Topological Analysis of Phase Equilibria in the Hg – H₂O System

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Abstract. The analysis of the joint stability of phases and valence forms of mercury in the Hg – H₂O system in the \( \lg f_{\text{O}_2} - 1/T \) coordinates for the temperature range from -50 to +360°C was carried out by method of F. Schreinemakers. Analysis of equilibrium valence forms showed that for the composition of fluid phases, the non-autonomy of the oxide film as a phase on the surface of liquid mercury is key.

1 Introduction

The valence states of mercury are well known: Hg(0), Hg(I) and Hg(II), whose domination in natural environments is determined by the redox conditions. Therefore, the choice of oxygen fugacity as a decisive intensive parameter, along with temperature, was inevitable when analysing phase relationships. Consideration included 6 phases: L₁ - liquid mercury phase, L₂ - liquid aqueous phase, G - gas, I - ice of water, S₀ - solid elemental mercury and S₁ - mercury (II) oxide. The phase of the composition of Hg₂O (S₂) and the reasons for its instability, as well as the nature of the thermodynamic instability of the solid phase Hg(OH)₂, are considered. When analysing the stability, it was not necessary to resort to the methods of complete topological analysis [1-3]; it was enough to use the existing thermochemical bases and well-known equilibrium constants of the forms of mercury. The specific problem of the stability of the CO₂-5.75H₂O compound, carbon dioxide gas hydrate, was solved, which for the first time in world practice allowed us to show [1, 2] the inevitability of formation and stability of this gas hydrate on the polar caps of Mars. The return to this approach is caused by loud publications [4, 5] about mercury content in permafrost, in the ice sheets of the Earth, in the absence of good versions of the nature of these inputs, phase forms of immobilization and the reality of secondary emission.

2 Research methods

An analysis of the joint stability of phases and valence forms of mercury in the Hg - H₂O system in the coordinates \( \lg f_{\text{O}_2} - 1/T \) was performed by the F. Schreinemakers method [6]. For the Hg - H₂O multisystem, the key task was the analysis of the compositions of the
phases and the dominant dissolved complexes under the monovariant equilibrium $L_1L_2G$ (Fig. 1), where both liquid phases change with varying $fO_2$ and temperature.

Fig. 1. Mercury solubility as a function of temperature.

In water, the main forms are $\text{Hg}^{(aq.)}$, the neutral hydroxocomplexes $\text{Hg}_2^{2+}(OH)^{2-}$ and $\text{Hg}^{2+}(OH)^{2-}$ with complete dominance of the complex - $\text{Hg}^{(I)}$. The presence in the aqueous phase of all three valence states at atmospheric $fO_2 = 0.208$ and the well-studied [7] tendency of mercury mineral phases to form structures with the covalent pair $-\text{Hg} - \text{Hg}-$, also well known. The surface of $\text{Hg}^{(liq.)}$ coated with non-autonomous oxide film up to $110^\circ$C and $\text{Hg}_2\text{O}$, $\text{HgO}$ - minerals do not dissolve in $\text{Hg}^{(liq.)}$. We are developing this version for the first time, but the lack of experimental data on the composition of the phase $G$ forces us to resort to both topological analysis for water solution $L_2$ and oxide film with variable oxygen fugacity and temperature. The end point equilibrium $L_1L_2G$ is a nonvariant point $IL_1L_2G$ with parameters very close to the triple point of water ($T = -0.01^\circ$C and $lg P = -2.236$), and the stability of the three water phases with liquid mercury is beyond doubt (Fig. 1). The second such non-invariant point $S_0IL_1G$, is an analogue of the mercury triple point with well-known tabulated $P-T$ parameters ($T = -38.8344$, $lg P_{\text{atm}} = -9.25664$) + plus ice water. Third nonvariant points are $S_0IHG$ -point is the last (lower temperature) point of the final decomposition of the gas hydrate: $H \rightarrow I + S_0$ about 120 K, when for this reaction decomposition of the solid phases $\Delta V = 0$. Sublimation of two solid phases $I + S_0 \rightarrow G$ occurs: up to lowest temperatures [1, 3] ($\leq 120$ K) and water fugacity where effect of the sublimation on reaction $I + S_0 \rightarrow G$ is observed. All results of topological analysis are based on thermochemical data of particles and phases in a consistent system [8]. Using the data of standard energies of formation, the ratio of the molality of the three dominant valence forms was calculated: $\text{Hg}^{0(aq.)}$, $\text{Hg}_2^{2+}(OH)^{2-}$ and $\text{Hg}^{2+}(OH)^{2-}$ with the well-known (Fig. 1), repeatedly studied value of gross solubility ($lg m_\Sigma$). The dashed line in Fig. 1 is the line of temperature dependence of the Henry’s constant $\text{Hg}$ in terms of its fugacity with endless dilution $\text{Hg}^{\Theta(aq.)}$ (Fig. 1, 2). This calculation through the standard values of the
free energy of formation should be carried out by the reaction: \( \text{H}_2\text{O} + 0.5 \text{O}_2 + \text{Hg}_2(\text{OH})_2^0 \rightleftharpoons 2\text{Hg} (\text{OH})_0^0 \), but taking into account the fugacity of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) \((0.5 \log f_\text{O}_2 = -0.341)\). In this case, the molality of forms in water \((L_2)\) is equal to: \( \log m (\text{Hg}^0(\text{aq.})) = -8.01 \) [5]; \( \log m (\text{Hg} (\text{OH})_2^0) = -8.351 \) and \( \log 2m (\text{Hg}_2(\text{OH})_2^0) = -6.518 \).

![Fig. 2. The extremality of the Henry’s constant for Hg\(^0\) - 1/T in detailed coordinates, our data.](image)

A new task is the approach to the problem of instability of the Hg(0) gas hydrate, that is, the clathrate compound of mercury. The choice between the clathrate compound Hg\(\cdot\)5.75H\(_2\)O of mercury and Hg\(_2\)O\(_2\)5.75H\(_2\)O turned out to be a non-trivial task for similar values of the enthalpies according to the rules of supramolecular chemistry [9] and small values of the enthalpies of clathrate decay.

### 3 Results and discussion

All valence forms common in natural waters contrast with their solubility and migration mobility. Elementary mercury due to low solubility [10] (solubility of elemental mercury in the form of \( \text{Hg}^0(\text{aq.}) \) at 25°C is \( 0.977\cdot10^{-8} \text{ mol/l} \), but with total (gross) solubility the sum of three valence forms, that is, mercury dominates in the aqueous phase in the form of a hydroxocomplex of \( \text{Hg}_2(\text{OH})_2^0 \), \( \text{Hg} (\text{OH})_2^0 \) and \( \text{Hg}^0(\text{aq.}) \). The shift of the equilibrium in the presence of a zero-valent form is easily carried out both in the natural setting and under the anthropogenic impact. Any shift of equilibrium towards the formation of Hg(II) in the presence of Hg(I) leads to the generation of Hg(0), which either accumulates in the droplet liquid phase or enters the atmosphere as a gas vapor phase. Also, when Hg(II) binds to well-known chloride complexes, in the presence of liquid mercury, it requires a corresponding decrease in the concentration of the Hg\(_{2}\)\(^{2+}\) ion when the disproportionation equilibrium shifts to the right with the formation of liquid mercury and the Hg\(^{2+}\) ion. Taking into account the above, when assessing the geochemical situation, it is important to determine not so much the gross composition as the relationships between the various valence forms of mercury that control the subtle mechanisms of geochemical migration. Therefore, in the practice of analytical work it is necessary to have methods to calculate the shares of valence forms, or to determine them. The
task of analytical, (that is, preparative) separation of oxidized forms of mercury from the elementary form is insoluble due to the complete thermodynamic lability of all redox and hydration equilibria. Another problem of experimental geochemistry in studying the cycle of mercury is the question of how much an elementary mercury vapor can be hydrated in solution and in the gas phase. According to our data, elemental mercury in the form of Hg\textsuperscript{0}(aq.) is practically insoluble in water [10]. There is reason to believe that the value of 2.2 ng/l is somewhat overestimated, but under normal conditions (“standard atmosphere”) of the oxidizing environment with oxygen fugacity of 0.208 atm, the saturation of water upon contact with liquid mercury is provided by the hydroxo complex Hg(OH)\textsuperscript{2+}, and most importantly, Hg\textsubscript{2}(OH)\textsubscript{2} (up to 60 μg/l). First, elemental mercury itself, by its own chemical properties, should be close to other noble metals, whose solubility is 2 orders of magnitude lower, demonstrates duality of behaviour and causes a relatively high the ability to oxidize. Secondly, as we see (Fig. 1), it is in the high-temperature region, when Hg(0) begins to absolutely prevail over the oxidized forms and the \textit{lg} \textit{m} – 1/T dependence becomes an extremely simple linear function. and the solubility of mercury near room temperature does not give this dependence, that is, the concentration is too high compared with a linear law, which is associated with the appearance of already analytically significant quantities of oxidized forms of mercury, compared to Hg(0). So, using our data on the solubility of Hg(0) in a reducing environment [10] and tabulated data on vapor pressure over liquid mercury, it is easy to calculate the Henry’s constant (Fig. 2), as standard fugacity [11]. The exaggerated values of the Henry’s constant given in the literature, which are close to the constants of highly hydrated hydrogen sulfide and carbon dioxide, are associated precisely with the overestimation of the concentration of elemental mercury in calculating its solubility from the values of the so-called “solubility of liquid mercury”, which are usually given in the literature (Fig. 1). Exactly, it is these values, that demonstrate large concentrations of "supposedly elemental mercury" in solution due to the presence of dominant and better soluble forms of mercury of another valence state.

On first step we interpret this phase transition as a reaction for the formation of gas hydrate (H) from mercury vapor Hg(0) according to a simple scheme: Hg(g) + 5.75 H\textsubscript{2}O (g) = H, where H = Hg\textsubscript{5.75}H\textsubscript{2}O. According to [1-3] our topological analysis of the stability of gas hydrates in the systems H\textsubscript{2}O - CO\textsubscript{2} and H\textsubscript{2}O - H\textsubscript{2}S, the temperatures of the inevitable complete decomposition of solid solutions are close to 121 K (-150°C) and 126 (-147°C), respectively, and are controlled by the approach of saturated pressures steam over the “guests” molecules (CO\textsubscript{2}, H\textsubscript{2}S and Hg\textsubscript{2}O\textsubscript{2}) and ice water as the “host”. A reliable estimate of the lower temperature stability of Hg\textsubscript{5.75}H\textsubscript{2}O (H) without experimental data is difficult, but as a first approximation is possible. If, following [5], it is assumed that global accumulation (and preservation) of mercury (4 ppt) occurs in permafrost, but in the form of this gas hydrate, that is, it is entirely due to its stability with known thermodynamic fugacity Hg (0), corresponding to the content in the “standard air”, 2.2 ng/m\textsuperscript{3}, that is, with a partial pressure of Hg = 2.46\texttimes 10\textsuperscript{-13} in the air, and comparing this value with the content of mercury (4 ppt \texttimes \textit{X} = 3.6\texttimes 10\textsuperscript{-13} in permafrost ice, it is easy to calculate the typical composition of the gas hydrate Hg\textsubscript{6.05}H\textsubscript{2}O (H), but different from the theoretical, which corresponds to the complete filling of the structural cavities: Hg\textsubscript{2}O\textsubscript{2}\textsubscript{5.75}H\textsubscript{2}O.

Next step. The difference between the theoretical composition and the actually observed in the permafrost is due to the choice of the wrong stoichiometry. The real composition of gas hydrate Hg\textsubscript{2}O\textsubscript{2}\textsubscript{5.75}H\textsubscript{2}O and not Hg\textsubscript{6.05}H\textsubscript{2}O. After this transition operation, there is complete agreement between the stoichiometric and observed content (4 ppt) in permafrost.

Text analogies and references to the H\textsubscript{2}O - CO\textsubscript{2} system and the polar caps of Mars are absolutely not accidental. There are deep analogies between the migration of carbon dioxide and the formation of its gas hydrate on Mars, and another, but very similar process, which controls a stable level of mercury in the Earth’s atmosphere and permafrost.
An analysis of the equilibria of valence forms showed that, for the composition of the liquid phases, the non-autonomy of the oxide film as a phase on the surface of liquid mercury is key [5]. Their simultaneous participation in geochemical processes and the mercury cycle demonstrates the features of migration and distribution of valence forms of mercury in the atmosphere, hydrosphere and lithosphere.

4 Conclusions

1. Accumulation (and preservation) of mercury in permafrost occurs mainly in the form of ice-stabilized monovalent mercury gas hydrate (metal cycle O-Hg-Hg-O for each 5.75 H₂O). Its decay during the melting of ice serves as a source of valent forms entering the atmosphere: Hg (0), Hg (I) and Hg (II), but during the processes of redox-disproportion in the atmosphere, atomic vapors Hg (0) accumulate.

2. The Hg₂O₂- and HgO - oxides are easily hydrated and removed from the atmosphere by wet deposition, what determines short-period local changes in mercury content [12]. In gas hydrate structure transmutation: Hg₂O₂ → 2 HgO is a second-order phase transition, also.

3. The topological analysis of phase equilibria and the formation of dominant valence forms of mercury is preferably carried out in terms of oxygen and water fugacity, as relation (\(\lg f_{O_2}/\lg f_{H_2O}\)), which makes it possible to more reasonably refine the coordinates of nonvariant points and experimentally unexplored monovariant equilibria. Additional clarifying experiments are needed.

4. Key factor in the analysis of the structure of phase diagram in system Hg – O is the fact of non-autonomy of the oxide film on the surface of metallic mercury, which is associated with its place in the electrochemical activity range and its hydrophobicity, as well as the standardization of elemental mercury solution through the Henry constant [10] for GL₂ equilibrium line (in terms of the fugacity of elemental mercury), which allows us to determine the temperature dependence using the Krichevsky-Kazarnovsky equation. of Hg₂O₂:5.75 H₂O is only a usual tracer of formation of CO₂, N₂ and O₂ - hydrates in the atmosphere.

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References

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