

### CE 561 Homework 3: (assigned 9/14/09, due 9/21/09)

Consider the reaction mechanism and (fictional) data for the decomposition of aluminum chloride ( $\text{AlCl}_3$ ) in the presence of hydrogen ( $\text{H}_2$ ) that are given below. The mechanism includes forward and reverse rate parameters for each reaction at 1300 K and 0.1 bar, except for the first reaction in the forward direction. Using the given mechanism and rate parameters, apply a non-linear least squares analysis to determine the forward rate coefficient for reaction 1. Plot the resulting model prediction for the  $\text{AlCl}_3$  profile along with the experimental data. Compute the sensitivity of the  $\text{AlCl}_3$  concentration profile to each of the rate constants in the mechanism. How does the sensitivity of the model results to the rate coefficient being determined compare to the sensitivity of the model results to the other rate coefficients? Comment on the effect of uncertainties in the other rate constants on the fitted value of the rate constant being measured.

#### Al-H-Cl Reaction Mechanism with Rate Parameters

Reaction Number.	Reaction	$k_f$ (1300 K, 0.1 bar)	$k_r$ (1300 K, 0.1 bar) <sup>c</sup>
1	$\text{AlCl}_3 \leftrightarrow \text{AlCl}_2 + \text{Cl}$	To be determined	$3.92 \times 10^{19} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
2	$\text{AlCl}_2 \leftrightarrow \text{AlCl} + \text{Cl}$	$1.54 \times 10^6 \text{ s}^{-1}$	$5.86 \times 10^{17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
3	$\text{AlHCl} \leftrightarrow \text{AlCl} + \text{H}$	$5.87 \times 10^9 \text{ s}^{-1}$	$9.78 \times 10^{15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
4	$\text{H}_2 \leftrightarrow 2 \text{ H}$	$1.43 \times 10^{-8} \text{ s}^{-1}$	$1.13 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
5	$\text{HCl} \leftrightarrow \text{H} + \text{Cl}$	$1.64 \times 10^{-7} \text{ s}^{-1}$	$3.91 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
6	$\text{AlHCl}_2 \leftrightarrow \text{AlCl} + \text{HCl}$	$1.77 \times 10^5 \text{ s}^{-1}$	$4.64 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
7	$\text{AlCl}_3 + \text{H} \leftrightarrow \text{AlCl}_2 + \text{HCl}$	$3.29 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$1.28 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
8	$\text{AlCl}_2 + \text{Cl}_2 \leftrightarrow \text{AlCl}_3 + \text{Cl}$	$2.20 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$9.45 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
9	$\text{AlHCl}_2 + \text{H} \leftrightarrow \text{AlCl}_2 + \text{H}_2$	$3.42 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$7.13 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
10	$\text{AlHCl}_2 + \text{H} \leftrightarrow \text{AlHCl} + \text{HCl}$	$1.26 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$1.99 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
11	$\text{AlHCl}_2 + \text{Cl} \leftrightarrow \text{AlCl}_2 + \text{HCl}$	$7.50 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$5.18 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
12	$\text{AlHCl} + \text{Cl}_2 \leftrightarrow \text{AlHCl}_2 + \text{Cl}$	$2.20 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$2.33 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
13	$\text{AlCl} + \text{HCl} \leftrightarrow \text{AlCl}_2 + \text{H}$	$3.07 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$1.92 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
14	$\text{AlCl} + \text{Cl}_2 \leftrightarrow \text{AlCl}_2 + \text{Cl}$	$5.18 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$5.42 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
15	$\text{AlHCl} + \text{H} \leftrightarrow \text{AlCl} + \text{H}_2$	$1.00 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$2.11 \times 10^2 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
16	$\text{AlHCl} + \text{Cl} \leftrightarrow \text{AlCl} + \text{HCl}$	$1.00 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$7.00 \times 10^1 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
17	$\text{Cl}_2 + \text{H} \leftrightarrow \text{Cl} + \text{HCl}$	$1.08 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$1.81 \times 10^6 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
18	$\text{H}_2 + \text{Cl} \leftrightarrow \text{HCl} + \text{H}$	$6.94 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$2.30 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

A plot of the fictional  $\text{AlCl}_3$  concentration vs. time data for initial conditions of 1300 K, 0.1 bar total pressure,  $\text{H}_2$  mole fraction of 0.99, and  $\text{AlCl}_3$  mole fraction of 0.01 is given on the following page. To download this data as a plain text file, in which the first column is the time and the second column is the  $\text{AlCl}_3$  concentration (in  $\text{mol}/\text{cm}^3$ ), click [here](#).

