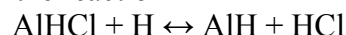


CE 561 Homework 5: (assigned 10/01/09, due 10/05/09)

- (1) Consider the reaction



for which high-level quantum chemistry calculations have been used to compute the energies and vibrational frequencies of the reactants, transition state, and products.

These calculations predict that the transition state is 3.3 kcal/mol higher in energy than the reactants, and the products are 18.9 kcal/mol lower in energy than the reactants (22.2 kcal/mol lower in energy than the transition state). These energy differences include zero-point energy, but not any thermal energy (they are energy differences at 0 K).

The vibrational frequencies and moments of inertia for the molecules were computed to be:

Species	Vibrational Frequencies (cm^{-1})	Moments of Inertia ($\text{amu} \text{ \AA}^2$)
AlHCl	495 552 1734	2.0 71.9 73.9
AlH	1596	2.7
Transition State	1275i 113 285 309 429 524	233 255 478
HCl	2845	1.6

Apply transition state theory to estimate the forward and reverse rate constants for this reaction at several temperatures ranging from 300 K to 2000 K. Fit the results to the modified Arrhenius form: $k = A T^b \exp(-E_a/RT)$. Note that AlHCl and the H atom are free radicals with one unpaired electron. Therefore, their electronic ground state has a degeneracy of 2.

- (2) Another possible reaction among the atoms involved in problem 1 above is the thermal decomposition of AlH_2Cl to $\text{AlH} + \text{HCl}$. In the high pressure limit, the first-order rate constant for this reaction is approximately $2 \times 10^{14} \exp(-32000/T)$, with T in Kelvins. Analyze the pressure dependence of this unimolecular decomposition reaction using the quantum Rice-Ramsberger-Kassel (QRRK) theory.
- What oscillator frequency (vibrational frequency) is required to match the experimental high-pressure pre-exponential factor?
 - Calculate the energy dependent rate constant $k(E)$ for energies from E_0 to $3E_0$.
 - Assuming a hard-sphere collision diameter of 3.0 \AA for AlH_2Cl , calculate the hard-sphere collision rate at 600, 1200, and 1800 K for pressures from 0.1 mbar to 10 bar. Assume that the reaction takes place under conditions where AlH_2Cl is present in very low concentrations in N_2 .
 - Prepare plots of $(k_{\text{uni}}/k_{\infty})$ vs. pressure from 0.1 mbar to 10 bar at temperatures of 600, 1200, and 1800 K, based on the QRRK predictions of the pressure dependence.