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Thermodynamics and kinetics of gaseous metal hydroxide formation from oxides relevant to power and propulsion applications



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ABSTRACT

The thermodynamics and kinetics of gaseous metal hydroxide formation from simple oxides important for power and propulsion applications are reviewed. The transpiration technique for determining thermodynamics of gaseous metal hydroxide is highlighted. The status of thermodynamic data for $\text{CrO}_2(\text{OH})_2(\text{g})$, $\text{Si}(\text{OH})_4(\text{g})$, and $\text{Al}(\text{OH})_3(\text{g})$ in available databases is described. A thermodynamic argument is presented for the trend that gaseous metal hydroxides with more $-\text{OH}$ groups will have a greater pressure dependence and a lower temperature dependence of reaction from their condensed phase oxide than those gaseous metal hydroxides with few $-\text{OH}$ groups. Finally, the need for thermodynamic data for Ti-, Mn-, Y-, and Ta-gaseous metal hydroxides is summarized.

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1. Introduction

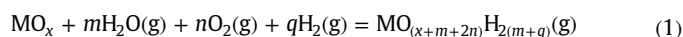
Structural metals and ceramics utilized in high temperature propulsion and power applications can react with water vapor present in these environments to form gaseous metal hydroxides, thereby consuming the underlying material at unacceptably high rates. The thermodynamics and kinetics of these reactions have been under study for many years [1,2]. Available thermodynamic data have been recently reviewed [3]. This paper focuses on a subset of these species that are particularly important for materials in power and propulsion applications in which water vapor is present at high partial pressures, on the order of 1 bar and higher. The objectives of this paper are to review 1) the thermodynamics and rate limiting step for gaseous metal hydroxide formation; 2) experimental methods to determine thermodynamics and kinetics of gaseous metal hydroxide formation at relatively high water vapor partial pressures; 3) current status of available data in thermodynamic databases; 4) thermodynamic trends for formation of gaseous metal hydroxides; and 5) gaps in available data for technologically relevant materials.

2. Gaseous metal hydroxide formation

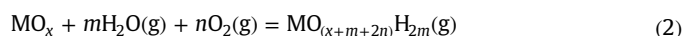
2.1. Thermodynamics

A generic reaction can be written for gaseous metal hydroxide

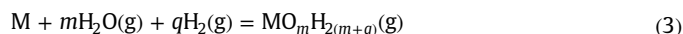
formation as given by Eq. (1).



where M stands for any metal. This reaction can be utilized for metal oxides forming gaseous metal hydroxides in oxidizing $\text{O}_2(\text{g})\text{--H}_2\text{O}(\text{g})$ mixtures typical of combustion environments where $q=0$, given in Eq. (2), as will be the focus of this paper.



In addition, an appropriate reaction can be realized for metals reacting to form gaseous metal hydroxides in more reducing $\text{H}_2(\text{g})\text{--H}_2\text{O}(\text{g})$ gas mixtures where x and n in Eq. (1) are both set equal to zero, as given by Eq. (3).



Given an unknown gaseous metal hydroxide formation reaction, the stoichiometry of the volatile species can be identified by systematically varying the reactant partial pressures for a material of known x and measuring the resultant partial pressure of the volatile species at constant temperature, so that m , n , and q can be identified.

$$P_{\text{MO}_{(x+m+2n)}\text{H}_{2(m+q)}} \propto P_{\text{H}_2\text{O}}^m \cdot P_{\text{O}_2}^n \cdot P_{\text{H}_2}^q \quad (4)$$

Once the identity of the gaseous metal hydroxide species is known, the temperature dependence of the reaction can be used to determine thermodynamic data for the reaction. An expression

for the equilibrium constant, K , can be written as:

$$K = \frac{P_{\text{MO}_{(x+m+2n)\text{H}_2(m+q)}}}{a_{\text{MO}_x} \cdot P_{\text{H}_2\text{O}}^m \cdot P_{\text{O}_2}^n \cdot P_{\text{H}_2}^q} \quad (5)$$

Then using the Van't Hoff Equation or second law method, [4] the enthalpy ΔH and entropy ΔS of reaction (1) can be determined from the slope and intercept of a plot of the natural log of the equilibrium constant versus inverse temperature in degrees Kelvin:

$$\ln K = -\frac{\Delta H_{rxn}}{RT} + \frac{\Delta S_{rxn}}{R} \quad (6)$$

Alternatively, if the structure, mass, vibrational frequencies, and electronic energy levels of the gaseous metal hydroxide are known or estimated, the Gibbs Energy Function, Δg_{efT} , can be calculated by evaluating the partition function of the gas molecule [4,5]. A third law determination of the enthalpy of reaction can be calculated from each experimentally determined equilibrium constant data point using Eq. (7) [4].

$$\frac{\Delta H_{rxn}}{T} = -R \ln K - \Delta g_{efT} \quad (7)$$

Assuming thermodynamic data exist for all the reactants, the enthalpy of formation and absolute entropy for the gaseous metal hydroxide species can be calculated at the experimental temperature. If the heat capacity of the gaseous metal hydroxide can be calculated by again evaluating the partition function of the molecule, the enthalpy of formation and absolute entropy for the gaseous metal hydroxide species can be calculated at 298 K providing the data needed for inclusion in thermodynamic data bases.

2.2. Kinetics

Once thermodynamic data are available to calculate the equilibrium partial pressures of gaseous metal hydroxides formed from a metal or metal oxide in high temperature water vapor-containing environments of technological interest, the kinetics of the solid-gas reaction are needed to predict material lifetimes. Reactions forming gaseous products can be limited by 1) transport of reactants to the surface, 2) the surface reaction, or 3) transport of the gaseous products away from the surface. The first type of limiting kinetics – transport of reactant inward – is typically observed when the reactant partial pressure is low, as for example in the studies of iron oxidation in nitrogen with small amounts of oxygen [6]. Most power and propulsion environments operate at pressures of one bar or greater with high partial pressures of water vapor, thus reactant transport to the surface is not limiting. Surface reaction limiting kinetics are typically observed at low temperatures, as for well-known carbon, silicon and SiC oxidation studies [7–10]. Temperatures in power and propulsion applications are high such that surface reactions occur rapidly. Gaseous metal hydroxides in steam-containing power and propulsion environments typically form at low partial pressures ($< 10^{-3}$ bar). Volatilization reactions are therefore typically limited by transport of the gaseous metal hydroxide species outward through the reactant gas boundary layer rather than by reactant transport inward through the gaseous boundary layer or surface reaction rates.

Product gas transport through a laminar gas boundary layer is shown in Fig. 1 assuming a flat plate geometry for simplicity. In this case, the flux of volatile species, J , is given by: [11]

$$J = 0.664 Re^{1/2} Sc^{1/3} \frac{D\rho}{L} \quad (8)$$

where Re is the dimensionless Reynolds number describing flow characteristics in the gaseous boundary layer, Sc is the

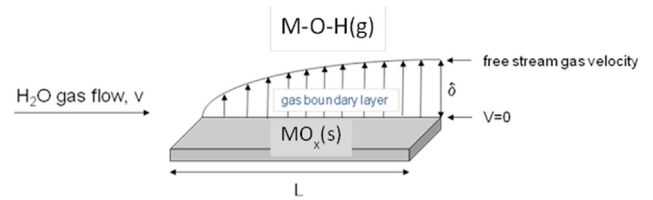


Fig. 1. Gas boundary layer formation over a flat plate.

dimensionless Schmidt number describing transport characteristics in the gaseous boundary layer, D is the interdiffusion of the gaseous metal hydroxide in the O_2 – H_2O boundary layer, ρ is the density of the gaseous metal hydroxide derived from the equilibrium partial pressure of the gaseous metal hydroxide, and L is the characteristic dimension of the flat plate in the flow direction. The Reynolds and Schmidt number can be expanded as follows:

$$J = 0.664 \left(\frac{\rho' v L}{\eta} \right)^{1/2} \left(\frac{\eta}{\rho' D} \right)^{1/3} \frac{D\rho}{L} \quad (9)$$

where ρ' is the gas density of the boundary layer, v is the free stream gas velocity, η is the boundary layer gas viscosity, and all other terms have been previously defined.

Note that as the gas velocity increases, the gas boundary layer thickness, δ , will decrease and the flux of volatile species will increase with the square root of the gas velocity. The flux of the gaseous metal hydroxide species will increase with pressure according to the stoichiometric coefficients of the reactants in Eq. (1), while the interdiffusion coefficient D is inversely proportional to the total pressure. The overall pressure dependence varies with each gaseous metal hydroxide, as will be described in Section 5 below. Finally, the temperature dependence of the flux arises from the temperature dependence of the gaseous metal hydroxide formation reaction and is therefore related to the enthalpy of reaction given by Eq. (1). From Eqs. (5) and (6), and at constant reactant partial pressures, the following relationship for the temperature dependence can be written:

$$P_{\text{MO}_{x+m+2n}\text{H}_2(m+q)} \propto \exp\left(-\frac{\Delta H_{rxn}}{RT}\right) \quad (10)$$

The temperature dependence of the gaseous diffusion coefficient is weak, $T^{3/2}$, relative to the exponential dependence of the enthalpy of formation given by Eq. (10), and can therefore be neglected.

3. Experimental techniques for characterizing gaseous metal hydroxide formation

The predominant gaseous metal hydroxide species observed are a strong function of the overall system pressure. Thus techniques used to study formation of these species most relevant to power and propulsion applications are those which can be conducted at high pressures (≥ 1 bar). This section features three techniques most relevant for these high pressure conditions: transpiration, high pressure sampling mass spectrometry, and thermogravimetric analysis.

3.1. Transpiration technique

In Section 2.1 of this paper, it was stated that the equilibrium constant for reaction (1) could be obtained by determining the temperature dependence of the equilibrium constant as given by Eq. (5). However, the stoichiometry of the gaseous metal hydroxide vapor species (coefficients m , n , and q , as appropriate) must

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