

Review

A review of the sources of uncertainties in atmospheric mercury modeling II. Mercury surface and heterogeneous chemistry – A missing link

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Despite direct and indirect evidence suggesting that heterogeneous surfaces potentially play a key role in mercury chemistry, there is little known about mercury reactions and equilibrium processes that take place at atmospherically relevant surfaces. The lack of knowledge of mercury surface chemistry is a major gap for adequate modeling of mercury cycling. In part I of this review, we assessed the sources of uncertainty associated with existing kinetic parameters. In this part, we present evidence that supports surface–mercury interactions in the ecosystem elucidating the importance of heterogeneous and interfacial chemistry from a fundamental viewpoint. Consequently, we draw attention to the chemical processes that are missing and/or are inadequately incorporated in the atmospheric mercury models and highlight some of the recent advances in this field. We reveal that adsorption equilibrium of mercury species, most of which are not well characterized, to natural surfaces such as atmospheric particles and air/water interface are not known. Gas–liquid partitioning of mercury and its compounds are not adequately implemented. Equilibrium constants for aqueous phase complex formation with dissolved organic matters and formation of possible solid mercury clusters and nanoparticles are not considered in the global models. Potential heterogeneous mercury reduction reactions that can be important in mercury cycling require further evaluation which includes characterizing the influence of surfaces on mercury chemistry. The implementation of chemical processes for which information is available but not currently included in the models bears the potential of greatly reducing the uncertainties that are currently present in the models.

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1. Introduction

The complex chemical interactions that occur in the atmosphere are not limited to pure gas or aqueous phase chemistry. For instance, the observed magnitude of ozone depletion in the last three decades could not be explained via pure gas-phase reactions and instead heterogeneous halogen chemistry on the surfaces of polar stratospheric clouds at cold temperatures was shown to play a major role (Solomon, 1999; Solomon et al., 1986). Likewise, heterogeneous reactions of NO_x on cirrus clouds in the troposphere were found to be significant in its cycling (Zondlo et al., 2000). In general, as has been highlighted in recent years (Finlayson-Pitts, 2009; Prather et al., 2008; Rubashinghe et al., 2010), understanding the

chemical reactions occurring in the presence of atmospheric surfaces is of fundamental necessity yet the heterogeneous chemistry in the current atmospheric models is either entirely ignored or poorly described. Aerosols and clouds are the major heterogeneous components in the atmosphere. Along with atmospheric surfaces, namely aerosols, clouds, ice, and other environmental surfaces such as snow covers, soil, vegetation, and air–water interfaces can also serve as sites of surface catalyzed mercury reactions (Fig. 1).

Mercury chemistry is also influenced by the presence of ill-defined heterogeneous chemical mixtures of dissolved organic matter (DOM) or dissolved organic compounds (DOC) in the aquatic environment (Zhang, 2006). Possible heterogeneous reduction of mercury in volcanic and power plant plumes can also have a large impact on mercury cycling (Glasow, 2010; Lohman et al., 2006; Vijayaraghavan et al., 2008).

Numerous direct and indirect observations, some of which are presented in this review, point to the fact that these surfaces influence mercury chemistry. Nevertheless, systematic understanding of mercury surface and heterogeneous chemistry is lacking

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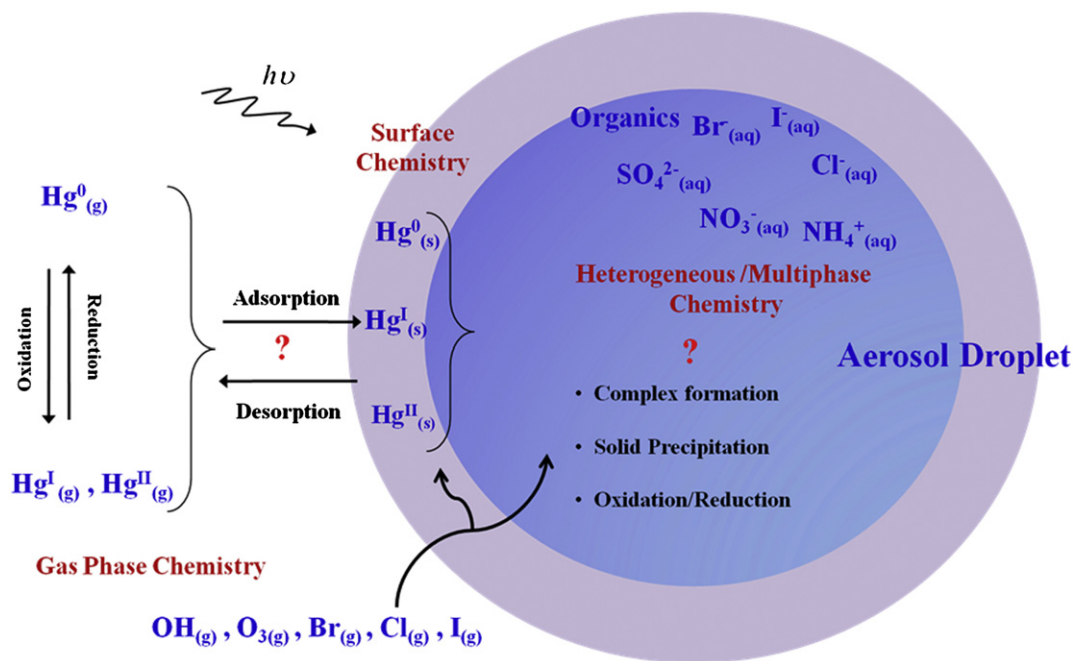


Fig. 1. A model representation of chemical interactions of mercury species with an aerosol particle. One of the major sources of uncertainty is our lack of knowledge of mercury surface and heterogeneous chemistry, emphasized by the question marks. Mercury reactions and equilibrium processes occurring at the surface of an aerosol particle and inside its heterogeneous mixture have yet to be investigated. Some of these processes include adsorption (and desorption) of mercury species (Hg^0 , Hg^{I} , Hg^{II}) to (and from) the aerosol surface and their subsequent diffusion to the bulk solution, for which systematic studies are lacking. The existence of Hg^{I} in the atmosphere is unlikely but is included in this figure to emphasize the lack of chemical identification of mercury species. The subscript (i) represents interfacial mercury compounds to distinguish them from their corresponding bulk species. Reduction and oxidation reactions and complex formation at the surface and inside the aerosol have yet to be studied. Note: knowledge of interfacial chemistry occurring at various other surfaces (ice, cloud, environmental water) is limited.

and the implementation of the corresponding chemical parameters in mercury modeling is limited. This insufficient knowledge of mercury interactions with various surfaces constitutes one of the major missing links in mercury modeling chemistry. We herein present the current knowledge and the uncertainties associated with these chemical parameters. Additionally, to provide a future direction to reduce uncertainty in modeling atmospheric cycling of mercury, we highlight some recent advances in this area throughout the review.

2. Importance of atmospheric and environmental surfaces and heterogeneity: relevance to mercury chemistry

2.1. Underlying importance of surface and heterogeneous (or multiphase) chemistry

In this section, we briefly discuss the significance of surfaces and heterogeneous chemistry from a fundamental perspective and give an overview of the surfaces available in the environment and the atmosphere. A surface, or more generally – interface, is defined as the boundary between two bulk media (Levine, 2002). Surfaces are ubiquitous in nature; for example, about two-third of the earth's surface is an air/water interface. Interfaces are also available in the heterogeneous mixture of soil, snow covers, and DOM in the aquatic environment. The primary reason interfaces are important is that the species adsorbed at an interface can exhibit different physical and chemical properties compared to their corresponding bulk properties. Surface bound molecules are known to exhibit different chemical reactivity since unique characteristics of interfaces can stabilize certain reaction intermediates and products (Adamson and Gast, 1997; Butt et al., 2006). Chemical equilibrium and spectral properties of molecules can also shift when adsorbed

at planar and/or particle surfaces (Eisenenthal, 1996, 2006). The shift in equilibrium can alter chemical speciation and spectral changes are important in photochemistry.

In the atmosphere, suspended airborne solid and liquid (heterogeneous/multiphase) particles, technically defined as aerosols (Seinfeld and Pandis, 2006), provide sufficient surfaces for gas phase atoms and molecules to adsorb, deposit, or collide. In the context of tropospheric chemistry involving condensed systems, heterogeneous processes refer to chemistry taking place at the surface of a solid whereas multiphase chemistry takes place in the bulk of a liquid (Ravishankara, 1997). Despite this distinction, we use both terms (“heterogeneous” and “multiphase”) interchangeably throughout this review since we would like to put emphasis on both for reactions involving mercury species. Aerosols are prime examples of chemical systems where both heterogeneous and multiphase processes are likely. Depending on their sources of emission, these airborne particles can be composed of inorganic salts, organic compounds, mineral dusts (Rubashingege et al., 2010), as well as microorganisms (Ariya et al., 2009b). Fig. 1 depicts some of the chemical interactions between mercury and aerosol particles.

Adsorption of gaseous mercury species can occur on atmospheric surfaces and subsequently they can desorb, undergo surface enhanced (photo)chemical reactions or diffuse to the inner aqueous compartment where they can exhibit heterogeneous reactions. Studies suggest that important oxidants such as OH radicals and O_3 , which can react with mercury, prefer surface adsorption over bulk solvation in water and in salt solutions (Laskin et al., 2003) resembling seawaters and aerosol conditions. Based on the composition of the aerosols, mercury compounds may undergo complex formation, phase change or re-adsorb to the surface. Both molecular dynamic (MD) simulations and experimental evidences

suggest that halide ions, Cl^- , Br^- , and I^- , which can form stable complexes with oxidized mercury (Clever et al., 1985), adsorb to air/water interfaces and are applicable to the conditions of sea salt aerosols (Jungwirth and Tobias, 2006; Petersen and Saykally, 2006). Although the adsorption process is illustrated for an aerosol (Fig. 1), it is also relevant to particles present in plumes and to the heterogeneous mixtures present in aquatic environments. For solid particles only the adsorption–desorption and surface reactions are possible.

Aerosols provide large surface-area to volume ratios (Heimenz, 1986; Lyklema, 1995) allowing most of their constituents to be concentrated on their surfaces. It is estimated that for a spherical particle of 1 μm in diameter about 1 percent of molecules will be at the surface. Under similar assumptions, the percentage of molecules at the surface reaches 100 when the particle diameter is 3 nm (Finlayson-Pitts, 2009). Hence, as the particle size decreases, the influence of surface chemistry becomes even more important. The varying size distribution (~ 1 nm to ~ 100 μm) and composition of aerosols (Finlayson-Pitts, 2009; Seinfeld and Pandis, 2006) make systematic understanding of its surface chemistry challenging (Prather et al., 2008). To better understand these complex systems, integration of field, laboratory, and theoretical studies has been emphasized (Finlayson-Pitts, 2009; Prather et al., 2008). In fact, selective investigation of even planar surfaces, such as an air/water interface, is experimentally difficult. The progress in this research area is dynamic and beyond the scope of this review. The significance of this issue, however, lies in the following questions: do the surface and heterogeneous interactions play a role in mercury cycling and, if so, what steps must be taken to reduce the uncertainty in model predictions?

2.2. Evidence of mercury surface and heterogeneous chemistry

The major surfaces interacting with mercury species are aerosols, cloud droplets, and interfaces such as snow, lake and ocean surfaces as well as soil, vegetation, and DOM in aquatic environments. These interfaces are sites for redox reactions and mercury exchange with the atmosphere. While a large volume of field and laboratory studies have been reported, only select examples representing different types of surface interactions are presented. A comprehensive line of evidence can be found elsewhere (Ariya et al., 2009a).

2.2.1. Mercury and atmospheric particles

In the atmosphere, mercury is assumed to be in the form of gaseous elemental mercury (GEM), reactive gaseous mercury (RGM) or gaseous oxidized mercury (GOM), and particulate mercury (Hg_p). RGM or GOM, and Hg_p are only operationally defined terms and are further discussed later in this review with respect to the uncertainties in mercury chemical speciation. Hg_p is likely to encompass solid or liquid materials which may be either homogeneous or heterogeneous with respect to physical and/or chemical composition or shape (Lynam and Keeler, 2005). Particulate-phase mercury, which range from sub-micrometers to a few micrometers in size (Keeler et al., 1995), are generally sampled using aerosol filtration techniques which embed many measurement errors (Lynam and Keeler, 2005). Although the observation of Hg_p is a strong indication that mercury species do interact with atmospheric surfaces, adequate characterization of the adsorption process and speciation of mercury for different compositions of aerosols are only beginning to emerge. These studies are reviewed in section 3.

2.2.2. Mercury in snow packs

Snow packs are matrices which resemble heterogeneous chemical systems, providing large surface areas for mercury

transformation and exchange to occur and have been shown to play an important role in mercury depletion events (Steffen et al., 2008). It has been demonstrated that in suburban and temperate areas, about 50% of mercury is released to the atmosphere as a result of photo-reduction of Hg^{2+} to Hg^0 in the snow pack by natural sunlight (Lalonde et al., 2002). Snow in forested areas with diverse vegetations surfaces exhibits higher levels of mercury than snow in more open areas, such as frozen lake surfaces, where photo-reduction can occur more efficiently (Poulain et al., 2007b,d). Laboratory simulation of Hg^0 emissions from heterogeneous snow packs also revealed that oxidized mercury, Hg^II , can have a shorter lifetime in snow (Dommergue et al., 2007). Oxidation of elemental mercury by Br and Cl radicals is also prominent in snow packs and on aerosol ice surfaces (Lindeberg et al., 2002). A recent review article (Durnford and Dastoor, 2011) discusses further examples and implications of mercury chemistry on snow surfaces.

2.2.3. Mercury interaction in surface waters

Ocean and lake surfaces are known to be major sites for mercury exchange at a global scale. About 39% of global emissions of Hg^0 may occur at the ocean surface (Mason and Sheu, 2002) with chemical transformations of Hg^{2+} to Hg^0 occurring predominantly due to photochemical reduction (Rolfhus and Fitzgerald, 2004). Oxidation of elemental mercury is also prevalent at the seawater surface and is influenced by halogen chemistry (Lalonde et al., 2001; Sheu and Mason, 2004). Enhanced photo-reduction of Hg^{2+} ions dominates near the surface of lakes (Amyot et al., 1994) and is possibly mediated by heterogeneous mixtures of DOC (Fitzgerald et al., 2007) such as iron(III) (Zhang and Lindberg, 2001), humic acid substances (Allard and Arsenie, 1991), and microbes (Siciliano et al., 2002) present in lakes. The importance of microbial mediate reduction of oxidized mercury in interfacial waters has also been reported (Poulain et al., 2007a,c). These observations imply that surface water, which accounts for up to 50% of natural mercury emissions (Pirrone et al., 2008; Pirrone and Mason, 2009), may be influenced by heterogeneous or interfacial chemistry. It has been suggested that further investigations are required to better evaluate the role of sea spray and formation of dissolved gaseous mercury (DGM) in the top water micro-layer, both of which drive the gaseous mercury exchange mechanisms at the air–water interface (Pirrone et al., 2008). Direct investigation of mercury chemistry occurring at the air–water interface is lacking, partly due to the difficulty in probing interfacial mercury species, reactants, intermediates and products selectively.

2.2.4. Additional sites for heterogeneous and surface enhanced chemistry – soil, vegetation, and plumes

Soil represents a complex chemical system as diverse compositions of reactants, moisture, pH, and sorption properties make it a site where heterogeneous reactions can occur. Mercury chemistry in the presence of soil is poorly understood. Mercury air–soil exchange has been recognized as an important component of the mercury cycle (Grigal, 2002; Xin and Gustin, 2007). It has been shown that in untreated soils mercury can exist as spherical particles covered with a thin layer of $\text{HgO}_{(\text{s})}$ and/or $\text{HgSO}_{4(\text{s})}$, preventing Hg^0 to vaporize (Taube et al., 2008). Plant/air interfaces are a site of both passive and active exchange of Hg^{2+} and Hg^0 . Atmospheric particulate mercury and RGM have been shown to adsorb on leaf surfaces through dry deposition (Hanson et al., 1995) whereas stomata actively take up Hg^0 (Lee et al., 2000). Leaf surfaces have also been shown to be a site of photochemical transformation of deposited Hg^{2+} to Hg^0 . Lastly, enhanced surface chemistry pertaining to interactions of particles in volcanic (Glasow, 2010) and power plant (Edgerton et al., 2006; Lohman et al., 2006) plumes is being recognized as having a dominant impact on mercury cycling.

3. Modeling uncertainties pertaining to mercury surface and heterogeneous chemistry

The fundamental importance of surface and heterogeneous chemistry, along with the direct and indirect observations highlighted in the previous section, goes to show that mercury–surface interactions in the atmosphere and the environment can plausibly affect the global cycling of mercury. This entails that mercury models must incorporate surface effects. Consequently, the quantitative analysis of mercury surface chemistry, which would yield appropriate chemical parameters to be implemented in the models, is necessary. The chemical processes and mechanisms that require systematic investigations are: (1) proper chemical identification of mercury compounds in the gas and aqueous phase, (2) adsorption of gaseous or aqueous mercury to specific surfaces and their subsequent identification, (3) complex formation and phase transitions leading to mercury speciation in heterogeneous mixtures, and (4) rates of reactions at or in contact with these surfaces.

Acknowledging that the current understanding of the corresponding chemical parameters is limited and hence is a source of uncertainty, laboratory-based experiments and modeling studies are facilitating progress in this area. To the best of our knowledge, theoretical investigation of mercury–surface interactions is missing. Integrating the findings of all these approaches has the potential to reduce modeling uncertainties of mercury cycling. In this section, we discuss in detail the chemical parameters of interest, highlight recent scientific advances, and suggest future research directions.

3.1. Mercury speciation in the gas and aqueous phase

It is recognized that knowledge of the different forms or speciation of atmospheric mercury is crucial for predicting its surface adsorption and deposition and understanding its biogeochemical cycling (Horvat, 2005; Landis et al., 2005). However, existing methods of determination provide limited information on the chemical identification of mercury compounds. Currently, based on measurement techniques, mercury is categorized as: gaseous elemental mercury ($\text{Hg}^0_{(\text{g})}$), gaseous oxidized mercury (GOM) (or most commonly known as reactive gaseous mercury (RGM)), and particulate mercury, Hg_p . The chemical composition of RGM is not characterized but based on limited physicochemical properties and laboratory measurement techniques it is assumed to be gaseous oxidized mercury (Hg^{II}) complexes such as $\text{HgCl}_{2(\text{g})}$, HgBr_2 , and HgOBr (Mason, 2009) and references therein.

There are numerous reports of uncertainty associated with these measurement techniques for RGM and Hg_p in gas and aqueous phases (Horvat, 2005; Jokai and Fodor, 2009; Lyman et al., 2010; Lynam and Keeler, 2005; Malcolm and Keeler, 2007). Accordingly, the composition of different atmospheric Hg species remains poorly understood. Do these particles constitute Hg^{II} , Hg^0 , even transient Hg^{I} intermediate complexes, or a mixture of them? Are these mercury species adsorbed at the surface or dissolved in the aqueous compartment of aerosols? How are they formed, i.e., do Hg^0 and Hg^{II} compounds initiate particle formation or do they adsorb onto other particles? And if the latter is true, with what affinity do these species bind to different types of aerosols? These are some of the fundamental questions that need to be addressed to properly understand the impact of mercury–surface interactions on its global cycling. But identifying individual mercury compounds in atmospheric particulate matters should be the primary focus in order to elucidate the chemistry they would exhibit in the gas phase.

3.2. Adsorption of mercury and mercury compounds to natural surfaces

The first step for mercury to undergo a surface reaction is adsorption. Here we distinguish the process of adsorption from deposition and scavenging by particles. For instance, chemical species can either exhibit physisorption or chemisorption. In physisorption, a most common type of adsorption process for gas and aqueous species, weak Van-der-Waals type forces are involved whereas chemisorption is governed by formation of new chemical bonds (Adamson and Gast, 1997). Experimental determination of physisorption requires obtaining an adsorption isotherm curve and calculation of free energy of adsorption. From this point of view, adsorption of elemental mercury and mercury compounds from the gas phase to the surface of aerosols, ice, or clouds has yet to be studied.

Reports of Hg^{II} adsorption to different sorbents, mostly irrelevant to the atmosphere, in the aqueous phase (Budinova et al., 2003; Karabulut et al., 2001; Manohar et al., 2002; Sanchez-Polo and Rivera-Utrilla, 2002; Seigneur et al., 1998; Xiao and Thomas, 2004; Yin et al., 1997) have been reviewed earlier (Lin et al., 2006). From these studies, it is apparent that due to the heterogeneous nature of particles in their physical and chemical properties, such as size distribution, surface charge density and chemical constituents, it is difficult to obtain reliable information on mercury adsorption onto these particles. The inconsistency in these adsorption constants is of four orders of magnitude (Lin et al., 2006). Interestingly, this exceeds the uncertainty of most existing gas phase kinetic rate constants discussed in part I of this review.

Experimental investigations have demonstrated that RGM adsorption/partitioning strongly depends on the composition of the aerosol particles. Preferential partitioning of RGM to dry NaNO_3 , KCl and NaCl particles has been identified and RGM was observed to favor the gas phase for ammonium sulfate and organic aerosols (Rutter and Schauer, 2007b). Table 1 lists the measured partitioning coefficients for these particles along with other chemical parameters involving surface and heterogeneous interactions. Additional studies showed that partitioning was strongly dependent on temperature (Rutter and Schauer, 2007a). Based on desorption enthalpies RGM was shown to exhibit weak chemisorptions rather than physisorption for ambient particles investigated. However, specific chemical bonding was not confirmed. A separate study showed strong affinity of HgCl_2 , presumably one of the major components of RGM, for sea salt (NaCl) aerosols (Malcolm et al., 2009). In situ investigation of aerosols from the lower stratosphere has suggested that particulate mercury in this region originated locally from the gas phase rather than being transported there (Murphy et al., 2006). Interestingly, this study suggested some support for the growth of particles less than 20 nm initiated by mercury. Although semi-quantitative, this study provides some insight into a possible mechanism of Hg_p formation in the atmosphere.

3.3. Gas–liquid partitioning of mercury – inaccurate use of Henry's constant

The Henry's Law constant, K_H , describes the partitioning of chemical species from the liquid to gas phase (or vice versa). For quick reference, some of the common Henry's law constants used in mercury modeling are listed in the appendix (Table A.1). However, it is often not recognized that these values only hold true for pure two-phase systems (Levine, 2002). Atmospheric water droplets and aerosol particles are known to contain organic and bioorganic chemicals and high concentrations of halide ions, which can

Table 1

List of some chemical parameters not incorporated in models or recently determined.

Chemical parameters	Mathematical expressions or values	References
Gas-particle partitioning coefficients	$K_p = \frac{[\text{Hg}^{2+}\text{X}]_{(p)}}{[\text{Hg}^{2+}\text{X}]_{(g)}} \left(\frac{\text{m}^3 \text{ of air}}{\mu\text{g of particles}} \right)$ <p>TPM = Total particle mass Range of K_p values: NaCl + HgCl₂ (20–30), NaNO₃ + Hg(NO₃)₂ (300–600), KCl + HgCl₂ (30–200), (NH₄)₂SO₄ + HgCl₂ (1–8)</p>	(Rutter and Schauer, 2007b)
Salting coefficients	$k_s = \frac{1}{C_s} \log \left(\frac{C_0}{C} \right)$ <p>K_s values: NaCl (0.079), NaNO₃ (0.062), Na₂SO₄ (0.308), NaBr (0.017), KCl (0.07), NaClO₄ (0.117)</p>	(Sanemasa et al., 1981)
Henry's constant	<p>For pure water $K_H = \exp[-2404.3/T + 6.92]$ For 1.5M NaCl $K_H = \exp[-1871.6/T + 5.28]$</p>	(Andersson et al., 2008)
Complex formation	$\text{Hg}_{(aq)}^{2+} + \text{DOM}_{(aq)} \rightleftharpoons \text{Hg} - \text{DOM}_{(aq)}$ $K_f \sim 0.22\text{--}1028$	(Miller et al., 2007)
Heterogeneous reduction of Hg ^{II} by SO ₂	$k \leq 6.0 \times 10^{-17} \text{ molecules cm}^{-3} \text{ s}^{-1}$	(Seigneur et al., 2006)

influence the solubility of mercury and mercury compounds. Therefore, the use of Henry's constants corresponding to a pure gas and liquid phase is not suitable in such scenarios (Finlayson-Pitts and James N. Pitts, 1986). In sea salt aerosols, the Cl[−] ion concentration can reach up to 5 M (Hedgecock and Pirrone, 2005). The following investigations highlight the importance of using accurate Henry's constants for elemental mercury for the cases of sea salt aerosols and ocean waters.

The effect of salt type and concentration on Hg⁰ solubility at 25 °C has been reported for salt concentrations up to 1M (Sanemasa et al., 1981). The salt effect parameters, k_s , for selected electrolyte solutions are provided in Table 1. Based on the mathematical expression given, $C/C_0 = 10^{-k_s C_s}$, the solubility ratio as a function of salt concentration, C_s , for elemental mercury for some salt solution relevant to aerosol and seawaters has been plotted in Fig. 2a. In this expression, C and C_0 correspond to Hg⁰ solubility in electrolyte and pure aqueous solution, respectively. Although it was not clear if saturation was achieved in all solutions or if Hg⁰ was subject to oxidation (Clever et al., 1985), this study clearly indicated that solubility of Hg⁰ was reduced in the presence of salt. This effect is greatest for Na₂SO₄ salt and decreases for NaCl > NaNO₃ > NaBr. The question, however, remains of whether salting out led Hg⁰ in these solutions to adsorb at the air/water interface or escape into the gas phase.

A recent investigation (Andersson et al., 2008) determined Henry's constants of mercury for an artificial sea salt solution and a solution containing 1.5 M NaCl which is of relevance to atmospheric waters in coastal areas. The empirical equations that were determined describing the Henry's constant of mercury for the seawater, which was found to be the same as pure water, and 1.5 M NaCl solutions for the temperature range of 5 °C to 35 °C are given in Table 1. Based on this result, it is apparent that at 25 °C the K_H of mercury in 1.5 M NaCl solution is greater by factor of approximately 1.2 compared to its K_H in pure water. This implies that when a liquid phase containing high levels of Cl[−] ions (note that this is a typical situation in aerosols) the mercury content in the gas phase will be higher compared to a Henry's constant for a pure two phase system. This was explained by the salting out effect. The absence of salting out in artificial seawater was not investigated but the presence of magnesium and calcium in seawater was attributed as a possible cause (Andersson et al., 2008). It was also shown that at lower temperature less mercury is likely to be dissolved in the salt solution (see Fig. 2b).

3.4. Mercury speciation in heterogeneous mixtures – mercury complexes and solids

Mercury complex formation predominantly occurs in the aqueous phase, which can be found in environmental waters, atmospheric water droplets, and aerosols. Table A.1 showcases selected chemical equilibria of complexes along with the corresponding stability constant, K_f , relevant to the mercury cycling.

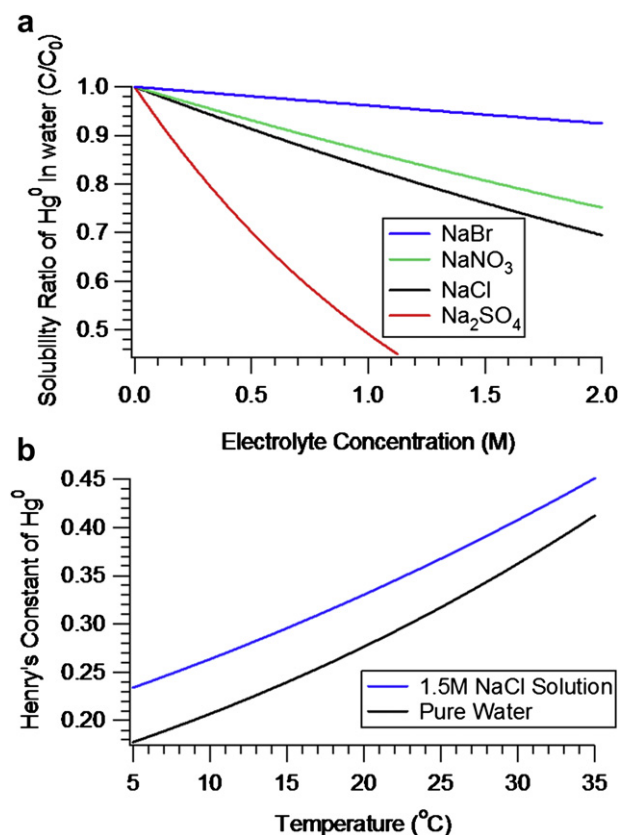


Fig. 2. The effect of salt type and concentration on the solubility of elemental mercury (a) and the effect of temperature on Henry's constant of Hg⁰ (b).

Although only a limited number of mercury complex equilibria are incorporated in the models, they are suitably representative of most atmospheric conditions. This section highlights some of the assumptions with complex formations and provides other hypothetical complex and solid formations.

Aqueous Hg^{2+} concentrations are much smaller relative to the concentrations of the ligands present in environmental waters and atmospheric water droplets. The total ligand concentration is the determining factor that predicts which complex will form. The ligand concentration can vary throughout the aqueous phase. Therefore, knowledge of the concentration profile of these ligands in different environments is important to predict mercury complex formation accurately. Currently, because of their large stability constants and relatively high abundance in atmospheric water droplets, chloride and sulfite (SO_3^{2-}) ions are considered to be important ligands (Erel et al., 1993; Lin et al., 2006; Schell et al., 1997; Seinfeld and Pandis, 1997). Complexes of Hg^{2+} with nitrate (NO_3^-) and sulfate (SO_4^{2-}) are considered to have negligible contribution to mercury cycling due to their small binding stability which is on the order of 10^0 – 10^3 (Lin et al., 2006). Moreover, HgCl_2 is assumed to be the primary form of Hg^{II} in the aqueous phase because the lifetime of S(IV) is only a few hours (Lin et al., 2006). For conditions with higher halide ion concentration, complex formation of the type HgX_4^{2-} , where $\text{X} = \text{Br}^-$, Cl^- , or I^- , are very likely, at least, at neutral pH. Some recent models do incorporate these complexes associated with Br and Cl (Hedgecock et al., 2005).

In general, complexes involving Hg^{2+} ion are considered. Complexation with Hg^0 is also possible. Evidence of complexes of Hg^0 with dissolved organic matter (DOM) is emerging (Bian et al., 2010). The implication of the Hg^0 -DOM complex formation on mercury cycling has yet to be explored. The presence or lack of oxygen in the aquatic environment can also influence the speciation of mercury. For instance, inorganic sulfides (HS^-) bind very strongly to $\text{Hg}^{2+}_{(\text{aq})}$ in anoxic environments and influence its bioavailability for microbial methylation (Benoit et al., 1999; Miller et al., 2007; Ravichandran, 2004). Organic ligands and dissolved organic matter can also bind to mercury very strongly (Ravichandran, 2004; Zhang, 2006). Although the concentrations of organic ligands and DOM are not significant in atmospheric droplets, their influence on mercury speciation is noteworthy in aquatic environments. The published stability constant for mercury binding with DOM varies from $10^{4.7}$ to $>10^{30}$. However, more recent studies suggest that the stability constant should be within 10^{22} to 10^{28} (Miller et al., 2007). The six orders of magnitude of uncertainty in this parameter has been attributed to the heterogeneous nature of DOM and the different approaches used to determine these constants (Miller et al., 2007; Ravichandran, 2004). To the best of our knowledge, mercury complex formation equilibria with DOM in environmental water interfaces are not been taken into account in atmospheric models.

In sedimentation and aquatic environments, particle formation from pure mercury or mercury compounds is also possible. Namely, there is an evidence of spherical particles in the soil with elemental mercury, $\text{Hg}^0_{(\text{l})}$, in the core (Taube et al., 2008). This is possible because liquid mercury exhibits high surface tension, 485.5 mN m^{-1} at 25°C (CRC, 2010). A few studies also suggest the formation of nanoparticles of oxidized mercury compounds. Formation of $\text{HgS}_{(\text{s})}$ nanoparticles in natural waters has been reported (Deonaraine and Hsu-Kim, 2009; Gondikas et al., 2010; Slowey, 2010). Their stability and structural organizations are heavily dependent on DOM concentration. Evidence of nanoparticles of HgI_2 , HgBr_2 , and HgCl_2 also exists (Shaopu et al., 2002). However, their formation in atmospheric conditions needs to be verified. Further evaluation of these mercury solid nanoclusters is

necessary with respect to their impact on global cycling of mercury throughout the ecosystem.

3.5. Heterogeneous redox reactions

In most atmospheric models, the reduction of oxidized mercury (Hg^{II}) species to Hg^0 is assumed to occur only in the aqueous phase. Furthermore, particulate mercury, Hg_p , is treated as chemically inert and it is assumed to have no influence on mercury redox reactions (Seigneur et al., 2006). The aqueous phase, present in the form of clouds, fog, and rain, serves as the effective media for mercury reduction reactions in the atmosphere. Some aerosols containing approximately 30–50% water by mass can also provide sufficient aqueous phase and heterogeneous reactions to occur. In addition to atmospheric water droplets, environmental waters can also host a multitude of mercury complexes which can undergo reduction reactions. The possibility exists that the rate of oxidation can accelerate when atmospheric heterogeneity and surfaces are taken into account. Further, mercury solid complex formation (see section 3.4) along with subsequent sedimentation can serve as an additional removal pathway for mercury. The identification and accurate determination of Hg^{II} reduction pathways, which can counterbalance the loss of Hg^0 , become important in order to accurately depict mercury cycling in the atmosphere.

The reduction of Hg^{II} , the most stable oxidized form of mercury, depends on the specific complexes it forms in the aquatic environment (Lin and Pehkonen, 1997; Munthe et al., 1991). It is recognized that photo-reduction pathways of Hg^{2+} involving various halides and organo- Hg^{2+} complexes can occur via ligand-metal charge transfer upon UV light absorption (Griffiths and Anderson, 1991; Horvath and Vogler, 1994; Kunkely et al., 1997). Solar radiation can cause mercury compounds to react directly or indirectly by generating precursors that subsequently react with the mercury. Electronic transitions for most mercury complexes occur below 298 nm which is not available in the lower atmosphere. Despite this fact, as mentioned earlier, spectral shift can occur when these complexes are adsorbed on atmospheric particle surfaces. In such a scenario, efficient absorption of light can occur and photoreduction may proceed. Some of the complexes such as iodo-mercurate complexes absorb light in the near-UV region but their presence in atmospheric water droplets is not likely. As a result, photoreduction processes of these mercury complexes are not considered in atmospheric models (Lin and Pehkonen, 1999). Organic ligands such as formate, acetate, and oxalate complexes of mercury are currently deemed to play a minimal role in the reduction of Hg^{2+} under atmospheric conditions because they require UV irradiation (Pehkonen and Lin, 1998).

Another potential reduction process that is missing from atmospheric models is the reaction of mercury in environmental waters and in soils in the presence of heterogeneous mixtures of DOM. Dissolved organic matter binds strongly to mercury (section 3.4) and can enhance the reduction of oxidized mercury. Much evidence has been documented of enhanced reduction of $\text{Hg}^{2+}_{(\text{aq})}$ initiated by microorganisms or humic substances in the presence or absence of light (Ravichandran, 2004; Zhang, 2006). These reduction mechanisms have been found to be strongly influenced by pH and concentrations of dissolved oxygen, chloride and mercury. The presence of dissolved organic compounds and DOM enhances the photoreduction of mercury. However, subsequent re-oxidation of a portion of oxidized mercury in the presence of selected dissolved organic compounds, instead of volatilization of elemental mercury, has also been observed (Si and Ariya, 2008). Naturally found iron particles, such as goethite, hematite, and maghematite, along with organic compounds can also influence the redox chemistry of mercury (Lin and Pehkonen, 1997; Ravichandran, 2004; Zhang,

Table 2

Summary of the uncertainties in the chemical parameters important in mercury atmospheric models.

Chemical parameters	Key points	Research questions/future directions
Henry's constants K_H	<ul style="list-style-type: none"> Henry's law constant holds for pure two phase dilute solutions and is not applicable for atmospheric water droplets and aerosol particles, which contain inorganic and organic species. Recent studies are providing new information pertaining to atmospheric and environmental chemistry on the influence of non-ideal solutions on the Henry's law constant. 	<ul style="list-style-type: none"> Determination of K_H values applicable to aerosol and other non-ideal solutions should be continued. The updated Henry's constant should be implemented in mercury models.
Adsorption constant K_{ad}	<ul style="list-style-type: none"> Mercury is known to adsorb to many different surfaces. The reported values of K_{ad} show a wide range of inconsistency and are not relevant to atmospheric surfaces. Adsorption is the first step for surface reactions to occur. 	<ul style="list-style-type: none"> What are the adsorption mechanisms for different mercury compounds to the surfaces of aerosol, ice, clouds, sea water, plants, etc? What is the influence of these surfaces on the reactions of mercury?
Complex formation constants K_f	<ul style="list-style-type: none"> Hg^0, Hg^I, and Hg^{II} form complexes with numerous inorganic and organic ligands in the aqueous phase. These complexes can exhibit photochemical reactivity. Complex formation of mercury with dissolved organic matter (DOM) is strong in environmental water. Complex formation is dependent on pH, temperature, and ligand concentration. 	<ul style="list-style-type: none"> What are the mercury complexes formed inside the heterogeneous mixture of aerosols? What is their photochemical reactivity? Organic/biological matter is also found in aerosols. What is its contribution in mercury complex formation? Investigation and incorporation of pH, temperature, and ligand concentration profiles in atmospheric models.
Rate constants k	<ul style="list-style-type: none"> An in-depth analysis of available rate constants is presented in part I of this review 	<ul style="list-style-type: none"> Investigation of surface and heterogeneous reactions of mercury is imperative in minimizing uncertainties in the atmospheric modeling of mercury.

2006; Zhang and Lindberg, 2001). These potentially relevant reactions involve complex heterogeneous chemistry that are poorly understood and will require scientific focus in order to accurately depict the atmospheric cycling of mercury.

Lastly, solid–gas heterogeneous reduction of $HgO_{(s)}$ by $SO_{2(g)}$ was apparently observed with formation of Hg_2SO_4 , turning into HgS and $HgSO_4$ adsorbates (Scott et al., 2003). However, the reaction was deemed to be complex. Unfortunately, no further experimental or theoretical study exists for this reaction. The impact of this reaction in power plant and volcanic plumes, where heterogeneous particle and $SO_{2(g)}$ are available, can be significant (Glasow, 2010; Lohman et al., 2006; Vijayaraghavan et al., 2008). The implication of this reduction pathway has been tested and is discussed in the following section. It is important to note that indication of heterogeneous oxidation of Hg^0 in the presence of $SO_{2(g)}$ in flame has also been reported (Schofield, 2004). This implies that heterogeneous redox reaction of mercury in flue gases is complicated and needs to be thoroughly investigated.

4. Recent advances in modeling – impact of mercury heterogeneous and surface chemistry on mercury fate and transport

Recent modeling studies have begun incorporating surface effects. Surface resistance parameters for deposition velocity, which in turn depend on the properties of the surface and depositing species (Lin et al., 2007; Yarwood et al., 2003), are included in current models. To simulate the observed evasion fluxes of mercury, temporally and spatially resolved natural mercury emissions from vegetation, water surfaces and soils have been developed based on a simplified mechanistic (Bash et al., 2004) or a regression (Lin et al., 2005) model. Developments in Environment Canada's atmospheric mercury model (GRAHM) include evasion of mercury from the snow pack as a function of solar radiation. This model is also being coupled to terrestrial and ocean models to better depict surface interactions (Dastoor and Davignon, 2009; Dastoor et al., 2008). A recent review (Bash et al., 2007) evaluates some of the existing models for treating air-surface processes. However, these models only describe the physical processes, such as mercury evasion and deposition, but not the biogeochemistry that mercury exhibits at these surfaces.

Due to lack of experimental data and broad uncertainties, adsorption of mercury to aerosol particles from the fundamental perspective as described here are not used in models. However, similar pathways have recently been incorporated. In some cases it is assumed that 50/50 partitioning takes place between gaseous Hg^{II} and aerosol phase (Holmes et al., 2010). Modeling studies implementing the hypothetical reduction of mercury in power plant plumes with SO_2 have shown to improve model performance (Lohman et al., 2006; Vijayaraghavan et al., 2008). The empirically derived rate constant of this reduction, $k = 6.0 \times 10^{-17}$ molecules $cm^{-3} s^{-1}$ (Seigneur et al., 2006), also leads to a significant shift of mercury chemical speciation in volcanic plumes (Glasow, 2010). Interestingly, this heterogeneous reduction of Hg^{II} has not been well studied and is thus subject to uncertainty.

5. Concluding remarks

The discrepancy between measured and modeled concentrations of atmospheric mercury is likely a combination of a range of factors including (but not limited to) the uncertainties in measurements, emission inventories and mercury chemistry used in the models. With regard to measurements, possible sources of uncertainty are: RGM caught as $Hg^0_{(g)}$, ozone interference resulting in underestimation of RGM, that the true composition and fraction of RGM captured by the Tekran system is unknown, and improper emission inventories. As an example, primary mercury species emissions from anthropogenic sources, particularly point sources such as coal fired power plants, used in the models have significantly higher proportions of oxidized mercury at the stack ($Hg^0:Hg^{II}$ ratio of ~60:40) compared to what is measured at the observation sites downwind. This indicates either emission speciation at the stack is wrong as presented in the inventories or there is reduction following emission. Uncertainties in chemistry predominantly involve missing processes such adsorption of mercury species to particle surfaces and heterogeneous reductions in plumes and at the surfaces of atmospheric and environmental particles.

To realistically describe the transformation and transport of mercury throughout the atmosphere, accurate knowledge of physical and chemical parameters that describe the atmospheric processes along with field observations are essential. In this two part review, we discussed the sources of uncertainties that exist in

the currently available chemical kinetic parameters (part I) and addressed the influence of atmospheric and environmental surfaces and heterogeneity on mercury chemistry (part II). The uncertainties associated with the chemical parameters critical in describing mercury chemistry in the atmosphere are summarized in Table 2. This table also lists the immediate research areas that must be pursued in order to minimize the current uncertainties in mercury models. It is apparent that accurate simulation of mercury cycling entails complete parameterization of mercury heterogeneous chemistry. However, due to a lack of knowledge in mercury surface chemistry, it is a major source of uncertainty in the existing atmospheric models. Along with the implementation of chemical processes for which information is available but not currently

included in the models, integration of field measurements, laboratory experiments and theoretical calculations pertaining to mercury–surface interactions bear the potential of greatly reducing the uncertainties that are currently present in the models.

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Appendix

Table A.1

Selected chemical equilibria relevant to mercury chemistry. Source: (Bullock, 2005; Lin et al., 2006; Lin and Pehkonen, 1999; Seigneur et al., 2009, 2006) and references therein.

Complex formation equilibrium	Equilibrium expression	K_f
$\text{Hg}_{(\text{aq})}^{2+} + 2\text{Cl}_{(\text{aq})}^- \rightleftharpoons \text{HgCl}_{2(\text{aq})}$	$\frac{[\text{HgCl}_2]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{Cl}^-]_{\text{aq}}^2}$	10^{14} M^{-2}
$\text{Hg}_{(\text{aq})}^{2+} + \text{SO}_3^{2-}(\text{aq}) \rightleftharpoons \text{HgSO}_3(\text{aq})$	$\frac{[\text{HgSO}_3]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{SO}_3^{2-}]_{\text{aq}}}$	$5 \times 10^{12} \text{ M}^{-1}$
$\text{HgSO}_3(\text{aq}) + \text{SO}_3^{2-}(\text{aq}) \rightleftharpoons \text{HgSO}_3^{2-}(\text{aq})$	$\frac{[\text{HgSO}_3]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{SO}_3^{2-}]_{\text{aq}}}$	$2.5 \times 10^{11} \text{ M}^{-1}$
$\text{Hg}_{(\text{aq})}^{2+} + \text{OH}_{(\text{aq})}^- \rightleftharpoons \text{HgOH}_{(\text{aq})}^+$	$\frac{[\text{HgOH}^+]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{OH}^-]_{\text{aq}}}$	$4.0 \times 10^{10} \text{ M}^{-1}$
$\text{HgOH}_{(\text{aq})}^+ + \text{OH}_{(\text{aq})}^- \rightleftharpoons \text{Hg}(\text{OH})_{2(\text{aq})}$	$\frac{[\text{Hg}(\text{OH})_2]_{\text{aq}}}{[\text{HgOH}^+]_{\text{aq}}[\text{OH}^-]_{\text{aq}}}$	$1.6 \times 10^{11} \text{ M}^{-1}$
$\text{Hg}_{(\text{aq})}^{2+} + 2\text{Br}_{(\text{aq})}^- \rightleftharpoons \text{HgBr}_{2(\text{aq})}$	$\frac{[\text{HgBr}_2]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{Br}^-]_{\text{aq}}^2}$	$1.9 \times 10^{17} \text{ M}^{-2}$
$\text{Hg}_{(\text{aq})}^{2+} + \text{OH}_{(\text{aq})}^- + \text{Br}_{(\text{aq})}^- \rightleftharpoons \text{HgOHBr}_{(\text{aq})}$	$\frac{[\text{HgOHBr}]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{OH}^-]_{\text{aq}}[\text{Br}^-]_{\text{aq}}}$	$5.0 \times 10^{19} \text{ M}^{-2}$
$\text{Hg}_{(\text{aq})}^{2+} + \text{OH}_{(\text{aq})}^- + \text{Cl}_{(\text{aq})}^- \rightleftharpoons \text{HgOHCl}_{(\text{aq})}$	$\frac{[\text{HgOHCl}]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{OH}^-]_{\text{aq}}[\text{Cl}^-]_{\text{aq}}}$	$1.8 \times 10^{18} \text{ M}^{-2}$
$\text{Hg}_{(\text{aq})}^{2+} + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{HgCO}_3(\text{aq})$	$\frac{[\text{HgCO}_3]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{CO}_3^{2-}]_{\text{aq}}}$	$1.0 \times 10^{11} \text{ M}^{-1}$
$\text{Hg}_{(\text{aq})}^{2+} + 2\text{HS}_{(\text{aq})}^- \rightleftharpoons \text{Hg}(\text{HS})_{2(\text{aq})}$	$\frac{[\text{Hg}(\text{SH})_2]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{HS}^-]_{\text{aq}}^2}$	$5.0 \times 10^{37} \text{ M}^{-2}$
Aqueous-gas equilibria	Equilibrium expression	K_H
$\text{Hg}_{(\text{g})}^0 \rightleftharpoons \text{Hg}_{(\text{aq})}^0$	$\frac{\text{Hg}_{(\text{g})}^0}{\text{Hg}_{(\text{aq})}^0}$	9.1 atm M^{-1}
$\text{HgCl}_{2(\text{g})} \rightleftharpoons \text{HgCl}_{2(\text{aq})}$	$\frac{\text{HgCl}_{2(\text{g})}}{\text{HgCl}_{2(\text{aq})}}$	$7.1 \times 10^{-7} \text{ atm M}^{-1}$
$\text{Hg}(\text{OH})_{2(\text{g})} \rightleftharpoons \text{Hg}(\text{OH})_{2(\text{aq})}$	$\frac{\text{Hg}(\text{OH})_{2(\text{g})}}{\text{Hg}(\text{OH})_{2(\text{aq})}}$	$8.3 \times 10^{-5} \text{ atm M}^{-1}$
$\text{HgO}_{(\text{g})} \rightleftharpoons \text{HgO}_{(\text{aq})}$	$\frac{\text{HgO}_{(\text{g})}}{\text{HgO}_{(\text{aq})}}$	$3.7 \times 10^{-13} \text{ atm M}^{-1}$
$\text{HgBr}_{2(\text{g})} \rightleftharpoons \text{HgBr}_{2(\text{aq})}$	$\frac{\text{HgBr}_{2(\text{g})}}{\text{HgBr}_{2(\text{aq})}}$	$3.6 \times 10^{-7} \text{ atm M}^{-1}$
$\text{Hg}_{(\text{aq})}^{2+} + 2\text{HS}_{(\text{aq})}^- \rightleftharpoons \text{HgS}_2\text{H}_{(\text{aq})}^- + \text{H}_{(\text{aq})}^+$	$\frac{[\text{HgS}_2\text{H}^-]_{\text{aq}}[\text{H}^+]_{(\text{aq})}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{HS}^-]_{(\text{aq})}^2}$	$3.2 \times 10^{31} \text{ M}^{-1}$
$\text{Hg}_{(\text{aq})}^{2+} + 2\text{HS}_{(\text{aq})}^- \rightleftharpoons \text{HgS}_2^{2-} + 2\text{H}_{(\text{aq})}^+$	$\frac{[\text{HgS}_2\text{H}^-]_{\text{aq}}[\text{H}^+]_{(\text{aq})}^2}{[\text{Hg}^{2+}]_{\text{aq}}[\text{HS}^-]_{(\text{aq})}^2}$	1.6×10^{23}
$\text{Hg}_{(\text{aq})}^{2+} + \text{HS}_{(\text{aq})}^- \rightleftharpoons \text{HgSH}_{(\text{aq})}^+$	$\frac{[\text{HgSH}^+]_{\text{aq}}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{HS}^-]_{(\text{aq})}}$	$1.6 \times 10^{30} \text{ M}^{-1}$
$\text{Hg}_{(\text{aq})}^{2+} + \text{HS}_{(\text{aq})}^- \rightleftharpoons \text{HgS}_{(\text{aq})} + \text{H}_{(\text{aq})}^+$	$\frac{[\text{HgS}]_{\text{aq}}[\text{H}^+]_{(\text{aq})}}{[\text{Hg}^{2+}]_{\text{aq}}[\text{HS}^-]_{(\text{aq})}}$	1.0×10^{26}

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