

EXPERIMENTAL DETERMINATION OF THERMODYNAMIC PROPERTIES OF Ca-, Al- and Si-HYDROXIDE GAS MOLECULES AND APPLICATION TO THE SOLAR NEBULA; A. Hashimoto, Harvard-Smithsonian Center for Astrophysics, Cambridge, MA 02138, USA

The standard model nebula containing the elements in cosmic proportions [1] has approximately two oxygens and one carbon for every 3,000 hydrogen atoms. As a result, the partial pressures of H_2O and CO are about one thousandth that of H_2 at temperatures $>500\text{K}$. Major metallic elements such as Mg, Si, Fe, Ca and Al, whether in the gaseous or condensed states, are only 1/20-1/100 times as abundant as the H_2O molecule. Under these circumstances the gaseous hydroxide species $\text{M}(\text{OH})_n$ may be more abundant than the metallic (M) and oxide (MO_x) gas species combined, if the temperature of the nebula is not very high. However, the classic calculation of gas-mineral equilibria for the standard model nebula, the "condensation sequence" [2], did not consider the molecular species $\text{Fe}(\text{OH})_n$ ($n=1,2$), $\text{Ca}(\text{OH})_n$ ($n=1,2$), $\text{Al}(\text{OH})_n$ ($n=2,3$), or $\text{Si}(\text{OH})_n$ ($n=1-4$).

Recent studies of chondrules and Ca,Al-rich inclusions (CAIs) in chondritic meteorites have shown that the redox states recorded by their minerals are far more oxidizing than the canonical average oxygen fugacity of the standard model nebula [3]. There are two major effects an oxidizing environment would have on the state of metallic elements in the nebula, compared with their situation in a gas of cosmic composition: (1) the abundance of metallic and oxygen-deficient metal-oxide molecules in the gas phase would be diminished, as a result of their conversion into solid oxides by reaction with the increased oxygen; (2) the abundances of hydroxide gas species would increase as a result of enhanced H_2O pressure (which results from the increased oxygen fugacity of the nebula). Therefore hydroxide molecules might be the predominant metal-containing gas species, even at high temperatures, in regions of the nebula that were more oxidizing than the standard model assumes.

A quantitative estimate of how the inclusion of hydroxide gas species would affect the calculation of gas-mineral equilibria depends critically on the quality of the thermodynamic data available for these species. Unfortunately, however, among hydroxides of the five major metallic elements mentioned above, precise values of entropy and heat of formation are known only for $\text{Mg}(\text{OH})_2(\text{g})$ [4] and $\text{Fe}(\text{OH})_2(\text{g})$ [5].

An experimental investigation I began four years ago [6] is now complete, and this paper reports determinations of the heat of formation and entropy for $\text{Ca}(\text{OH})_2(\text{g})$, $\text{Al}(\text{OH})_3(\text{g})$, and $\text{Si}(\text{OH})_4(\text{g})$, the hydroxide species expected to be most abundant under the physical conditions assumed by current astrophysical theories. These thermodynamic properties can be derived from the vapor pressures of the species named, in equilibrium with solid calcium-, aluminum-, and silicon-oxides (respectively) in an atmosphere containing $\text{H}_2\text{O}(\text{g})$. The so-called transpiration technique was used to determine these vapor pressures; as an example of the technique, I describe measurement of the vapor pressure of $\text{Ca}(\text{OH})_2$. A controlled mixture of O_2 and H_2O at 1 atm is flowed through a noble-metal reaction cell containing solid CaO at the experimental temperature. The gas reacts with solid CaO , becomes saturated with $\text{Ca}(\text{OH})_2$ vapor species, then flows out of the cell through a long cool noble-metal tube where the $\text{Ca}(\text{OH})_2$ condenses on the walls as the oxide or hydroxide. The condensate is dissolved in acid, its Ca content measured by ion chromatography, and the amount of Ca vaporized per unit of gas flowed through is determined. From this the vapor pressure of the hydroxide species is calculated, using the equation of state for ideal gases. The heat of formation for $\text{Ca}(\text{OH})_2(\text{g})$ is then derived from the vapor pressure by the thermodynamic third-law method, and the heat of formation and entropy by the second-law method.

The temperature ranges investigated were 1225-1500°C, 1250-1475°C, and 1100-1500°C for Ca, Al and Si, respectively. Good linear correlations were observed between $\log(\text{vapor pressure})$ of Ca, Al and Si species and $\log(\text{H}_2\text{O pressure})$ of the gas flow at constant temperatures. Slopes of the lines obtained, 0.99 ± 0.05 (2σ) (close to 1), 1.49 ± 0.06 (~ 1.5), and 1.94 ± 0.09 (~ 2), respectively, indicate that the vapor species detected were $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and $\text{Si}(\text{OH})_4$. Insensitivity of results to the flow rate (over a range of 5x) shows that equilibrium was maintained in the cell. The thermodynamic quantities derived by the two methods agree very well (their average values shown in Table 1), vindicating the validity of the experiments.

These data (and literature thermodynamic data) were used to calculate the relative abundances of M, MO_x , and $\text{M}(\text{OH})_n$ gas species and the relative volatilities of Fe, Mg, Si, Ca and Al for ranges of temperature, total pressure (P_T), and H/O abundance ratios corresponding to plausible ranges of physical conditions in the nebula. Figure 1 shows the total vapor pressures of Si, Ca, and Al as a function of H/O abundance ratio for various temperatures, in a system with $P_T = 10^{-3}$ atm. In these figures vapor pressure curves are drawn as solid lines when the total vapor pressure is dominated by hydroxide vapor species, and as dashed curves when non-hydroxides (such as M and MO_x) predominate. As shown in the figures, non-hydroxide species dominate among all Si-bearing vapor species

Ca-, Al- and Si-HYDROXIDE GAS MOLECULES: Hashimoto, A.

(and also among all Mg- and Fe-bearing vapor species) at high and medium temperatures over the entire H/O range studied, while this is the case only at high temperatures and under reducing conditions for Al. Ca shows an intermediate trend.

If H/O varied locally during the evolution of the solar nebula, as the meteoritic evidence suggests it did, evaporation or condensation could occur even at constant temperatures, simply because of a change in H/O. At high temperatures, e.g., 1800K, all the elements except Fe become less volatile as $\log(\text{H/O})$ decreases from the solar value (3.16) to 0.3 (that for H_2O); this means that metal-bearing vapors would have tended to condense if the nebular environment became more oxidizing. The same trend continues for Si and Mg down to $\sim 900\text{K}$, while Ca and Al behave in the opposite way below 1200K and 1700K: their vapor pressures increase as $\log(\text{H/O})$ decreases. As a result Ca and Al would evaporate while Si and Mg condense if the physicochemical state of the nebula changed from reducing to oxidizing in the temperature range 900-1200K. Adoption of 10^{-6} atm as the total nebular pressure makes the stability fields of hydroxide vapors shift to lower temperatures, decreasing the critical temperatures at which the evaporation/condensation behaviors of the elements are reversed by 200-300K.

These results assist in understanding how the alteration of CAIs occurred in the nebula. Petrographic studies of the alteration zones of CAIs [7] indicate that Ca (and Al) were removed from them and Si, Mg, Fe, alkalis, Cl, Zn, H_2O , etc. were added. Several studies have concluded that the alteration temperature was $\sim 1000\text{K}$ or less [8]. Therefore, the removal and addition of these characteristic sets of elements during alteration of CAIs are very likely to have resulted from evaporation and condensation that occurred in the nebula when physical conditions changed from reducing to oxidizing at a moderate temperature.

REFERENCES: [1] Cameron, A.G.W. & Pine, M.R. (1973) *Icarus* 18, 377. [2] Grossman, L. (1972) *GCA* 36, 597. [3] Wood, J.A. (1988) *Ann. Rev. Earth Planet. Sci.* 16, 53; Fegley, B.Jr. & Palme, H. (1985) *EPSL* 72, 311. [4] Maeda, E. *et al.* (1978) *Yogyo-Kyokai-Shi* 86, 491. [5] Chase, M.W. *et al.* (1986) *JANAF*, 3rd ed. [6] Hashimoto, A. *et al.* (1987) *Meteoritics* 22, 405. [7] Wark, D.A. (1981) *LPS XII*, 1145. [8] Hutcheon, I.D. & Newton, R.C. (1981) *LPS XII*, 491; Barber, D.J. *et al.* (1984) *GCA* 48, 769. [9] Glushko, V.P. *et al.* (1978) "Thermodynamic Properties of Pure Substances".

Table 1. Heats of formation and entropies of gaseous hydroxides.

	$\text{Ca}(\text{OH})_2$		$\text{Al}(\text{OH})_3$		$\text{Si}(\text{OH})_4$	
	This work	Literature**	This work	Literature***	This work	Literature
ΔH_f° (kcal/mol)	-147.0 \pm 1.7	-146.0 \pm 9.0	-240.0 \pm 3.6	-242 \pm 24	-320.9 \pm 0.6****	--
S°_{298} (cal/mol-K)	68.0 \pm 1.9	68.2 \pm 2.0	75.0 \pm 1.9	72.0 \pm 3.4	141.6 \pm 0.3****	--

* Errors are 2σ . ** JANAF [5]. *** Glushko *et al.* [9]. **** At 1600K.

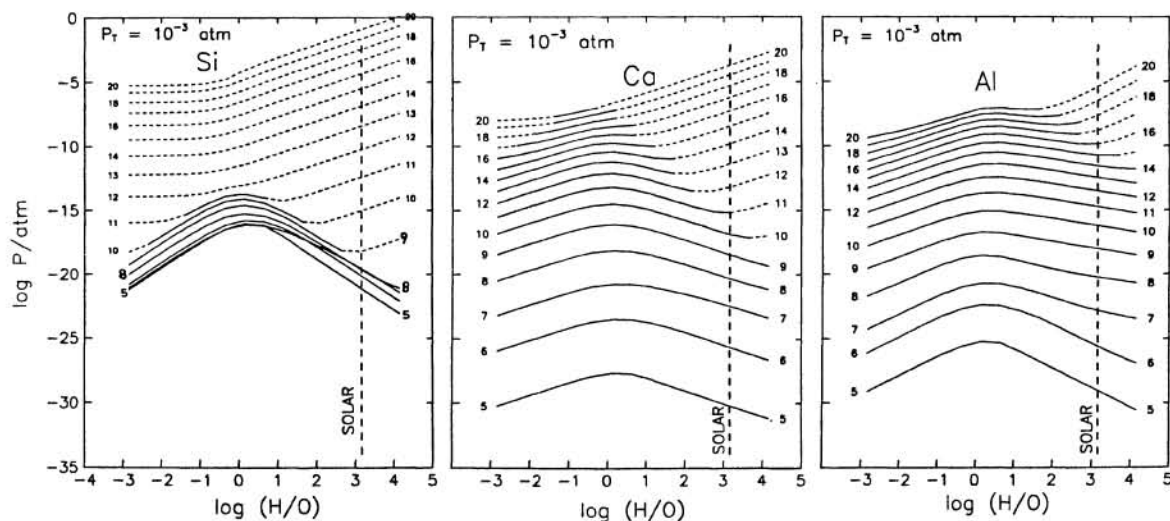


Figure 1. Total vapor pressures of Si, Ca, and Al as a function of the H/O abundance ratio in the model nebula. Pure oxides were assumed to be the only condensed phases in this calculation, to illustrate the relative volatilities of the elements. Solid lines indicate that hydroxide gas species dominate, dashed lines that non-hydroxide vapors do. Numbers in the figure are temperatures/100 (K). "SOLAR" indicates the solar H/O ratio.