady state reaction chamber or fast flow tubes and a single study has been carried on the analysis on field data. Both relative and absolute techniques were used in these studies. Both absolute and relative techniques have advantages and disadvantages.

Table 15.1 Compilation of known gas-phase kinetics of mercury

Gas Phase Reaction	Reaction Type ¹	Gas Type, Press	Temp (K)	Rate ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$) [$R] = J K^{-1} \text{mol}^{-1} [T] = \text{Kelvin}$]	Reference
$\text{Hg}(6^3\text{P}_0) + \text{N}_2 \rightarrow \text{Hg}(6^3\text{P}_0)$	Abs	N_2 , 1 atm	298	$3.9\text{--}7.1 \times 10^{-12}$	Hall et al., 2005
$\text{Hg}(6^3\text{P}_0) + \text{N}_2 \rightarrow \text{Hg}(6^3\text{P}_0)$	Abs	N_2 , 1 atm	296 ± 1	6.1×10^{-15}	Raofie et al., 2008
$\text{Hg} + \text{I}_2 \rightarrow \text{HgI}_2 + \text{HgOI}$	Abs	Air , N_2 , 1 atm	298 ± 1	$< 1.27 \times 10^{-19}$	Ariya et al., 2002
$\text{Hg} + \text{Br}_2 \rightarrow \text{HgBr}_2$	Abs	air, 1 atm	~298	No reaction detected	Summer et al., 2005
$\text{Hg} + \text{BrO} \rightarrow \text{HgBrO}$	Rel rate	N_2 , 1 atm	298	$10^{-15} < k < 10^{-13}$	Raofie and Ariya, 2003
$\text{Hg} + \text{Br} \rightarrow \text{HgBr}$	Ab initio	N/A, 1 atm	Range?	$1.01 \times 10^{-12} \text{ e}^{0.738/\text{RT}}$	Khalizov et al., 2003
	RRKM/B3LYP	N/A, 1 atm	180–400	2.1×10^{-12}	Goodsite et al., 2004
	Abs	He, 0.26–0.79 atm	298	1.1×10^{-12} (T/298) ^{2.37}	Donohoue et al., 2006
	CCSD(T)	1 atm	298	$(1.46 \pm 0.36) \times 10^{-32} [\text{cm}^6/\text{molecule}^2 \text{ s}^{-1}]$ $(\text{T}/298)^{(-1.86 \pm 1.49)}$	
	Rel	Ar, 1 atm	260	$(3.6 \pm 0.9) \times 10^{-13}$	Shepler et al., 2007
	Abs, fitted equation	Air , N_2 , 1 atm	298 ± 1	1.2×10^{-12}	Ariya et al., 2002
	Abs	CF_3Br , 0.26 atm	397	$(3.2 \pm 0.3) \times 10^{-12}$	Greig, G., et al., 1970
	Abs	CF_3Br , 0.26 atm	397	$\sim 3 \times 10^{-16} \text{ molec}^{-1} \text{ s}^{-1}$	Greig, G., et al., 1970
	Abs, fitted equation	CF_3Br , 0.26 atm	397	$7 \times 10^{17} \text{ molec}^{-1} \text{ s}^{-1}$	
	Abs	Air , N_2 , 1 atm	298 ± 1	$(2.1 \pm 1.3) \times 10^{-14} \text{ molec}^{-1} \text{ s}^{-1}$	
	Abs	Humid air	273	$(2.6 \pm 0.2) \times 10^{-18}$	Ariya et al., 2002
	Abs	Air	293–973	$0.4(\text{dry}) - 2.5(80\% \text{ RH}) \times 10^{-15}$	Menke and Wallis, 1980;
	Abs	air, 1 atm	~298	5.6×10^{15}	Seigneur et al., 1994
	Abs	N_2 , 1 atm	673–1173	$(2.5 \pm 0.9) \times 10^{-18}$	Sliker, et al., 2000
	Abs		673	$0.386(\text{units?}) \text{ exp}^{(-607/\text{RT})}$	Summer et al., 2005
	Abs			$3.65 \times 10^{-14} \text{ exp}^{(-6400/\text{RT})}$	Agarwal et al., 2007
	Abs			4.8×10^{-15}	Widmer, et al., 1998

(continued)

Table 15.1 (continued)

Gas Phase Reaction	Reaction Type ¹	Gas Type, Press	Temp (K)	Rate ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$) $[R] = J K^{-1} \text{mol}^{-1} [T] = \text{Kelvin}$	Reference
$\text{HgCl} + \text{HCl} \rightarrow \text{HgCl}_2 + \text{H}$	Ab initio QCISD/1997	1 atm	298-2000 298	$3.2 \times 10^{-15} \exp^{-(10640/\text{RT})}$ 1.5×10^{-33}	Wilcox et al., 2003
$\text{HgCl} + \text{M} \rightarrow \text{Hg} + \text{Cl} + \text{M}$	Ab initio QCISD/1997	1 atm	298-2000 298	$9.0 \times 10^{-11} \exp^{-(89800/\text{RT})}$ 1.6×10^{-26}	
$\text{Hg} + \text{Cl} \rightarrow \text{HgCl}$	Ab initio	N/A, 1 atm	298	$1.38 \times 10^{-12} e^{1720/\text{RT}}$	Khalizov et al., 2003
	Abs	He	243-293	2.8×10^{-12} $(2.2 \pm 0.5) \times 10^{-32} e^{(680 \pm 400)/(T/1298)}$ cm^6 $\text{molecule}^{-2} \text{s}^{-1}$	Donohoue et al. 2005
	Abs, fitted equation	Ar, 0.93 atm	383-443	$(3.2 \pm 1.7) \times 10^{-11}$	Horne et al., 1968
	Abs	Air, N ₂ , 1 atm	298 ± 1	$(1.0 \pm 0.2) \times 10^{-11}$	Ariya, et al., 2002
	Abs	Ar, 0.95 atm	397	$1.5 \times 10^{-14} \text{ molec}^{-1} \text{ s}^{-1}$	Greig, et al., 1970
	Abs	?	> 873	$30 - 2.5 \times 10^{-11}$	Senior, et al., 2000
$\text{HgCl} + \text{HgCl} \rightarrow \text{Hg}_2\text{Cl}_2$	Abs	Ar, 0.95 atm	397	$(3 \pm 2) \times 10^{-13} \text{ molec}^{-1} \text{ s}^{-1}$	Greig et al., 1970
$\text{Hg} + \text{F}_2 \rightarrow \text{Prod}$	Abs	air, 1 atm	~298	$(1.8 \pm 0.4) \times 10^{-15}$	Sumner et al., 2005
$\text{Hg} + \text{F} \rightarrow \text{HgF}$	Ab initio	N/A	298	$9.2 \times 10^{-13} e^{1720/\text{RT}}$ 1.9×10^{-12}	Khalizov, et al., 2003
$\text{Me}_2\text{Hg} + \text{OH} \rightarrow \text{MeHgOH}$ + Me	Rel rate	Air, 0.92 atm	~298	$(1.9 \pm 0.2) \times 10^{-11}$ 2.72×10^{-13} $< 10^{-21}$	Niki et al., 1983 Lin and Pehkonen, 1999
$\text{Me}_2\text{Hg} + \text{O}_3 \rightarrow ?$					
$\text{Me}_2\text{Hg} + \text{Cl} \rightarrow \text{CH}_3\text{HgCl}$				$(2.75 \pm 0.30) \times 10^{-10}$	
$\text{Me}_2\text{Hg} + \text{NO}_3 \rightarrow \text{Hg}^0\text{HgO(s)}$				$(7.4 \pm 2.6) \times 10^{-14}$	
$\text{Me}_2\text{Hg} + \text{NO}_3 \rightarrow \text{O}(\text{1p})\text{HgO}$				$(2.5 \pm 0.20) \times 10^{-11}$	
$\text{Me}_2\text{Hg} + \text{F} \rightarrow ?$				$(4.7 \pm 0.5) \times 10^{-10}$	
$\text{Hg} + \text{OH} \rightarrow \text{HgOH}$	Rel rate	N ₂ , 1 atm	283-353 298	$3.55 \times 10^{-14} e^{-(2440 \pm 130)/\text{RT}}$ $(9.0 \pm 1.3) \times 10^{-14}$	Pal and Ariya, 2004
	Abs	He, 1 atm	298	$< 1.2 \times 10^{-13}$	Bauer et al., 2003
	RRKM/ B3LYP	N/A, 1 atm	180-400	$3.2 \times 10^{-13} \times (T/298)^{3.06}$	Goodsite et al., 2004
	Rel.	Air, 1 atm	298	$(8.7 \pm 2.8) \times 10^{-14}$	Sommar et al., 2001

$\text{Hg}^0(\text{g}) + \text{h}\nu \text{ } \frac{1}{2}\text{O}_2 \rightarrow \text{Hg}^0(\text{g}/\text{s})$	Abs., 3-step reaction	Air, 1 atm	293	1×10^{23}	Hall et al., 1995
			973	4×10^{23}	
$\text{Hg} + \text{O}_3 \rightarrow \text{HgO}(\text{s}) + \text{O}_2$	Abs., extrapolated	N_2 , 1 atm	283-323	$8.43 \times 10^{-17} e^{(11700 \pm 270)/RT}$	Pal and Ariya, 2004
			298	$(7.5 \pm 0.9) \times 10^{-19}$	
	Abs., S/V extrapolated	N_2/O_2 , 1 atm	293	$(3 \pm 2) \times 10^{-20}$	Hall, 1995
	Abs.	air, 1 atm	~298	$(6.4 \pm 2.3) \times 10^{-19}$	Sumner, et al., 2005
	Abs., re-plotted	1 atm	293	4.9×10^{-18} (?)	Schroeder et al., 1991,
	data		303	8.4×10^{-18} (?)	P'yankov, 1949
			293	4.2×10^{-19} (?)	Slemr, 1985, P'yankov,
					1949
	Abs.,	Air, 1 atm	293	$\sim 1.7 \times 10^{-18}$	Iverfeldt, and Lindqvist,
					1986
	QCIS(T)/MP2;	1 atm	~298	$1.2 \times 10^{-9} e^{-176.500/RT}$	Xu et al., 2008
	TST theory		298	1.4×10^{-40} (?)	
$\text{Hg} + \text{NO}_2 \rightarrow$	Abs.	N_2 , 1 atm	293	$(2.8 \pm 0.5) \times 10^{-35} \text{ molec}^{-2} \text{ s}^{-1}$, 2 nd	Hall et al., 1995
				order in $[\text{NO}_2]$	
	S/V Extrapolation	N_2 , 5-10 $\times 10^{-3}$	294 \pm 2	$< 4 \times 10^{-15}$	Sommar, et al., 1997
		atm			
$\text{Hg} + \text{NO}_3 \rightarrow \text{HgO} + \text{NO}_2$	Rel	air, 1 atm	~298	$< 7 \times 10^{-15}$, $< 1.3 \times 10^{-14}$, 3×10^{-14}	Sumner et al., 2005
	Abs	N_2	293	$< 8.5 \times 10^{-19}$	Tokos et al., 1998

See Lee et al., (2004) for recent discussion of theoretical and experimental mercury kinetics gas phase reactions.

¹ab initio, semi-empirical, rel., abs., extrapolated

²unless otherwise stated

Table 15.2 Liquid (water)-phase kinetics of mercury

Liquid	Type of study	Environment pH	Temp (K)	Rate ($M^{-1}s^{-1}$, unless otherwise stated)	Reference
$Hg^{0(aq)} + hv \rightarrow Hg^{0(aq)}$	Field study	lake water, daylight radiation	ambient	$2.4 - 9$ times $Hg^{0(aq)}$ production than dark. $1.6\%/h$	Amyot et al., 1994, 1997
$Hg^{0(aq)} + O_3 + H_2O \rightarrow Hg^{2+} + OH^- + O_2$	Field	Water, pH = 4.5-9.5	~298 (T-ind)	$(4.7 \pm 2.2) \times 10^7$	Munthe, 1992
$Hg^{0(aq)} + H_2O + hv \rightarrow Hg(OH)_2$	Field	pH = 7	ambient	$1.2 \times 10^{-4} s^{-1}$	Zhang, 2006
$Hg^{0(aq)} + HOCl + H^+ \rightarrow Hg^{2+} + Cl^- + H_2O$	Lab	Water	Ambient	$(2.09 \pm 0.06) \times 10^6$	Lin and Pehkonen, 1998
$Hg^{0(aq)} + OCl^- + H_2O \rightarrow Hg^{2+} + Cl^- + 2OH^-$	Lab	Water	Ambient	$(1.99 \pm 0.05) \times 10^6$	
$HgCl_2 + e^- \rightarrow Cl^- + HgCl$	Avg'd Lit Cit.	pH = 5	Ambient	4.0×10^{10}	
$HgBr_2 + e^- \rightarrow Br^- + HgBr$	Avg'd Lit Cit.		Ambient	3.7×10^{10}	
$HgI_2 + e^- \rightarrow I^- + HgI$	Avg'd Lit Cit.		Ambient	3.0×10^{10}	
$Hg(CN)_2 + e^- \rightarrow CN^- + HgCN$	Avg'd Lit Cit.		Ambient	1.4×10^{10}	
$Hg(SCN)_2 + e^- \rightarrow SCN^- + HgSCN$	Avg'd Lit Cit.		Ambient	4.5×10^{10}	
$Hg(EDTA)^{2-} + e^- \rightarrow Products$	Avg'd Lit Cit.		Ambient	$2.1, 5.1 \times 10^9$	Buxton et al., 1998
$Hg(CN)_2 + e^- \rightarrow CN^- + HgCN$	Avg'd Lit Cit.		Ambient	1.4×10^{10}	
$Hg^{0(aq)} + e^- \rightarrow Hg(l)$	Avg'd Lit Cit.		Ambient	7.1×10^9	Zhang, 2006
$H + Hg_2^{2+} \rightarrow H^+ + Hg^+$	Lit. Cit.	pH = 1.0	Ambient	4.7×10^9	Buxton et al., 1988
$H + Hg_2^+ \rightarrow H^+ + Hg^+$	Lit. Cit.	pH = 1.5	Ambient	2.0×10^9	
$H + Hg(OH)_2 \rightarrow H_2O + HgOH$	Lit. Cit.	pH = 7	Ambient	2.4×10^9	
$H + HgCl_2 \rightarrow HCl + HgCl$	Lit. Cit.	pH = 1	Ambient	$1.0, 1.5 \times 10^9$	
$H + Hg_2^{2+} \rightarrow Hg_2^{+}(aq)$	Lit. Cit.		Ambient	1.5×10^9	
$OH + HgCl \rightarrow OH^- + HgCl^+$	Lit. Cit.	pH = 5	Ambient	$\sim 1 \times 10^{10}$	Buxton et al., 1988
$OH + HgBr_2 \rightarrow Br^- + HgBrOH$	Lit. Cit.		Ambient	$> 9 \times 10^8$	
$OH + HgCN \rightarrow products$	Lit. Cit.		Ambient	3.1×10^9	

$\text{Hg}^{\text{II}}(\text{aq}) + \text{OH}^- \rightarrow \text{Hg}^+ + \text{OH}^-$	Rel. Lab expt	Water	298	$(2.4 \pm 0.3) \times 10^9$	Gardfeldt et al., 2001
	Field	Water, pH = 3.9	298 ± 2	2.0×10^9	Lin and Pehkonen, 1997
	Lab	Ambient		5.5×10^9	Hines and Brezonik, 2004
$\text{Hg}^{\text{I}}(\text{aq}) + \text{OH}^- \rightarrow \text{Hg}^{2+} + \text{OH}^-$	Lab			1×10^{10}	Zhang, 2006
$\text{Hg}^{\text{I}}(\text{aq}) + \text{OH}^- \rightarrow \text{HgOH}$	Lab			2.4×10^9	
$\text{HgOH} + \text{OH}^- \rightarrow \text{Hg}(\text{OH})_2$	Lab			1×10^{10}	
$\text{HgOH} + \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{Hg}(\text{OH})_2 + \text{H}^+ + \text{O}_2^-$	Lab			10^9	
$\text{HO}_2 + \text{Hg}^{2+} \rightarrow \text{Hg}^+ + \text{O}_2 + \text{H}^+$	Lab	Ambient		1.7×10^4	Pehkonen and Lin, 1998
$\text{Hg}(\text{HSO}_3^-)_{\text{aq}} + \text{h}\nu \rightarrow \text{Hg}^{\text{I}}(\text{aq}) + \text{S(VI)}$				1.1×10^4 (chloride present)	
$\text{Hg}(\text{HSO}_3^-)_2 + \text{h}\nu \rightarrow \text{Hg}^{\text{I}}(\text{aq}) + \text{S(VI)}$				$4 \times 10^{-6} \text{ s}^{-1}$	Lin and Pehkonen, 1997
$\text{HgSO}_3(\text{aq}) + \text{h}\nu \rightarrow \text{Hg}^+ + \text{SO}_3^- \rightarrow \text{Hg}^{\text{I}}(\text{aq})$	Lab expt			$< 10^{-4} \text{ s}^{-1}$	
$\text{Hg}(\text{OH})_{2,\text{aq}} \rightarrow \text{Hg}^{\text{I}}(\text{aq}) + \text{prod.}$	Expt			0.6 s^{-1}	Lin and Pehkonen, 1999
$\text{Hg}^{\text{I}}(\text{aq}) + \text{Cl}^- \rightarrow \text{Hg}^{2+} + \text{Cl}^-$	Lab study	Sea water	298	$3 \times 10^{-7} \text{ s}^{-1}$	Yamamoto, 1996
$\text{Hg}^{\text{I}}(\text{aq}) + \text{Cl}^- + \text{h}\nu(\text{UV}) + \text{benzo-quinone} \rightarrow \text{Hg}^{\text{II}}$	Lab study	Pure water spiked	298	$0.28 - 1.1 \times 10^{-4} \text{ s}^{-1}$	Lalonde et al., 2001
$\text{Hg}^{\text{I}}(\text{aq}) + \text{bacteria exudates} + \text{Cl}^- \rightarrow \text{Hg}^{\text{II}}$	Lab study	Spiked water	298	$1.7 \times 10^{-4} \text{ s}^{-1}$	
$\text{HgMe} + \text{OH}^- \rightarrow \text{products}$	Lab expt	pH = 6.2 - 8.2	293	Dark reactions; 40% decrease in $\text{Hg}^{\text{I}}(\text{aq})$	Poulain et al., 2007
$\text{Hg}^{\text{II}} + \text{h}\nu \rightarrow \text{Hg}^{\text{I}}(\text{aq})$	Field expt	Lake water	Ambient	1.2×10^9	Zepp et al., 1987
		River water		UV-A: $7.76 \times 10^{-5} \text{ s}^{-1}$	O'Driscoll et al., 2006
				UV-B: $8.91 \times 10^{-5} \text{ s}^{-1}$	
				UV-A: $1.78 \times 10^{-4} \text{ s}^{-1}$	
				UV-B: $1.81 \times 10^{-4} \text{ s}^{-1}$	

(continued)

Table 15.2 (continued)

Liquid	Type of study	Environment pH	Temp (K)	Rate ($M^{-1}s^{-1}$, unless otherwise stated)	Reference
$Hg^{0}(aq) \rightarrow Hg^{(II)}$	Lab expt; oxid ⁿ isolated from red.	Coastal water, dark	Ambient	$2.6 - 5.3 \times 10^{-4} s^{-1}$	Whalin and Mason, 2006
$Hg^{0}(aq) + \text{fulvic acid} \rightarrow Hg^{(II)}$		Fresh water, dark		$8 - 15 \times 10^{-4} s^{-1}$	
$Hg^{0}(aq) + \text{semiquinones} + Cl^{-} \rightarrow Hg^{(II)}$				$10 - 20 \times 10^{-4} s^{-1}$	
$Hg^{0}(aq) + \text{saline water} \rightarrow Hg^{(II)}$		Artificial water		$0.28 \times 10^{-4} s^{-1}$	
$Hg^{0}(aq) + hv \rightarrow Hg^{(II)}$		Artificial water, 0.5 M HCl		$0.17 \times 10^{-4} s^{-1}$	
$Hg^{0}(aq) + UV + DOC \rightarrow Hg^{(II)}$		Saline water, dark		$1.4 - 1.6 \times 10^{-4} s^{-1}$	
$Hg^{0}(aq) + KCl(aq) \rightarrow Hg^{(II)}$		Saline water, UV		$0.7 \times 10^{-4} s^{-1}$	
$Hg^{0}(aq) + hv \rightarrow Hg^{(II)}$		Lake water			
$Hg^{0}(aq) + hv \rightarrow Hg^{(II)}$		Lake water			
$Hg^{0}(aq) + hv \rightarrow Hg^{(II)}$		Freshwater	Ambient	$1.6 \times 10^{-4} s^{-1}$	Whalin and Mason, 2006
$Hg^{0}(aq) + hv \rightarrow Hg^{(II)}$		Freshwater, Vis light			
$Hg^{0}(aq) + hv \rightarrow Hg^{(II)}$		Freshwater, UV light			
$Hg^{0}(aq) + hv \rightarrow Hg^{(II)}$		Sea water + UV		$< 0.1 \times 10^{-4} s^{-1}$	Whalin and Mason, 2006;
$Hg^{(II)} + hv \rightarrow Hg^{0}(aq)$		Sea water + UV		$0.25 \times 10^{-4} s^{-1}$	Lalonde, et al., 2004
$Hg^{(II)} + Fe(III) \rightarrow Hg^{0}(g)$		Sea water + UV		$1.6 - 1.9 \times 10^{-4} s^{-1}$	
$Hg^{(II)} + Fe(III) + hv \rightarrow Hg^{0}(g)$		Freshwater, dark (prev. UV expos.)			
		Freshwater, UV exposed		$0.3 - 3.9 \times 10^{-4} s^{-1}$	Poulain et al., 2007
				$1.2 - 4.4 \times 10^{-4} s^{-1}$	
				$0.6 - 0.8 \times 10^{-4} s^{-1}$	Zhang and Lindberg, 2001;
					Whalin and Mason, 2006
					Zhang and Lindberg, 2001
					470% increase in Hg^{0} production in 4h; $0.3 - 0.6 \times 10^{-4} s^{-1}$

$\text{Hg}^{(II)} + \text{MerA bacteria} \rightarrow \text{Hg}^{(0)}(\text{aq})$	pH = 7.0	MerA, intact cells	Ambient	4 - 18 nmol Hg^{2+} min^{-1} mg protein^{-1}	Philippidis et al., 1991
$\text{Hg}^{(0)}(\text{aq}) + \text{hv} \rightarrow \text{Hg}^{(II)}$		Natural water, UV exposure	River water	Hg^0 loss: $0.6 \times 10^{-4} \text{ s}^{-1}$ $\text{Hg}^{(II)}$ production: $0.9 \times 10^{-4} \text{ s}^{-1}$	
$\text{Hg}^{(0)}(\text{aq}) + \text{hv} \rightarrow \text{Hg}^{(II)}$			Sea Water	Hg^0 loss: $1.2 \times 10^{-4} \text{ s}^{-1}$ $\text{Hg}^{(II)}$ production: $1.2 \times 10^{-4} \text{ s}^{-1}$	
$\text{Hg}^{(0)}(\text{aq}) + \text{hv} \rightarrow \text{Hg}^{(II)} (\text{HgO}?)$		Lake water + Hg lamp	Ambient Temp	$1.1 - 2.1 \times 10^{-4} \text{ s}^{-1}$ $1.4 \times 10^{-4} \text{ s}^{-1}$	Hines and Brezonik, 2004; Whalin and Mason, 2006
$\text{Hg}^{(0)}(\text{aq}) + \text{NO}_3^- + \text{hv} \rightarrow \text{Hg}^{(II)}$		Lake water		$15.3 \times 10^{-4} \text{ s}^{-1}$	
$\text{Hg}^{(0)}(\text{aq}) + \text{Cl}^- + \text{hv} \rightarrow \text{Hg}^{(II)}$		Lake water		$0.006 \times 10^{-4} \text{ s}^{-1}$	
$\text{Hg}^{(0)}(\text{aq}) \rightarrow \text{Hg}^{(II)}$		HPLC water, dark		$0.06 \times 10^{-4} \text{ s}^{-1}$	
$\text{Hg}^{(0)}(\text{aq}) + \text{NO}_3^- + \text{hv} \rightarrow \text{Hg}^{(II)}$		Lake water, dark			
$\text{Hg}^{(0)}(\text{aq}) + \text{NO}_3^- + \text{hv} \rightarrow \text{Hg}^{(II)}$		Q-water	Ambient temp	$8.7 \times 10^{-4} \text{ s}^{-1}$ $46 \times 10^{-4} \text{ s}^{-1}$	Hines and Brezonik, 2004; Mason et al., 2001
$\text{Hg}^{(0)}(\text{aq}) + \text{Cl}^- + \text{NO}_3^- + \text{hv} \rightarrow \text{Hg}^{(II)}$		Q-water			
$\text{Hg}^{(0)}(\text{aq}) + \text{Br}_2 \rightarrow \text{P}$	Lab expt	pH = 2	296 - 298	0.20 ± 0.03	Wang and Pehkonen, 2004
$\text{Hg}^{(0)}(\text{aq}) + \text{HOBr} \rightarrow \text{P}$		pH = 6.8		0.28 ± 0.02	
$\text{Hg}^{(0)}(\text{aq}) + \text{OBr}^- \rightarrow \text{P}$		pH = 11.7		0.27 ± 0.04	
$\text{Hg}^{(0)}(\text{aq}) + \text{H}_2\text{O}_2 \rightarrow \text{HgO}(\text{s}) + \text{Hg}^{2+} + \text{H}_2\text{O}$	Lab			6.0	Munthe and Mcelroy, 1992
$\text{HgSO}_3(\text{aq}) \rightarrow \text{Hg}^+ + \text{SO}_3^-(\text{aq})$	Lab			0.6 s^{-1}	Munthe et al., 1991

Table 15.3 Inter-phase (heterogeneous/surface) kinetics and emission rates of mercury

Surfaces	Type of expt	Interface	Temp (K)	Rates/rate constants/results;		Reference
				No general units		
$\text{Hg}^0(\text{g}) \rightarrow \text{Hg}^0(\text{ads})$	Abs	N_2 , 1 atm, N_2/Teflon wall ($s/v = 0.58 \text{ cm}^{-1}$)	293 323 348	$4.5 \times 10^{-6} \text{ s}^{-1}$ $1.7 \times 10^{-5} \text{ s}^{-1}$ $3.0 \times 10^{-5} \text{ s}^{-1}$	Hall, 1995	
$\text{Hg}^0(\text{g}) \rightarrow \text{Hg}^0(\text{ads})$	Abs	air, 1 atm, air/carbon	293 423-523 573	$90-120 \times 10^{-4} \text{ s}^{-1}$ $1.3-5.0 \times 10^{-4} \text{ s}^{-1}$ $\sim 0 \text{ s}^{-1}$	Hall et al., 1995	
	Abs	air, 1 atm, air/fly ash	293	$81 \times 10^{-4} \text{ s}^{-1}$		
$\text{Hg}^0/\text{HgF}_2/\text{HgNO}_3(\text{aq}) + \text{hv} \rightarrow \text{Hg}(\text{l})$	Lab, Hg lamp	Water/ TiO_2 surface	423-523 573	$11.2-27.2 \times 10^{-4} \text{ s}^{-1}$ $6.8-7.7 \times 10^{-4} \text{ s}^{-1}$	Habibi et al., 2003	
$\text{Hg}(\text{l}) + \Delta \rightarrow \text{Hg}^0(\text{g})$		TiO_2 surface/ N_2 flow	423	Removes Hg^0 in ~ 1 hour		
$\text{Hg}^0(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{O}_2(\text{g}) + \text{hv} \rightarrow \text{HgO}(\text{s})$	Lab	Air/ TiO_2 surface	297-408	$k = \text{Ae}^{-(E_s-A)/RT} \frac{d[\text{Hg}]}{dt} = k[\text{Hg}]^{1.4 \pm 0.1} [\text{J}_{\text{UV}}]^{(0.35 \pm 0.05)}$	Lee et al., 2004	
$\text{HgCl}_2 + \text{dodecyl sulfate}(\text{DS}) + \text{hv} \rightarrow \text{Hg}^0(\text{s})$	Lab	Water/ TiO_2 surface	Ambient	97% reduction in 6 min	Zhang, 2006,	
$\text{HgCl}_2 + \text{hv} + \text{cetyltrimethylammonium}(\text{CTA}^+) \rightarrow \text{Hg}^0(\text{s})$	Lab	Water/ TiO_2 surface	Ambient	99% reduction in 25 min	Horvath et al., 2005	
$\text{HgCl}_2 + \text{hv} + \text{arginine} \rightarrow \text{Hg}^0(\text{s})$	Lab	Water/ TiO_2 surface	Ambient?	arginine binds Hg^0 to TiO_2 , facilitates charge transfer	Skubal and Meshkov, 2002	
$\text{HgCl}_2(\text{aq}) + \text{UV} \rightarrow \text{Hg}^0(\text{aq}) + 2\text{Cl}^-$	Lab	Water/ TiO_2 semiconductor	293 \pm 5	$E = 0.41\text{V}$, poss. catalytic TiO_2 action, rate oxid = $0.051 \sqrt{[\text{Hg}]}$	Prairie et al., 1993	
$\text{Hg}^0(\text{g}) + \text{H}_2\text{O} + \text{UV} \rightarrow \text{HgO}(\text{s})$	Lab	Humid Air + TiO_2 surface	298	Surface mechanism developed, remov. rate incr. with $[\text{H}_2\text{O}]$, Hg removal < 80%, > 30%.	Rodríguez et al., 2004	
$\text{Hg}^0(\text{g}) + \text{H}_2\text{O} + \text{UV} \rightarrow \text{HgO}(\text{s})$	Lab	Humid Air+ $\text{SiO}_2/\text{TiO}_2$ surface	298	L-H mech., remov. rate decreases with $[\text{H}_2\text{O}]$, up to 95% removal when dry.	Li and Wu, 2007	
$\text{Hg}^0(\text{g}) \rightarrow \text{Hg}^0(\text{ads})$	Model/field data	Air/Forest floor	Ambient	0.12 cm s^{-1} 0.006 cm s^{-1}	Lindberg et al., 1992	

$\text{Hg}^0(\text{g}) \rightarrow \text{Hg}^0(\text{ads})$	Field study	Air/ground dry deposition	Ambient	0.5 cm s^{-1} (particulate; Hg_p) 0.1 cm s^{-1} ($\text{Hg}^0(\text{g})$)	Schroeder et al., 1998
$\text{Hg}(\text{II})/\text{humic acid} + \text{hv} \rightarrow \text{Hg}(\text{g})$	Lab study, xenon radiation	Air/(snow/ barren ground)	Ambient	$12.5 \pm 2.5 \text{ pmol m}^{-2} \text{ h}^{-1}$	Xiao et al., 1995
$\text{Hg}(\text{OH})_2 + \text{hv} \rightarrow \text{Hg}(\text{g})$	Field study	Water/air	Ambient	$2 \times 10^{-2} \text{ s}^{-1}$ $1.2 \times 10^{-4} \text{ s}^{-1}$	Lahoutifard et al., 2006
$\text{Hg}^0(\text{g}) + \text{H}_2\text{O}_2(\text{ads}) + \text{hv} \rightarrow \text{Hg}^0(\text{II})$	Field study	Air/snow pack	Ambient	5-fold increase in $\text{Hg}^0(\text{g})$ deposition with H_2O_2 -spiked snow	Lindberg et al., 2002 Ferrari et al., 2004
$\text{Hg}^0(\text{I/II})^? \rightarrow \text{Hg}^0(\text{I/II})_{\text{ads}}$	Field study	Air/snow; dry dep.	Ambient	1 cm s^{-1}	Ariya et al., 2004
$\text{Hg}^{2+}(\text{ads}) \rightarrow \text{Hg}^{2+}(\text{snowpack})$	Field study	Snow/Snow vertical diffusion	273	$5.8 - 7.0 \text{ pg m}^{-2} \text{ h}^{-1}$	Lalonde et al., 2003 Fain et al., 2007
$\text{Hg}^0(\text{ads, II}) + \text{hv} \rightarrow \text{Hg}^0(\text{g})$	Field study	Snow/air	273?	> 20% reduction loss in 3h	Dommergue et al., 2007
$\text{Hg}^0(\text{g}) + \text{hv} \rightarrow \text{Hg}^0(\text{ads,II})$	Lab study, Xe-lamp	Air/snow	258 - 313	$6.9 \times 10^{-5} \text{ s}^{-1}$, $5.0 \times 10^{-5} \text{ s}^{-1}$	Zhang, 2006
$\text{HgS}^{2-} + \text{hv} \rightarrow \text{Hg}^0(\text{aq})$	Field	Water/air	ambient	Not significant	Schuter et al., 2000
$\text{Hg}^0/\text{Hg}(\text{CH}_3)_2 \rightarrow \text{Hg}^0(\text{g})/\text{Hg}(\text{CH}_3)_2(\text{g})$	Field study	Soil/air	ambient	< $1 \text{ nmol m}^{-2} \text{ h}^{-1}$	Grigal, 2002
$\text{Hg}^0(\text{ads, II}) \rightarrow \text{Hg}^0(\text{g})$	Field study	Temperate, boreal Contaminated	ambient	$55 \text{ pmol m}^{-2} \text{ h}^{-1}$	
$\text{Hg}^0(\text{g}) \rightarrow \text{Hg}^0(\text{ads, II})$	Field study	Open, temperate Air/soil	ambient	$\sim 6500 \text{ pmol m}^{-2} \text{ h}^{-1}$	
	Field study	Temperate Forest Air/soil	ambient	$12 \text{ pmol m}^{-2} \text{ h}^{-1}$	
		soil	ambient	$47 \text{ pmol m}^{-2} \text{ h}^{-1}$	
		Throughfall/ litterfall	ambient	$190 \text{ nmol m}^{-2} \text{ a}^{-1}$	
$\text{Hg}^0(\text{ads, II}) \rightarrow \text{Hg}^0(\text{ads, II})$	Lit. Cit. Field study	Soil sequestration	ambient	$25 \text{ nmol m}^{-2} \text{ a}^{-1}$	Zhang, 2006
$\text{Hg}^0(\text{aq}) \rightarrow \text{Hg}^0(\text{g})$		Water/air	ambient	$25 \text{ pmol m}^{-2} \text{ h}^{-1}$	Lindberg et al., 1992
$\text{Hg}^{\text{III}}[\text{Cl}/\text{NO}_3] + \text{surface sediment} \rightarrow \text{Hg}^0(\text{aq})$	Model/Field study	Forest soil/d/air	ambient	$250 \text{ pmol m}^{-2} \text{ h}^{-1}$	Peretyazhko et al., 2007
	Field	Lake water/ sediment	~ 298	$\sim 10^{-5} - 10^{-6} \text{ min}^{-1}$	

(continued)

Table 15.3 (continued)

Surfaces	Type of expt	Interface	Temp (K)	Rates/rate constants/results; No general units	Reference
$\text{Hg}^0(\text{aq}) \rightarrow \text{Hg}^0(\text{g})$	Model fit, empirical data	Water/air	298	5.7 pmol $\text{m}^{-2} \text{h}^{-1}$ loss	Hines and Brezonik, 2004
$\text{Hg}^0(\text{aq}) + h\nu \rightarrow \text{Hg}(\text{g})$	Field study Lab study	Lake water/air River water/air Sea water/air	298? ambient	16 pmol $\text{m}^{-2} \text{h}^{-1}$ loss (0.6% h^{-1}) $0.2 \times 10^{-4} \text{ s}^{-1}$ $0.3 \times 10^{-4} \text{ s}^{-1}$	Amyot et al., 1994 Amyot et al., 1997
$\text{Hg}^0(\text{ads}) + \text{Br} \rightarrow \text{HgBr}$	Field study	In snow (20-60 cm deep)	~263	$2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$	Fain et al., 2006[97]
$\text{Hg}(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow (\text{HgCl})_n(\text{s})$	Lab Lab	Air/surface Air/water	525	50 second reaction Some enhancement	Medhekar et al., 1979 Skare and Johansson, 1992
$\text{Hg}^0(\text{g}) + \text{Cl}_2(\text{aq}) \rightarrow \text{Hg}^{2+} + 2\text{Cl}^-$	Lab Abs Abs	Air/water +sulfite Water + NaOCl Water + NaOCl	298 298 328	$6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $1.7 \times 10^{15} \text{ M}^{-1} \text{ s}^{-1}$ (too fast?) $1.4 \times 10^{17} \text{ M}^{-1} \text{ s}^{-1}$	Roy and Rochelle, 2004 Zhao and Rochelle, 1999
$\text{Hg}^0(\text{g,ads}) + \text{O}_2(\text{g,ads}) \rightarrow \text{Product}$	Langmuir-Hinshelwood mech.	Air/Fly ash surface	373-573	$1.5 - 6.5 \times 10^{-12} (\text{cm}^{-3} \text{ molec}^{-1})^{0.5} \text{ s}^{-1}$	Hall et al., 1991
$\text{Hg}^0(\text{g}) + \text{SO}_2 + \text{O}_2 \rightarrow \text{HgSO}_4(\text{s})$	Lab	Air/Pt	348-673	3.5 mg Hg/hr (348-600K)	Schofield, 2004
$\text{Hg}^0(\text{g}) \rightarrow \text{Product}$	Field test	Air/Pd Air/SCR catalyst Air/TMT-15 catalyst*	450	93% oxidation 62% oxidation Inconclusive; intended to prevent re-emission of Hg	EPRI, 2005 Blythe, 2006 Norton et al., 2003
$\text{Hg}^0(\text{g}) + \text{SO}_2 + \text{NO}_2 + \text{HCl} \rightarrow \text{Hg}(\text{s})^{2+}$	Lab	Air/Fly Ash	453	~30 % Hg(g) oxidation	
$\text{Hg}^0(\text{g}) \rightarrow \text{Hg}(\text{ads})$	Lab	Air/Fly Ash + carbon	293, 313	More mercury adsorption at 20°C than 40°C	Hwang et al., 2002
$\text{Hg}^0(\text{g}) + h\nu \rightarrow \text{prod.}$	Lab, Xenon lamp	Air/quartz surface	293	$1.2 \times 10^{-5} \text{ s}^{-1}$ $4.0 \times 10^{-5} \text{ s}^{-1}$ $1.6 \times 10^{-3} \text{ s}^{-1}$ $1.7 \times 10^{-3} \text{ s}^{-1}$	Sheu and Mason, 2004
$\text{Hg}^0(\text{g}) + h\nu + \text{H}_2\text{O}(\text{l}) \rightarrow \text{prod}$					
$\text{Hg}^0(\text{g}) + h\nu + \text{NaCl} \rightarrow \text{prod}$					
$\text{Hg}^0(\text{g}) + h\nu + \text{NaCl} + \text{H}_2\text{O}(\text{l}) \rightarrow \text{prod}$					
$\text{HgCl}_2(\text{g}) + \text{H}_2 \rightarrow \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{HCl}$	Lab, laser	N ₂ /Stainless steel surface	473	Unkonwn mech	Wang et al., 1983

$\text{Hg}^0(\text{g}) + (\text{HCl}) \rightarrow \text{Hg}(\text{ads})$	Lab	$\text{N}_2/\text{Stainless steel surface}$ or PTFE teflon	423	HCl enhances Hg^0 removal SS: (0 \rightarrow 44 ng) SS: (66 \rightarrow 128 ng)	Turchi, 2000
$\text{Hg}(\text{g}) \rightarrow \text{Hg}(\text{ads})$	Lab work	N_2 and trace gas/Gold	411	25 nm thick Au sheet absorbs for 33 min vs. 5 min for 2.5 nm sheet. Hg penetrates Au.	Turchi, 2000
$\text{HgCl}_2(\text{g}) \rightarrow \text{HgCl}_2(\text{ads})$	Simulated flue gas	N_2/gold Trace gas	422	Acid gases (HCl or NO_2) + SO_2 reduce ads. cap. HgCl_2 adsorbs; no rxn. Similar to carbon surf. ads.	Li et al., 2007
$\text{Hg}^{2+}(\text{aq}) + \text{N719-TiO}_2 \rightarrow \text{Hg}_{\text{ads}}(\text{II})$	Lab expt	Water/N719-TiO2	-298	Hg^{2+} binding constant: $3 \times 10^5 \text{ M}^{-1}$ 65% scavenging eff.	Sen and De, 1987
$\text{Hg}(\text{NO}_3)_2(\text{aq}) \rightarrow \text{Hg}_{\text{ads}}(\text{II})$	Lab	Water/Fly ash	303	Freundlich parameters: $k = 1.230$, $1/n = 0.361$ @ pH = 4.2, > 90% adsorption	Mohan et al., 2000
$\text{Hg}^0(\text{II})_{\text{aq}} \rightarrow \text{Hg}(\text{II})_{\text{ads}}$	Lab	Water/Activated carbon	300 318 338	Freundlich parameters: $k = 0.1427$, $1/n = 0.71$ $k = 0.0663$, $1/n = 0.75$ $k = 0.01073$, $1/n = 1.38$	Zhao et al., 2006
$\text{Hg}^0(\text{g}) + \text{Cl}_2 \rightarrow \text{HgCl}_2$	Lab	Air/Au surface	448-498	40-60 % oxidation $k \sim 10^{-8} \text{ cm}^3/$ (molec/s) (473 K) ? Langmuir- Hinshelwood mechanism proposed	Barrosse-Antle, 2007
$\text{Hg}(\text{NO}_3)_2(\text{aq}) + 2\text{e}^- \rightarrow \text{HgAu}(\text{s})$	Lab	Au-coated microparticle surface	298	0.35 V causes AuHg amalgam formation	Wu et al., 2006
$\text{Hg}^0(\text{g}) + (\text{H}_2\text{S}) \rightarrow \text{HgS}(\text{s}) + \text{S}(\text{s})$	Simul. flue gas	Flue gas/ $\text{Fe}_2\text{O}_3(\text{N})$	353	H_2S initiates Hg removal rxn up to 65% Hg loss in stream. -no effect from H_2 or CO . H_2O reduces Hg adsorbance.	Wu et al., 2008
$\text{Hg}^0(\text{g}) + \text{HCl} \rightarrow \text{HgO}(\text{s})$	Lab, simul. flue comb.	Fe_2O_3 , $\text{Fe}_2\text{O}_3\text{-Ca}(\text{OH})_2$, FeS_2 , Fe_2O_3 (1% wt)/ TiO_2 surfaces	353	Fe_2O_3 : 50% removal $\text{Fe}_2\text{O}_3/\text{TiO}_2$: 80% $\text{Fe}_2\text{O}_3\text{-Ca}(\text{OH})_2$: 70% FeS_2 : 60%	Li et al., in press
$\text{Hg}^0(\text{g}) + \text{UV} \rightarrow \text{HgO}(\text{s})$	Lab, simul. flue comb.	$\text{SiO}_2\text{-TiO}_2$ surface	408	HCl(g) suppressed Fe_2O_3 activity only 99% removal	

(continued)

Table 15.3 (continued)

Surfaces	Type of expt	Interface	Temp (K)	Rates/rate constants/results; No general units	Reference
$\text{Hg}^0(\text{g}) + \Delta \rightarrow \text{HgO}(\text{s})$	Lab, simul. flue comb.	Extensive list of metal oxide surface mixtures, Mars-Maessen mech.	410	$\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$, $\text{MnO}_2/\text{Al}_2\text{O}_3$, and MoS_2 show high Hg adsorption capacities.	Granite et al., 2000
$\text{Hg}^0(\text{g}) + \Delta \rightarrow \text{HgO}(\text{s})$	Lab, simul. flue comb.	Various metal surface catalysts. Het. rate constants measured.	411	Rank: $\text{Ir} > \text{Ir}/\text{HCl} > \text{Darco} > \text{Thief}/\text{HCl}$ (in terms of oxidation efficiency)	Presto et al., 2006
$\text{HgBr}_2(\text{s}) + \text{Ag}_2\text{WO}_4(\text{s})$	Lab, glass tube diffusion	Solid-state reaction	413 – 463	$K = 1.10 \times 10^{-4} \text{ cm h}^{-1}$ @ 120°C (thick-ness) ² = Kt	Jain and Beg, 1995
$\text{HgCl}_2(\text{s}) + \text{Ag}_2\text{WO}_4(\text{s})$			438 – 481	$K = 2.25 \times 10^{-4} \text{ cm h}^{-1}$ @ 145°C	
$\text{HgWO}_4(\text{s}) + \text{AgCl}(\text{s})$					
$\text{Hg}^0(\text{g}) \rightarrow \text{Hg}^0(\text{ads})$	Lab, over activated C	Ptolemais lignite + S	323	300 – 900 ng Hg/mgAC addn of S incrss. ads	Skodras et al., 2007
$\text{HgCl}_2(\text{g}) \rightarrow \text{Hg}^0(\text{ads})$	Lab	Air/Cysteine over silica	298 – 398	Capture eff CE: 12mg/g < CE < 33 mgHg/g	Abu-Daabes and Pinto 2005

*TMT-15 is a 15 % aqueous solution of Trimercapto-s-triazine, a trisodium salt ($\text{C}_3\text{N}_3\text{S}_3\text{Na}_3$)

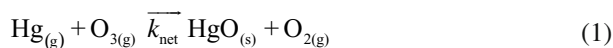
Additional information:

- For comparative discussion of $\text{Hg}^0(\text{g})$ oxidation surface mechanisms (Langmuir-Hinshelwood, Eley-Rideal, Mars-Maessen), see Presto and Granite, 2006.
- For large-scale fluxes to/from ocean, land, and anthropogenic sources, see Lindberg et al, 2007.
- For detailed photochemical information of mercury reactions in solid, liquid, and gas phases, see Zhang, 2000.
- Concentrations of $[\text{Hg}^0(\text{aq})]$ in various northern lakes: Peretyzhko et al, 2006.
- Large compilation of Henry's Law values for atmospherically relevant species: Sander, 1999.
- Compilation of aqueous rates of $\text{Hg}^0(\text{aq})$ oxidation by several combinations of semiquinones, Cl^- , fulvic acid, saline water, UV radiation, DOC, fresh water, lake water, sea water, NO_2^- , NO_3^- ,
- Other possible catalysis surfaces: Au, Ag, Cu, Ir, Pd, C (fly ash, thief carbon) (Presto and Granite, 2006), Fe_2O_3 , iron oxide— $\text{Ca}(\text{OH})_2$, FeS_2 (Wu et al., 2008), TiO_2 - SiO_2 (Li et al., in press). Expansive catalysts can often be deposited over a bed of Al_2O_3 , TiO_2 , or other comparatively cheaper metal oxides.
- $\text{Hg}^{2+}(\text{aq})$ complexes with: CH_3^- , Cl^- , H_2O , HCO_3^- , CO_3^{2-} , SO_4^{2-} , OH^- ; fulvic acid, humic acid, oxalate, citrate,...
- Detailed discussion of Hg emissions and deposition to/from soil, see Schluter [95], Giral [104], and Gabriel [195] (includes some details of aquatic Hg distribution).
- Estimated cost of removing mercury from coal fire plant (using SCR catalyst): 29,000 USD/lb (Turehi, 2000). Aerosol pH = 2-5; Surface water (lake, river, ocean) pH = 6-8

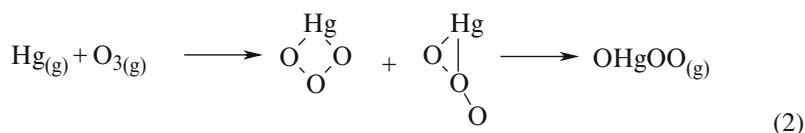
The disadvantage of the relative rate is that the calculated reaction rate constant is only as good as the original value of the reaction rate constant for the reference molecule used, and this why most detailed relative rate studies include several reference molecules to overcome this challenge. Another disadvantage is the complexity of the reactants and enhanced potential for side reactions. This challenge can be overcome with careful experimental setups and additional targeted experiments to minimize and characterize the extent of undesired reactions. An advantage of a detailed relative study is that one can readily perform the experiments under simulated tropospheric conditions, and also the reaction chambers can be coupled several state-of-the-art instruments for simultaneous analysis which allows detailed product analysis as well as kinetic determinations.

15.2.2 $Hg^0 + O_3$ and $Hg^0 + HO$

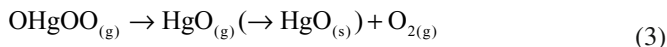
The advantage of the absolute method is clearly the fact that there is no need for incorporation of errors due to the reference molecules. However, in many absolute studies, one can follow merely one or two reactants, and considering the complexity of mercury reactions, and the extent of secondary reactions, the calculated values may be affected. Another challenge is some absolute studies are performed at lower pressure than tropospheric boundary layer pressure (~ 740 Torr) and concentrations orders of magnitude higher than tropospheric levels. Hence the data obtained under such conditions must be properly corrected for the ambient tropospheric situation, particularly in the case of complex mercury adduct reaction, and given the lack of detailed product analysis, and different carrier gases, this is not trivial. However, as it shown in Pal and Ariya (2004), both relative and absolute studies of the same reaction can yield the same values of rate constants within the experimental uncertainties and thus increase the confidence in the overall result. Ozone is an important atmospheric constituent and due to its atmospheric abundance, $O_3 + Hg^0$ has been a target of several laboratory studies. We have previously studied ozone-addition with elemental mercury under dry conditions (Pal and Ariya, 2004). The net reaction is written:



Calvert and Lindberg (2005) suggest reaction (1) could be proceed by an addition of ozone, followed by a re-arrangement into the linear species OHgOO:



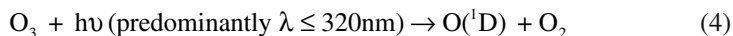
The reaction may be followed by dissociation into O_2 and $HgO_{(g)}$, the latter precipitating immediately to $HgO_{(s)}$.



The dissociation and precipitation are essentially irreversible steps. As shown in Table 15.1, the apparent rate constant, k_{net} , reaction (1), was previously found by our group (Pal and Ariya, 2004) to be $(7.5 \pm 0.9) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in good agreement with Sumner et al. (2005): $(6.4 \pm 2.3) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (performed in a much larger 17 m^3 chamber where the heterogeneous reactions were significantly reduced by direct increase in surface-to-volume ratios). Our rate constant was found to be larger than an earlier study by Hall (1995) $(0.3 \pm 0.2) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and smaller than both Schroeder et al.'s (1991) value $49 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (no error reported), and Iverfeldt and Lindqvist's (1986) value, $20 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (no error reported). In a new study by our group (Snider et al., 2008), for the first time, we have examined the effects of two atmospherically relevant polar compounds, $\text{H}_2\text{O}_{(g)}$ and $\text{CO}_{(g)}$, on the absolute observed rate coefficients of the O_3 -initiated oxidation rate of $\text{Hg}_{(g)}^0$, at $296 \pm 2 \text{ K}$ using gas chromatography coupled to mass spectrometry (GC-MS). In CO -added experiments, we observed a significant increase in the reaction rate that could be explained by pure gas-phase chemistry. In contrast, we found the apparent rate constant, k_{net} , varied with the surface-to-volume ratio (0.6 to 5.5 L flasks) in water-added experiments. We have observed small increases in k_{net} for nonzero relative humidity, $\text{RH} < 100\%$, but substantial increase at $\text{RH} < 100\%$. Product studies were performed using mass spectrometry and high resolution transmission electron microscopy coupled to an electron dispersive spectrometer (HRTEM-EDS). A water/surface/ozone independent ozone oxidation rate was estimated to be $(6.2 \pm (1.1; t\sigma/\sqrt{n}) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. There is furthermore $\pm 20\%$ accumulated uncertainties associated with the ensemble of the experimental setup used in this study.

In our previous study by Pal and Ariya (2004), we have observed HgO from gas-phase aerosols and as deposits using mass spectrometry techniques. Please note that our methodology could not allow us to evaluate the phase of the HgO at that stage. Most products were obtained as condensed matter deposited on the reaction walls, and with some aerosols identified on 2 micron filters. We had also obtained a very minor amount of mercury containing compounds from the gas phase (including suspended matter, i.e. aerosols that were not collected on 2 micron filter which included finer particles). We could not then identify the phase of these identified mercury compounds assumed to be HgO . Please also note that in chemical kinetics for gas phase oxidation reaction, we use terminologies such as "products observed in the course of gas-phase reaction of ...", it does not refer to the product as a gas, it just refers to the fact that the initial "reactants" were in the gas phase. In our recent study, as depicted in Figure 15.2, using high-resolution microscopy technique, we confirmed that HgO product is indeed solid ($\text{HgO}_{(s)}$). Our results gave evidence for enhanced chain growth of $\text{HgO}_{(s)}$ on a carbon grid at $\text{RH} = 50\%$. Clearly, due to importance of this reaction, further laboratory kinetic and mechanistic studies are desired.

Hydroxyl radical (HO) is considered to be the dominant daytime cleanser of the atmosphere. The major formation pathway in the troposphere is considered to involve photolysis of ozone followed by the reaction with water vapour:



In addition to the photolysis pathway, there are some dark reactions (ozonolysis) that have been proposed to be of significance at night or during the winter (Ariya et al., 2000). Typical background concentrations of ozone range from 20-30 ppbv (1 ppbv = $2.45 \times 10^{10} \text{ cm}^{-3}$), and can peak to a few hundred ppb during smog situations (Finlayson-Pitts and Pitts, 1999).

To date, there is very limited kinetic data on $\text{HO} + \text{Hg}^0_{(g)}$ as shown in Table 15.1. The results of (Sommar et al., 2001) are in excellent agreement with the recent results (Ariya et al., 2004). These reported values are both lower than Bauer et al. upper limit evaluations for HO initiated oxidation reaction. Again HgO was observed as product, and we can now confirm that it is $\text{HgO}_{(s)}$ (Figure 15.2). Further kinetic and mechanistic studies of this reaction are desirable.

15.2.3 $\text{NO}_3 + \text{Hg}^0_{(g)}$

The nitrate radical, NO_3 , is an important intermediate in the night time chemistry of the atmosphere. Upon sunrise, nitrate ions undergo photolysis to NO_2 or NO (Finlayson-Pitts and Pitts, 1999). Temperature dependence kinetics of elemental mercury, as well as dimethyl mercury, with NO_3 have been studied (Table 15.1). Sommar et al. (1997) employed a fast flow-discharge technique to study these reactions and obtained a second order rate constant value of $4 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

15.2.4 $\text{X}_2/\text{X}/\text{XO} (\text{X} = \text{Cl, Br, and I}) + \text{Hg}^0_{(g)}$

Mercury and halogen interaction has been experimentally studied under atmospheric conditions as summarized below.

Methyl iodide was shown to be non-reactive toward Hg^0 under atmospheric conditions ($k < 1 \times 10^{-21} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) (Tokos et al., 1998).

The first study of Hg^0 and chlorine atoms was published in 1968 (Horne et al., 1968). HgCl was measured by time resolved absorption spectroscopy in the temperature range 383 – 443 K

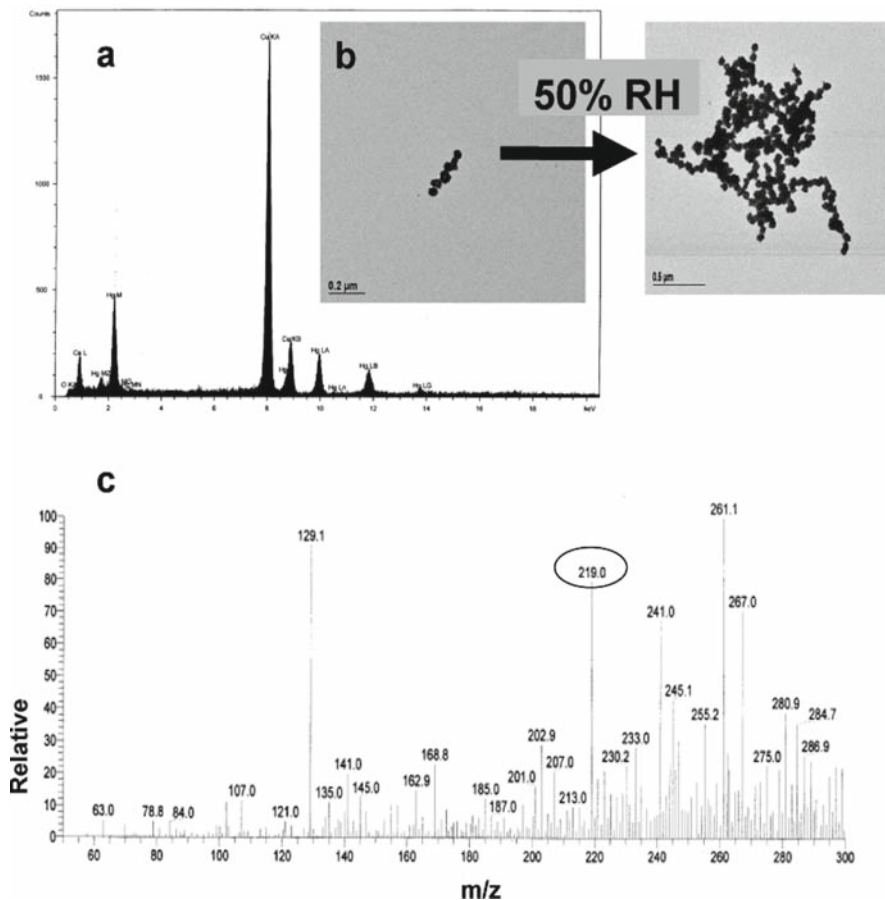


Figure 15.2 a) Energy dispersive spectroscopy (EDS) image of HgO b) Comparative HRTEM image of HgO deposit at RH = 0% and 50%, and c) CI of HgO product at RH = 0% and 50%. From Snider et al., 2008



The rate constant, k_1 , for the reaction of mercury with chlorine atoms was then derived to be $5.0 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ in 720 Torr CF_3Cl and $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ in 10 Torr $\text{CF}_3\text{Cl} + 710 \text{ Torr Ar}$. The authors (Horne et al., 1968) mentioned that k_1 has an uncertainty of a factor of three because of the accumulation of experimental errors in evaluating the separate terms and the rate constant can be considered to be more accurate than the order of magnitude when the results is transferred to atmospheric conditions.

Molecular chlorine was suggested to have a relatively modest reaction rate, $4 \times 10^{-16} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Schroeder et al, 1991; Menke and Wallis, 1980; Medhekar et al., 1979; Skare and Johansson, 1992; Seigneur et al, 1994) though

the reaction was found to be strongly surface catalysed, (Medhekar et al., 1979; Skare and Johansson, 1992) and the experimental value should be considered as an upper limit.

In 2002, extensive kinetic and product studies on the reactions of gaseous Hg^0 with molecular and atomic halogens (X/X_2 where $\text{X} = \text{Cl}, \text{Br}$) have been performed at atmospheric pressure (750 ± 1 Torr) and room temperature (298 ± 1 K) in air and N_2 and published (Ariya et al., 2002). Kinetics of the reactions with X/X_2 were studied using both relative and absolute techniques. Cold vapour atomic absorption spectroscopy (CVAAS) and gas chromatography with mass spectroscopic detection (GC-MS) were the analytical methods applied. The measured rate constants for the reactions of Hg^0 with Cl_2 , Cl , Br_2 , and Br were $(2.6 \pm 0.2) \times 10^{-18}$, $(1.0 \pm 0.2) \times 10^{-11}$, $< (0.9 \pm 0.2) \times 10^{-16}$, and $(3.2 \pm 0.3) \times 10^{-12}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Thus Cl_2 and Br_2 are not important reactants in the troposphere for the Cl_2 and Br_2 concentrations reported in literature. Please note that in the case Br reactions, in our laboratory, due to the existing experimental conditions, we only could deploy one reference molecules for the relative rate studies. As explained above, in relative studies the evaluation of the rate constants is very much dependant on the accuracy of the values of that the reference reactions. Hence, any challenge with the values of the reference reaction significantly affects the value of the reaction of interest, in this case, $\text{Br} + \text{Hg}^0$. At this stage, in our laboratories, we have acquired additional the state-of-the-art facilities to revisit the Br-atom reactions using both absolute and relative techniques.

Chlorine and bromine atoms were generated using UV and visible photolysis of molecular chlorine and bromine, respectively, in addition to UV ($300 \leq \lambda \leq 400$ nm) photolysis of chloroacetyl chloride and dibromomethane. The reaction products were analyzed in the gas-phase, in the suspended aerosols and on the wall of the reactor using MS, GC-MS and inductively coupled plasma mass spectrometry (ICP-MS). The major products identified were HgCl_2 and HgBr_2 adsorbed on the wall. Suspended aerosols, collected on the micron filters, contributed to less than 0.5% of the reaction products under the experimental conditions. Studies by Sumner et al. (2005) revisited both reactions using a 17.3 m^3 environmental chambers equipped with fluorescent lamps and sun lamps to mimic environmental reactions, and evaluated the rate constants to be in the order of 10^{-12} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and 10^{-11} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reactions of Br and Cl, respectively. Another research group (Donahue et al. 2005, 2006) has reported two other kinetic data sets for Cl and Br reactions using a pulsed laser photolysis-pulsed laser induced fluorescence spectroscopy (Table 15.1). These data sets are obtained using pseudo-first order conditions with respect to halogens or mercury. The authors of these studies indicate an uncertainty estimation of $\pm 50\%$ in the rate coefficients due to the determination of absolute concentrations of chlorine and Br atoms. These reactions are reported slower (factors of 9-15) that the other laboratory studies. Hence, further studies of these reactions are strongly desired.

Reactions of mercury with halogen oxide radicals drew major attention in the light of satellite BrO column measurements as well as simultaneous mercury and ozone depletion in the planetary boundary layer (Richter et al., 1998; 2002, Muller et al., 2002; Van Roozendaal et al., 2002; Goddsite et al., 2004). Experimental studies of XO

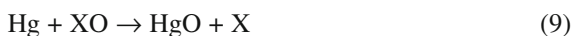
reactions are very scarce. To our knowledge there is only one published laboratory kinetic study on the reaction of BrO with elemental mercury (Raofie and Ariya, 2003) during which, using the relative rate methods, the room temperature bimolecular rate constant for $\text{BrO} + \text{Hg}^0_{(\text{g})}$ was estimated to lie within the range $10^{-15} < k < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The faster end of this range makes BrO a significant potential contributor to mercury depletion events in the Arctic. This is however in contradiction with theoretical calculations, see next section. A report was published on the first experimental product study of BrO-initiated oxidation of elemental mercury at atmospheric pressure of ~ 740 Torr and $T = 296 \pm 2$ K (Raofie and Ariya, 2004). The authors used chemical ionization and electron impact mass spectrometry, gas chromatography coupled to a mass spectrometer, a MALDI-TOF mass spectrometer, a cold vapour atomic fluorescence spectrometer, and high-resolution transmission electron microscopy coupled to energy dispersive spectrometry. BrO radicals were formed using visible and UV photolysis of Br_2 and CH_2Br_2 in the presence of ozone. They analyzed the products in the gas phase, on suspended aerosols and on wall deposits, and identified HgBr, HgOBr or HgBrO, and HgO as reaction products. Experimentally, they were unable to distinguish between HgBrO and HgOBr. The existence of stable $\text{Hg}^{(\text{I})}$ in form of HgBr, along with $\text{Hg}^{(\text{II})}$ upon BrO-initiated oxidation of Hg^0 , suggests that in field studies it is fundamental to selectively quantify various mercury species in mercury aerosols and deposits. The majority of mercury containing products were identified as deposits, however, aerosols accounted for a substantial portion of products. It is noteworthy that we anticipate the possibility of transformation of $\text{Hg}^{(\text{I})}$ to $\text{Hg}^{(\text{II})}$ at high humidity levels though care must be taken as previously mentioned to extrapolate the results to ambient concentration levels of the reactants. No definite conclusions on the potential primary or secondary reactions of BrO, can be made at this stage. Even considering one order of magnitude uncertainties in the existing kinetic data, Br reactions make it the likely radical to explain elemental mercury depletion in the Arctic. Two independent studies (Ariya et al., 2004; Goodsite et al., 2004) confirm this conclusion. The existing kinetic results indicate that the direct BrO impact is less important than Br, but further studies are required to examine this conclusion. For example, A Saiz-Lopez et al. (2007) have discovered via long path DOAS measurements, significant amounts of iodine oxide (IO) above the Antarctic ice, and that bromine persists there for several months throughout the summer, thus giving rise to a greater oxidizing effect than formerly though possible, given observations in the Arctic. However, there is a recent product studies on iodine compounds with elemental mercury, which are very much similar to those reported by Br counterparts (Snider et al., 2008). The reactions of molecular iodine are shown to be very slow to be significant in the atmosphere. Further kinetic studies on I and IO are desired.

15.3 Theoretical Evaluation of Kinetic Data

The possibility of theoretically predicting the thermochemistry of mercury-containing species of atmospheric interest is of strong importance due to the paucity of accurate experimental information. They also serve fundamentally to further comprehend

the complex reaction mechanisms. Accurate ab initio studies for measurements such as heats of formation, reaction enthalpies, and activation energies are particularly challenging, particularly in light of the large nuclear charge (80) and large number of electrons intrinsic to mercury. There is a detailed review on ab-initio thermochemical and kinetic studies on mercury reactions (Ariya and Peterson, 2005) and hence we discuss previous studies only in relation to experimental results. The existing theoretical kinetic data are also shown in Table 15.1. Ab initio calculations have to include e.g., careful choice of electron correlation method, treatment of relativistic effects, basis set truncation errors, etc., in order to obtain accurate kinetic data. The latter depends intimately on the underlying potential energy surface. A rigorous calculation of the rate coefficient for a given reaction generally involves either quantum scattering or classical trajectory calculations, which in turn require a global or semi-global potential energy surface (PES) calculated by ab initio methods. While these treatments are feasible for relatively small systems depending on the required accuracy of the underlying PES, most studies employ more approximate treatments of the reaction dynamics, e.g., transition state theory (TST) or RRKM theory (Rice-Ramsberger-Kassel-Marcus theory).

To the knowledge of the authors there are three studies by Goodsite et al, Khalizov et al, and Tossell (Goodsite et al., 2004, Khalizov et al., 2003, Tossell, 2003). The three groups looked on the reaction system of reactions:



where X is either Cl, Br or I.

Goodsite et al. (2004) and Khalizov et al. (2003) used the Gaussian 98 suite of programmes and the RRKM method. Goodsite et al. (2004) used the Steven Basch Kraus triple split CEP-121G basis set that account for some relativistic effects in the inner electrons of Hg. Khalizov et al. (2003) used two different basis sets. The first basis set was LanL2DZ which inner electrons substituted by effective core potentials and double- quality valence function for the heavier elements. The second basis set employs the ECP60MWB pseudo potential. Tossel used GAMESS, Gaussian 94 and Gaussian 98 software for the calculations also including relativistic effects.

Reaction 9 was investigated for X=Br to be endothermic and most probably without any importance in the atmosphere whereas reaction 2 is exothermic (Goodsite et al., 2004, Khalizov et al., 2003, Tossell, 2003). At room temperature Reaction 9 in all the studies was calculated to be exothermic. Khalizov et al. (2003) concluded that Hg + Br might be the dominant processes for atmospheric mercury depletion episodes (AMDE) occurring during Arctic Spring. This conclusion is further supported by Goodsite et al., (2004) that studied the temperature dependence of the reaction and showed that the HgBr intermediate is stabilised towards uni-molecular degradation at low temperatures which permits the addition

of another Br (reaction 3) and thus HgBr_2 is a possible candidate for the formation of the otherwise unknown RGM.

From the standpoint of theoretical quantum chemistry, accurate calculations on molecular species involving mercury are particularly challenging in comparison to light, main group elements. In part this is due to its large number of electrons like any late transition metal atom, but the main difficulties lie in the treatment of its strong relativistic effects that to a large degree dictate its chemistry. Fortunately one can account for these effects very conveniently and accurately by use of modern relativistic pseudopotentials (PPs), which are also referred to as effective core potentials (ECPs). Nearly all ab initio calculations involving mercury employ the PP approximation to recover both scalar and vector relativistic effects. The former includes the mass-velocity and Darwin terms of the relativistic Hamiltonian while the latter is dominated by the spin-orbit interaction. By using relativistic PPs, much of the machinery of state-of-the-art quantum chemistry that has been so successful for lighter elements can be utilized with only few modifications for mercury-containing species. In regards to prediction of accurate molecular structures (better than 0.01 Å in bond lengths) and thermochemistry (accuracies at or below 4 kJ/mol), the strategy can be generalized as outlined below.

- (i) The most accurate PP parameters available for mercury and perhaps other heavy atoms in the system of interest should be used. Those recently developed by the Stuttgart group (Figgen et al., 2005, Peterson, 2003) have been adjusted to multiconfigurational Dirac-Hartree-Fock calculations and appear to be the best choice at the present time for mercury and heavy main group elements, e.g., Br, I, Pb, etc.
- (ii) Gaussian basis sets that have been matched to the PP(s) being used in the calculation should be chosen carefully. For the newer Stuttgart PPs mentioned above, full series of correlation consistent basis sets, e.g., cc-pVnZ-PP ($n=D, T, Q, 5$), are now available (Ariya and Peterson, 2005, Balabanov and Peterson, 2003) and should be used if at all possible. These have the unique property of systematically converging computed quantities to the complete basis set limit as successive members of the series are used. This effectively removes this source of error in the calculation and is essential for accurate error estimates and eliminating fortuitous error cancellations that can lead to inaccurate predictions.
- (iii) In terms of the choice of electron correlation method, for thermochemistry and equilibrium structures the coupled cluster method, CCSD(T), has been shown to provide very accurate results for mercury species. For large scale potential energy surfaces or excited electronic states, multireference configuration interaction (MRCI) approaches must generally be used. Recent examples involving Hg include the low-lying electronic states of HgO and HgS, (Cressiot et al., 2007; Peterson et al., 2007; Shepler and Peterson, 2003) a quasiclassical trajectory study of the $\text{Hg}+\text{Br}$ recombination reaction (Shepler et al., 2007), and a global potential energy surface for HgBr_2 (Shepler et al., 2005). While density functional theory (DFT) is a very popular approach in quantum chemistry due

to its low scaling in terms of computational cost, it has not been shown to yield particularly accurate results for mercury-containing species. For example, previous large basis set DFT results (Khalizov et al., 2003) for the reaction enthalpies of $\text{Hg}+\text{Br}_2$ and $\text{Hg}+\text{Br}$ differed by nearly a factor of two from the analogous (presumably accurate) CCSD(T) values.

- (iv) While the relativistic PP will automatically account for scalar relativistic effects, some additional calculations incorporating spin-orbit coupling are generally warranted for mercury-containing systems. There are several avenues available for these calculations, but this remains one of the greater challenges for the accurate treatment of heavy-atom molecules and is not as amenable to the non-expert user. The reader is referred to Shepler and Peterson (2003) and Shepler et al., (2005) for some representative applications to mercury-containing systems.

Accurate quantum chemistry calculations using the methods briefly outlined above have played an important role in our current understanding of the oxidation of gas phase mercury in the atmosphere. High level ab initio calculations (Peterson et al., 2007; Shepler and Peterson, 2003) have conclusively demonstrated that $\text{HgO}_{(\text{g})}$ was not sufficiently stable to facilitate the reaction of Hg with the BrO radical. Before these calculations, oxidation of mercury by BrO was thought to be strongly exothermic since the experimental bond dissociation energy of Hg^0 was estimated to be near 50 kcal/mol instead of the value of about 4 kcal/mol conclusively obtained by theory. State-of-the-art quantum chemical calculations on a variety of mercury-halogen species (Goodsite et al., 2004; Khalizov et al., 2003; Tossell, 2003; Balabanov and Peterson, 2003; Shepler et al., 2005, 2007) led to the mechanism whereby the formation of the HgBr radical by atom-atom recombination is the rate determining step in the gas phase oxidation of mercury in the troposphere. Recently the quasiclassical trajectory approach has been used on an accurate HgBr-Ar potential energy surface (Shepler et al., 2007) to determine thermal rate coefficients for the recombination reaction over a wide range of temperatures. The results were in excellent agreement with recent laboratory measurements. Analogous calculations have also been carried out recently for the $\text{Hg}+\text{Br}_2$ and $\text{HgBr} + \text{Br}$ reactions on an accurate global HgBr₂ potential energy surface (Shepler et al., 2005). The latter surface exhibited a large barrier to insertion of Hg into the Br₂ bond, which provided a rationale for the very slow rate measured experimentally for that reaction. Reliable rate coefficient calculations for $\text{Hg} + \text{Br}$ and $\text{HgBr} + \text{Br}$ have also been carried out using RRKM methods (Goodsite et al., 2004).

In addition to the determination of thermal rate coefficients, one of the main contributions of quantum chemistry is the prediction and subsequent characterization of new products and intermediates from proposed mercury oxidation mechanisms. Since high accuracy methods can predict heats of formation and bond dissociation energies to better than 4 kJ/mol accuracy even for mercury compounds, this is more than sufficient to determine the stability of novel mercury species. One such study, which is ongoing in one of our research groups, is the characterization of the mercury hypohalite species, e.g., HgBrOBr, which have been proposed (Calvert and Lindberg, 2003) to be formed by the reaction of HgBr with halogen monoxides but have not

yet been observed by experiment. Our initial investigations find that they are thermodynamically very stable species.

15.4 Reactions at Interfaces: Heterogeneous Reactions

One of the first steps for mercury to undergo in a surface reaction is adsorption. There are two principal modes of adsorption of mercury molecules on any surface. The basis of distinction is the nature of the bonding between the molecule and the surface. In physical adsorption (physi-sorption), the bonding is by weak Van der Waals - type forces. There is no significant redistribution of electron density in either the molecule or at the substrate surface. In a chemisorption process a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character, and hence it is significantly stronger than physical adsorption (40-800 kJ/mol in comparison to 5-40 kJ/mol) (Atkins and de Paula, 2002). There are a few ways to distinguish physisorption and chemisorption. The temperature over which chemisorption occurs can be only over a small surface, but is almost unlimited. However, for physisorption the temperature range is around condensation point of a gas such as Hg^0 . Physisorption is generally reversible, non-dissociative, potentially multilayer and fast, whereas chemisorption is dissociative and often include an activated process with wide range kinetic desorption and limited to monolayers. To distinguish the type of adsorption, one can evaluate the vibrational frequency of substrate-adsorbate bond, or shift in energy or intensity of the valence orbitals in the substrate and adsorbate surface. For most mercury environmental surface studies shown in Table 15.1, the fundamental difference between chemi- and physi-sorption are not yet evaluated, and should be studied in future.

Environmental interfaces are very dynamic with respect to Hg cycling. The main surfaces interacting with the air compartment are soil, vegetation, snow, ocean and lake surfaces. These interfaces are sites of redox reactions and Hg exchange with the atmosphere. We here present an overview of Hg behavior at these interfaces, with respect to its reactivity and evasional flux.

15.4.1 Lake Surface

Lake surfaces represent about 1% of landmass surfaces, and are therefore not major players in controlling global fluxes (Mason and Sheu, 2002). However, evasion of Hg^0 from surfaces can significantly alter the Hg budget in these systems, with a potential impact on the contamination of fish. Results from a whole-ecosystem loading experiment (METAALICUS, Mercury Experiment to Assess Atmospheric Loading in Canada and the United States) have established that 45% of newly deposited Hg could be transformed near the water/air interface of a small boreal lake and returned to the

atmosphere (Amyot et al., 2004; Southworth et al., 2007). For one of the greatest freshwater systems, Lake Superior, Rolffhus et al., (2003) estimated that Hg evasion from the lake surface completely counterbalanced atmospheric Hg deposition.

Mercury transformations at the air/lake interface are usually dominated by the photoreduction of $\text{Hg}^{\text{(II)}}$ to Hg^0 (Amyot et al., 1994). This production of Hg^0 typically displays both diel and seasonal patterns with maxima under sunlit and warm conditions (Zhang, 2006). Photoreduction of $\text{Hg}^{\text{(II)}}$ can be induced by UV and, to a lesser extent, by visible radiation. The fact that visible radiation can induce this reduction suggests that DOC chromophores may be involved (Fitzgerald et al., 2007). Filtration experiments have shown that this photoreduction can be homogeneous. It can be mediated by iron(III) (Zhang and Lindberg, 2001) and humic acids (Allard and Arsenie, 1991). However, it can also be biologically-mediated (Siciliano et al., 2002). The relative importance of these mechanisms will differ with pH, light attenuation and DOC levels at the surface. An in-depth review on this topic is presented in Zhang and Wong, 2007.

Of lesser importance in lakes, (photo)oxidation of Hg^0 to $\text{Hg}^{\text{(II)}}$ has been observed and also follows a diel cycle (Garcia et al., 2005). This oxidation is mainly promoted by the UV-A waveband and can be driven by the formation of strong Hg oxidizing agents (e.g. OH radicals) or be indirectly caused by the photoproduction of hydrogen peroxide which, in turn, regulates microbial oxidation processes (Siciliano et al., 2002).

Current models do not predict well the formation of Hg^0 and its evasion from lake surfaces. Processes occurring in the surface microlayer need to be better assessed in order to establish the actual Hg^0 gradient at all water/air interfaces (for lakes, oceans and estuaries).

15.4.2 Surface of Oceans

Oceanic surfaces are a major site of Hg exchange at the global scale, with evasional fluxes accounting for about 39% of global Hg emissions (Mason and Sheu, 2002). Hg at this interface undergoes similar transformations to those described for lakes. Rolffhus and Fitzgerald (2004) estimated that about 70% of volatile Hg formed in coastal seawaters was of photochemical origin, 20% came from bacterial processes, and 10% from uncharacterized dark reduction.

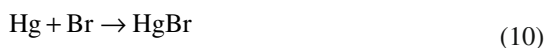
In addition, two major differences can be highlighted between freshwater and saltwater interfaces. First, in addition to Hg^0 , ocean waters also contain significant concentrations of another highly volatile species, dimethylHg. This species formed at depth can be brought up to the air/seawater interface by upwelling currents in coastal areas. Second, oxidation of Hg^0 to $\text{Hg}^{\text{(II)}}$ is far more prevalent in saltwaters and will hamper the evasional fluxes of Hg^0 . This oxidation is photo-induced and promoted by halogen chemistry both above and below the water/air interface (Sheu and Mason; 2004, Lalonde et al., 2001). In Sheu and Mason (2004), aqueous NaCl/NaBr salts were photolyzed in the presence of $\text{Hg}^0_{(\text{g})}$. It was discovered that $\text{Hg}^0_{(\text{g})}$,

in the presence of water, salt, and under a Xe-lamp, the oxidation rate constant increased 100-fold compared with irradiated salt-free water. Work was done at ambient temperatures in a quartz container. Mechanisms proposed involved volatilization of halogen species, which then react with mercury. Many secondary reactions of mercury were also considered (i.e. those with OH, BrO, ClO, and O₃), generally initiated by the presence of salt and light energy. Sheu and Mason (2004) also note reactions of Hg + Br were 25 faster than with Cl radicals.

Accidental Hg reduction by marine microorganisms has been proposed as a significant source of Hg⁰ in the mixing layer for a long time (Mason et al., 1995). There is evidence the bacterial mercuric reductase enzyme (MerA) will reduce MeHg and inorganic Hg^(II) species to Hg⁰(g) in Arctic coastal and marine environments (Poulain et al., 2007). It is noted this reduction is an apparently deliberate self-preservation of certain biota against methylmercury contamination in water. In addition to photoreduction recycling mercury, bacteria are capable of re-volatilizing the metal at comparable levels even with only 1% of cells active.

As mentioned for lakes, very few studies have focus on the sea surface microlayer, even though microscale processes in this layer may have an important impact on evasional fluxes.

Using *ab-initio* chemistry, Shepler et al., (2007b) noted water microsolvation (using 1-3 water molecules) favored the oxidation of mercury in the presence of bromine.



Reactions (10) and (11) were found more favorable in the presence of water, whereas reaction (12) was less favorable when solvated. They conclude it is probable the effects of ice, snow, and water surfaces enhance the scavenging of mercury by halogens.

15.4.3 Snow Surface

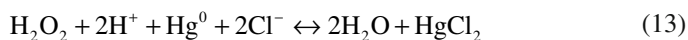
The role of the snow surface on the reactivity of Hg and its release to the atmosphere has been discussed for polar regions in Chapter 9 of Steffen et al. (2007). It has been demonstrated that in suburban and remote temperate areas, about 50% of newly deposited Hg is returned back to the atmosphere within 24 to 48 hours (Lalonde et al., 2002). This release results from the photoreduction of Hg^(II) to Hg⁰ in the snowpack, mostly induced by UV-B radiation (Lalonde et al., 2003). The processes leading to this reduction have not been elucidated.

In forested areas, the canopy has a significant impact on the behavior of Hg in the underlying snowpack (Poulain et al., 2007b). Snow under canopy has typically higher Hg levels than snow from open areas (e.g. frozen lake surfaces); photoreduction of Hg^(II) followed by evasion is less efficient in forested areas because of light attenuation by the canopy. Poulain et al. (2007c) calculated net winter gain of Hg in snow under canopies dominated by conifers whereas, under a deciduous canopy, the pool of Hg stored at the end of the winter was comparable to that of wet deposition. Coniferous trees were both a source of Hg to the forest floor (via throughfall) and an obstacle to Hg photoreduction in underlying snow. Snow over lakes acted as a winter source of Hg to the atmosphere. Whereas most Hg deposited by snow on lakes is lost before snowmelt, Hg deposited on the forested watershed is largely retained in snowpacks.

Snow can house a number of different Hg^(II) species, i.e. HgC₂O₄, Hg(OH)₂, HgOHCl, HgO (Ferrari et al., 2002), and possibly others. It is clear from experiments that Hg^(II) on snowpacks is photo-reduced by natural sunlight (Dommergue et al., 2007). Mercury over snow originates from atmospheric Hg⁰_(g) through dry deposition (Schroeder et al., 1998) and oxidation mainly via O₃, BrO, and Br (Ariya et al., 2004). Concentrations of arctic mercury on snowpacks are guided by incoming and outgoing fluxes, which depend on light intensity and oxidant concentration, respectively. Oxidation of mercury over snowpacks is part of a dynamic system of ice, snow, ozone, UV-Vis light, Cl, and Br radicals (see Lindberg et al., 2002). It is believed that aerosol ice surfaces catalyze oxidation of Hg⁰_(g) to HgO or HgBr₂/Cl₂ during the Arctic spring (Lindberg et al., 2002). Oxidation is aided by the destruction of ozone by Br over ice and formation of Hg⁰ oxidants (Ariya et al., 2004; Oltmans et al., 1989).

Methylmercury (MeHg^(I)) has been observed in Arctic snowpacks (St. Louis, et al., 2007). The origins of MeHg^(I) are aqueous (oceans, lakes), however its volatility is low: $K_p = [\text{HgMe}_{(g)}]/[\text{HgMe}_{(aq)}] = 2 \times 10^{-5}$, at 298 K (Schluter, 2000). By contrast, volatility of dimethylmercury (Me₂Hg) is much higher: $K_p = 0.31$ (Schluter, 2000). St Louis et al., (2007) hypothesize MeHg originates from nearby ocean sources as MeHg₂, then converts to MeHgCl in the salty snow. They note there is a positive correlation between total mercury and Cl concentrations over snowpacks. The salinity of Arctic snow can range anywhere between 20 – 2000 mg l⁻¹ (Ariya et al., 2004).

Snow spiked with hydrogen peroxide was observed to enhance Hg^(II) deposition five-fold under natural Arctic springtime sunlight (Lahoutifard et al., 2006). The mechanism of oxidation is not known, though it is suggested equilibrium can be formed with chlorine in acidic conditions:



Samples were spiked with 50 μM H₂O₂, similar to natural concentrations (30 μM). Hence H₂O₂ was suggested to play a significant role in Hg⁰ oxidation under UV light that should be further confirmed. Bromine, as well as Cl, can oxidize Hg⁰

in snow. Fain et al. (2006) calculated from field samples a mercury + bromine oxidation rate constant very similar to lab studies; $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at $-10 \text{ }^\circ\text{C}$.

Poulain et al., (2007) observe 100-fold higher concentrations of total mercury in snow found near Arctic sea/ice boundaries than inland. They note melting of the snow/ice during springtime further enhances mercury deposition (until enhanced light intensity of the spring re-volatilizes condensed mercury). Douglas et al., (2008) observe various crystalline morphologies of snow will exhibit varying degrees of $\text{Hg}^0_{(\text{g})}$ scavenging, with up to an order of magnitude difference in deposited concentrations. Heterogeneous mercury reactions evidently depend on surface morphology in addition to surface species present. Aspmo et al., (2006) observed $\text{Hg}^0_{(\text{g})}$ concentrations over sea ice, noting some increase in concentration (1.82 ng m^{-3}) compared with background north Atlantic ocean levels (1.53 ng m^{-3}). Analyses were done in the summer and spring, leading to the possibility of re-emission of $\text{Hg}^{\text{(II)}}$ over ice and snow. Depth profiles of mercury concentration over snow show generally higher levels than atmospheric background levels. Despite observed rapid mercury depletion events in the polar regions (Schroeder et al., 1998; Ebinghaus et al., 2002), but the over all fate is an subject of debate (Steffen et al., 2002). The total volume of mercury entering the Arctic circle is calculated to be about 300 Mg per year, via global model simulation (Ariya et al., 2004). This influx is largely scavenged over ice, snow, and water via bromine explosions (Tackett et al., 2007). However, this deposition in part is rapidly reduced to $\text{Hg}^0_{(\text{g})}$ later during Arctic springtime (Steffen et al., 2002).

Frost flowers have been a known source of halogen from sea ice for several years (Kaleschke et al., 2004). Now it is possible these ice crystals provide via high surface areas a scavenging of mercury (Douglas et al., 2008) It was found crystals formed in the vapour phase have higher mercury concentrations (2-10 times as much) than snow deposits. The only difference between frost flowers and snow deposits would appear to be their morphology; hence the surface design (diamond dust, surface hoar, blowing snow, glass trays) may also affect kinetics of $\text{Hg}(\text{II/I})$. A previous study already supposed Br radicals are released from the sea ice crystals (Gauchard et al., 2005), implying heterogeneous reactions are responsible in part for mercury oxidation. However, we point out that the $\text{Br/BrO} + \text{Hg}^0$ oxidation itself is gaseous. Trace species affecting Hg reduction/oxidation in snow include, but are not limited to, Br, Cl, microbes, and ice/snow morphology.

15.4.4 Soil Surface

Mercury air-soil exchange is an important component of the Hg cycle at regional and global scales (Grigal, 2002). Hg^0 volatilization from soils has been correlated to soil Hg concentration (Gustin et al., 1999), soil moisture (Gustin and Lindberg, 2005), atmospheric oxidants (Gustin et al., 2005), meteorological conditions (barometric pressure, temperature, wind speed and turbulence, and solar radiation).

Under low atmospheric Hg concentrations, barren soils can act as Hg sources to the atmosphere during the day or sinks of Hg at night (Xin and Gustin, 2007). Photochemical processes are likely the main driver of Hg⁰ formation and evasion when the substrate is moist or after rain events (Edwards et al., 2001), whereas solar-induced thermodesorption of Hg⁰ is probably more important under dry conditions (Poissant et al., 2004). The sorption properties of soils will be dictated by the mineralogical composition. For instance, the presence of kaolinite, montmorillonite, and goethite in soils has been shown to enhance the sorptive capacity of soils (Edwards et al., 2001).

Since soils can significantly differ in their sorption capacity and their reactivity, and current evasion estimates are site-specific, the overall global fluxes associated with soils are still poorly constrained and need further assessment.

15.4.5 *Vegetation Surface*

Vegetated areas are key players in global Hg cycling. According to Mason and Sheu (2002), net Hg evasion from land is 8 Mmol yr⁻¹; emissions from vegetated areas (forest, prairies and farmland) are estimated at 9 Mmol yr⁻¹ and uptake of Hg⁰ by plant drives a depositional flux of -7 Mmol yr⁻¹. Because of the magnitude of these vegetation fluxes, a far better understanding of these surfaces is needed to constrain flux estimates.

The plant/air interface is a site of both passive and active exchange of Hg^(II) and Hg⁰. For example, atmospheric particulate Hg and reactive gaseous Hg can be absorbed on leaf surfaces after dry deposition (Hanson et al., 1995). Stomata can actively take up atmospheric Hg⁰ (Lee et al., 2000). This assimilated Hg can come either from passing air masses or from soil Hg emissions below the canopy; in the latter case, this uptake results in a fast cycling of Hg within the forest. In contaminated sites, plants can translocate Hg from soils to leaves, with some Hg being released through stomata or through litterfall. The leaf surface has also been shown to be a site of photochemical transformations of deposited Hg^(II) to Hg⁰, followed by its evasion to the atmosphere. The UV band was shown to be the most efficient radiation in this reduction.

15.4.6 *Carbon (Fly Ash, Charcoal)*

Knowledge that coal combustion is a source for mercury dates back over 35 years (Joensuu, 1971). Residues of coal combustion in industrial power plants generate fly ash, composing mostly of SiO₂ and Al₂O₃. Fly ash composition and morphology make it suitable for zeolite synthesis (Querol et al., 1997). Flue gas may be comprised of CO₂, O₂, CO, NO, NO₂, SO₂, H₂S, HCl, NH₃, N₂O, and Hg (Hall et al., 1995). Incomplete combustion (T < 400 °C) leads to carbon in fly ash, usually enhancing

mercury adsorption (Pavlish et al., 2003). Presence of carbon also leads to high “Loss on ignition” (LOI), which is defined in the context of coal combustion as the fly ash weight loss at a given (elevated) temperature. Thus the carbon content may be expelled when sufficiently heated, possibly taking absorbed mercury with it. Presence of carbon was found to increase the BET surface area of fly ash, enhancing adsorption (Hower et al., 2000). Surface area per unit mass, and per unit area in the flue, is significant in describing adsorption. Carbon content ranges from 6 to 850 $\text{m}^2 \text{g}^{-1}$, with $\sim 70 \text{m}^2 \text{g}^{-1}$ in charcoal (Chen, 2007). The BET surface area of iron oxide is $62 \text{m}^2 \text{g}^{-1}$ (Wu et al., 2006). Soot/fly ash may disperse globally; fly ash has been shown to be a component of Arctic aerosols (Daisey et al., 1981). It is possible carbon in aerosols will affect mercury oxidation rates under environmental conditions.

Presto and Granite (2006) have efficiently summarized the significant contributions carbon, metal, metal oxide, and other surfaces in simulated and experimental coal-combustion conditions. We attempt to avoid duplication of their review material by further updating this subject, though some reference material of theirs is necessarily highlighted. We also refer the reader to Pavlish et al., (2003) for an earlier review of mercury capture in power plants.

Activated carbon can absorb mercury in aqueous solutions as well gaseous systems (Namasivayam and Kadirvelu, 1999; Ranganathan, 2002; Yardim et al., 2003). Sen and De (1987) found that aqueous $\text{Hg}(\text{NO}_3)_2$ was readily adsorbed by fly ash at a $\text{pH} = 3.5 - 4.5$. At a pH of 5, Hg^{II} was hypothesized to transform into $\text{Hg}(\text{OH})_2$ over the carbon (Namasivayam and Kadirvelu, 1999). Chen (2007) noted that $\text{H}_2\text{O}_{(\text{g})}$ did not affect mercury oxidation. Some experiments have noted humidity negatively affecting oxidation (Menke and Wallis, 1980; Seigneur et al., 1994).

It is clear that many factors affect the adsorption - hence redox - reactions of mercury over fly ash. The most important trace elements affecting the oxidation rate are HCl, ClO, and Cl_2 . Mechanistically, we suspect that the majority of oxidation in the presence of fly ash or carbon is heterogeneous based on the evidence of Presto and Granite (2006). Temperature is a significant factor in oxidation rate; optimal values must be achieved to balance reaction efficiency and total adsorption. Hall et al., (1995) discovered a mixture of oxygen and mercury at 100-300 °C would react in the presence of fly ash or carbon. There was a measurable oxidation rate constant of $\sim 10^{-4} \text{s}^{-1}$. Surface kinetics have been postulated to obey a Langmuir - Hinshelwood mechanism, where both mercury and oxygen adsorb onto the carbon surface before reacting. A temperature of about 200 °C was found optimal. Xu et al., (2008) (see also Change and Offen, 1995) compared mercury oxidation by different pathways using a combination of kinetic modeling and *ab initio* chemistry over a carbon surface. They conclude that $\text{Hg}^0 + \text{ClO}$ reactions may be more significant at $T > 130^\circ\text{C}$ than mercury reactions with either Cl_2 or HCl.

We conclude this section by stating the use of fly ash or charcoal in removing mercury is not cost-effective (Change and Offen, 1995), varying between 14,000 – 38,000 USD/lb Hg. The useful temperature range is not wide for carbon; the peak efficiency temperature is $\sim 200^\circ\text{C}$ (Hall et al., 1995). Carbon is not effective at high temperatures ($> 400^\circ\text{C}$) due to its LOI. Some studies find temperature to be inversely proportional to Hg^0 removal (Dunham et al.,

2003); it is found that carbon at 20 °C absorbs Hg^0 better than at 40 °C (Hwang et al., 2002). Fly ash is stable at high temperatures, however efficiency also decreases with increasing temperature. Fly ash also does not efficiently oxidize mercury unless other additives (HCl , H_2S) are present. Although carbon/fly ash injection is a very natural method to removing $\text{Hg}^0_{(\text{g})}$, it remains the engineers' and physical chemists' goal to achieve improved mercury absorbency by more robust and cheaper adsorbents.

15.5 Open Questions and Future Directions

The lack of knowledge in the gas phase and liquid phase looks insignificant in comparison to the lack of knowledge at the interfaces, and thus heterogeneous reactions. The knowledge of mercury chemical, physical and biological interactions at environmental surfaces is scarce at best. It is now evident that the existence of the surfaces, different types of surfaces, and different environmental conditions can alter the transformation of mercury in pure gas phase or aqueous phase. However, the quantification of the impact of surfaces is yet to be understood. The challenges facing surface chemistry includes:

1. As far as the theoretical calculations are concerned, one of the major challenges is the accurate inclusion of spin-orbit coupling effects, particularly for large molecules and clusters. Advances are currently being made in the area of two-component DFT theory and this may very well be a promising avenue for incorporating these effects. Of course the methods outlined above are also mostly limited to gas phase calculations. Accurate theoretical treatment of condensed phase system continues to be a great challenge. Both cluster models and ab initio molecular dynamics methods will certainly play a large role in future studies of the heterogeneous reactivity of mercury.
2. Despite the novel positive acquisitions of knowledge from experimental and theoretical studies of gas-phase elemental mercury chemistry there are still large gaps before a complete understanding of the fate of mercury in the atmosphere is obtained. It is essential to provide kinetic data, information about formed products.
3. There are some limited studies on the kinetics of gas-phase elemental mercury oxidation on surfaces (e.g., Lee et al, 2004; Flora et al., 1998; Vidic et al., 1998). However, experimental studies on uptake or kinetics of heterogeneous reactions of mercury on various environmentally relevant surfaces such as ice, snow, and aerosols and biomaterials, are needed.
4. Lack of knowledge of detailed mercury chemical speciation in the field studies. Currently, the existing techniques are quite poor in providing detailed chemical structure of mercury compounds at the environmental interfaces as at the matter of fact even in atmosphere, water and snow. The operational definitions are used to discern amongst different functional groups, however, as they are not based

on fundamental understanding of physical and chemical structures of molecules, it is very difficult to use them adequately for proper understanding of surface chemistry and physics of mercury. Further development of targeted techniques for detailed mercury analysis is essential.

5. Currently, the knowledge of chemical reactions involving mercury compounds in aerosols and clouds is limited, and sometimes contradictory, liquid phase chemistry kinetic data. However, there is an urgency of for research on heterogeneous mercury reactions at fundamental theoretical, kinetic and dynamic studies, as well as proper incorporation in atmospheric modeling.
6. Fundamental surface sciences during the last several decades have achieved break through understanding of interfaces at molecular and cluster levels. It is wise for mercury scientists to take advantage of this existing body of knowledge including techniques such as various types of electron microscopy (e.g. transmission to electron force) to further understand the physical property of the surfaces, and the nature of the bonds between substrate and surface, as well as substrate-substrate configuration changes upon interactions with surfaces. This case is particularly valid for surfaces such as snow, as well as aerosols and cloud droplets. It is of outmost interest to understand the mechanism(s) on or within these surface reactions.
7. The nature of diffusion of mercury species in surfaces and interfaces (e.g., snow/ice) should be characterized.
8. The importance of so-called "micro-layer" within the interface in relation to the entire surface should be studied.
9. There is an amazing range of biological surfaces available for mercury transformation. Reactions are shown to occur on the surfaces or be altered within the biological bodies. The detailed chemical transformation of such reactions implicating biological transformation of mercury and its impact on physical and chemical characteristics of mercury compounds in environment is a fascinating field of studies that should be attempted from nano to macro scales.
10. We know presently full well that to grasp the mercury transformation on this planet, the knowledge of pure gas, or condensed-phase physics and chemistry will not suffice. The feedbacks of gas phase on surfaces or liquid/solid/heterogeneous phase on environmental surfaces are ought to be characterized. The impact of heterogeneity on surfaces in local, regional and global scales is ought to be understood.
11. Anthropogenic activities in the domains of new materials and nanotechnology, has produces novel surfaces as product of by-product of such activities. These molecules are in addition to oxidized transition metals (Fe, Mn, V, Cu, Ti), noble metals (Au, Pd, Ag, Cu) and metal oxides, glass type structures that are known to be involved in mercury transformations or its removal. There is not much known on the interactions of human-made novel surfaces with mercury compounds. As anthropogenic activities currently represent the major mercury emission in the atmosphere, the importance of these surfaces on Hg transformation should be understood.

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