Supporting information

Shock Wave Mediated Plume Chemistry for Molecular Formation in Laser Ablation Plasmas

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Thermodynamics of Al I reactions in air

The elementary gas phase reactions producing AlO and the net reaction are listed in Table S1 along with the standard enthalpy of reaction, ΔH^o_{rxn}, standard Gibbs free energy of reaction, ΔG^o_{rxn}, and the equilibrium constants, K_{eq}, for three high temperatures. K_{eq} is related to ΔG^o_{rxn} by

$$K_{eq} = e^{-\frac{\Delta G^O_{rxn}}{RT}} = \frac{\Pi_{prod}\, p_i{}^{n_i}}{\Pi_{react}\, p_i{}^{n_i}} \qquad (1)$$

and is also equal to the ratio of the products of the partial pressures of the products, p_i, raised to the power of the coefficient in the equation for the reaction, n_i, divided by a similar product for the reactants.

The first reaction in Table S1 is slightly endothermic, which results in a small increase in K_{eq} for the reaction with temperature. At these high temperatures, the increase in entropy as this reaction proceeds from left to right results in a negative change in Gibbs free energy, ΔG^o_{rxn}, and hence K_{eq} of about 11 over this temperature range. In contrast, the analogous reaction to form AlN from molecular nitrogen is highly endothermic ($\Delta H^o_{rxn} \cong 680\ kJ/mol$) with $K_{eq} \sim 10^{-5}$. The second elementary reaction is written to include a third body, which does not affect the thermodynamics, but is necessary for the formation of AlO for longer than fraction of a picosecond. This reaction is strongly exothermic but also produces a relatively large decrease in entropy in the forward direction, which results in a large increase in ΔG^o_{rxn} with temperature and K_{eq} changing from favoring products ($K_{eq} > 1$) at 3000K to favoring reactants at the higher temperatures. The thermodynamics of the net reaction, given in the third row of Table S1, are dominated by the second reaction; exothermic but with a decrease in entropy. Especially at higher temperatures, such as those expected at early times of plasma evolution, the thermodynamics do not favor these reactions fully depleting the reactants to form AlO. Most of the enthalpy and free energy release from burning aluminum is from subsequent reactions that remove AlO and form liquid Al_2O_3.

Table S1: Thermodynamic quantities for reactions producing AlO at temperatures of 4000K, 5000K, and 6000K at a standard pressure of 1 bar and are per mole of product. These values are derived from standard heats and free energies of formation given in the NIST-JANAF tables.[i] The upper temperature is the maximum for which necessary data are listed in these tables, while the lowest temperature is a lower bound for the temperatures seen in this work.

Reaction	#	ΔH_{rxn}^o (kJ/mol)				ΔG_{rxn}^o (kJ/mol)				K_{eq}			
		3000K	4000K	5000K	6000K	3000K	4000K	5000K	6000K	3000K	4000K	5000K	6000K
$Al + O_2 \rightleftarrows AlO + O$	(1)	1.0	7.3	11.3	13.1	-56.7	-77.0	-98.5	-120.7	9.7	10	10.7	11.2
$Al + O + M \rightleftarrows AlO + M$	(2)	-512.4	-507.7	-504.8	-503.5	-165.4	-50.4	63.5	177.0	760	4.6	0.22	0.03
$Al + \dfrac{1}{2}O_2 \rightleftarrows AlO$		-255.2	-250.2	-246.7	-245.2	-111.0	-63.7	-17.5	28.1	86	6.8	1.5	0.57
$AlO + O_2 \rightleftarrows AlO_2 + O$	(3)	105.9	102.6	100.6	99.1	88.1	82.6	77.9	73.5	0.029	0.083	0.15	0.23
$O + O + M \rightleftarrows O_2 + M$	(4)	-513.5	-515.0	-516.0	-516.7	-108.7	26.5	162.0	297.7	78	0.45	0.020	0.0026

Equilibrium Concentrations

Equations for finding the equilibrium partial pressures for the coupled reactions in Table S1 include two initial conditions, two equations for conservation of the aluminum and oxygen atoms, and four equilibrium equations. With only five variables, the partial pressures of Al, AlO, AlO$_2$, O$_2$ and O, and six equations this might seem to be an over determined problem. However, with the constraints on the ΔG_{rxn}^o values for the reactions, only three of the equilibrium expressions are independent.

Conservation equations

$$P_{Al} + P_{AlO} + P_{AlO_2} = P_{Al}^0 \tag{2}$$

$$2 \cdot P_{O_2} + P_O + P_{AlO} + 2 \cdot P_{AlO_2} = 2 \cdot P_{O_2}^0 \tag{3}$$

where P_i is the partial pressure of species i and P_i^0 is the initial partial pressure of species i before any reaction. Multiplying these two conservations equations by V/RT converts each term to moles. The initial conditions are the values of P_{Al}^0 and $P_{O_2}^0$.

Equilibrium equations

$$\frac{P_{AlO} \cdot P_O}{P_{Al} \cdot P_{O_2}} = K_{eq}^1 = \exp(-\frac{\Delta G_{rxn-1}^o}{R \cdot T}) \tag{4}$$

$$\frac{P_{AlO}}{P_{Al} \cdot P_O} = K_{eq}^2 = \exp(-\frac{\Delta G_{rxn-2}^o}{R \cdot T}) \tag{5}$$

$$\frac{P_{AlO_2} \cdot P_O}{P_{AlO} \cdot P_{O_2}} = K_{eq}^3 = \exp(-\frac{\Delta G_{rxn-3}^o}{R \cdot T}) \tag{6}$$

$$\frac{P_{O_2}}{(P_O)^2} = K_{eq}^4 = \exp(-\frac{\Delta G_{rxn-4}^o}{R \cdot T}) \tag{7}$$

where the numbers correspond to the equation numbers in the paper and are also in Table S1. The ratio of the second equation divided by the first equation gives the bottom equation.

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[i] http://kinetics.nist.gov/janaf/.