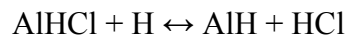


CE 561 Homework 5: (assigned 10/01/09, due 10/05/09)

(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 (amu Å 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.

I did this problem in a spreadsheet, shown below and linked [here](#).

Species	Vibrational Frequencies (1/cm)						Moments of Inertia (amu Å ²)		
AlHCl	495	552	1734				2	71.9	73.9
Transition State	1275i	113	285	309	429	524	233	255	478
AlH	1596						2.7		
HCl	2845						1.6		

Species	Vibrational Temperatures (K)						Rotational Temperatures (K)		
AlHCl	712.206	794.22	2494.9				12.12356	0.337	0.328
Transition State		162.58	410.06	444.59	617.25	753.93	0.104065	0.095	0.051
AlH	2296.3248						8.980416		
HCl	4093.386						15.15445		

Species	Vibrational Terms in Partition Function						Rotational Partition Function	Mass (amu)	Translational Partition Function (m ³)	Electronic Partition Function	Total Partition Function
AlHCl	1.103	1.076	1.000				7.95E+03	63.45	4.938E+32	2	9.32E+36
H								1.01	9.887E+29	2	1.98E+30
Transition State		2.390	1.342	1.294	1.146	1.088	4.11E+05	64.46	5.056E+32	1	1.08E+39
AlH	1.000						3.34E+01	28.00	1.447E+32	1	4.84E+33
HCl	1.000						1.98E+01	36.46	2.151E+32	1	4.26E+33

Forward barrier (kJ/mol)	13.8
Reverse barrier (kJ/mol)	92.9
Forward degeneracy	1
Reverse degeneracy	1
Forward Rate Constant (m ³ /s)	1.44E-18
Reverse Rate Constant (m ³ /s)	2.19E-32
Equilibrium Constant	6.57E+13

For convenience, I first converted the vibrational frequencies and moments of inertia to vibrational temperatures and rotational temperatures, defined as

Vibrational temperature: $\Theta_{v,i} = \frac{hc\bar{\nu}_i}{k}$, where h is Planck's constant (in J s), c is the speed of light (in cm/s), $\bar{\nu}_i$ is the i^{th} vibrational frequency (in cm^{-1}), and k is Boltzmann's constant (in J/K)

and

Rotational temperature: $\Theta_r = \frac{h^2}{8\pi^2Ik}$, where h is Planck's constant (in J s), k is Boltzmann's constant (in J/K), and I is the moment of inertia (one of three for nonlinear molecules) in kg m^2 . To convert I from amu \AA^2 to kg m^2 , you divide by Avagadro's number (to go from moles to molecules), divide by 10^{20} to go from \AA^2 to m^2 , and divide by 1000 to go from g to kg. Thus, overall, you divide the given values by 6.022×10^{46} .

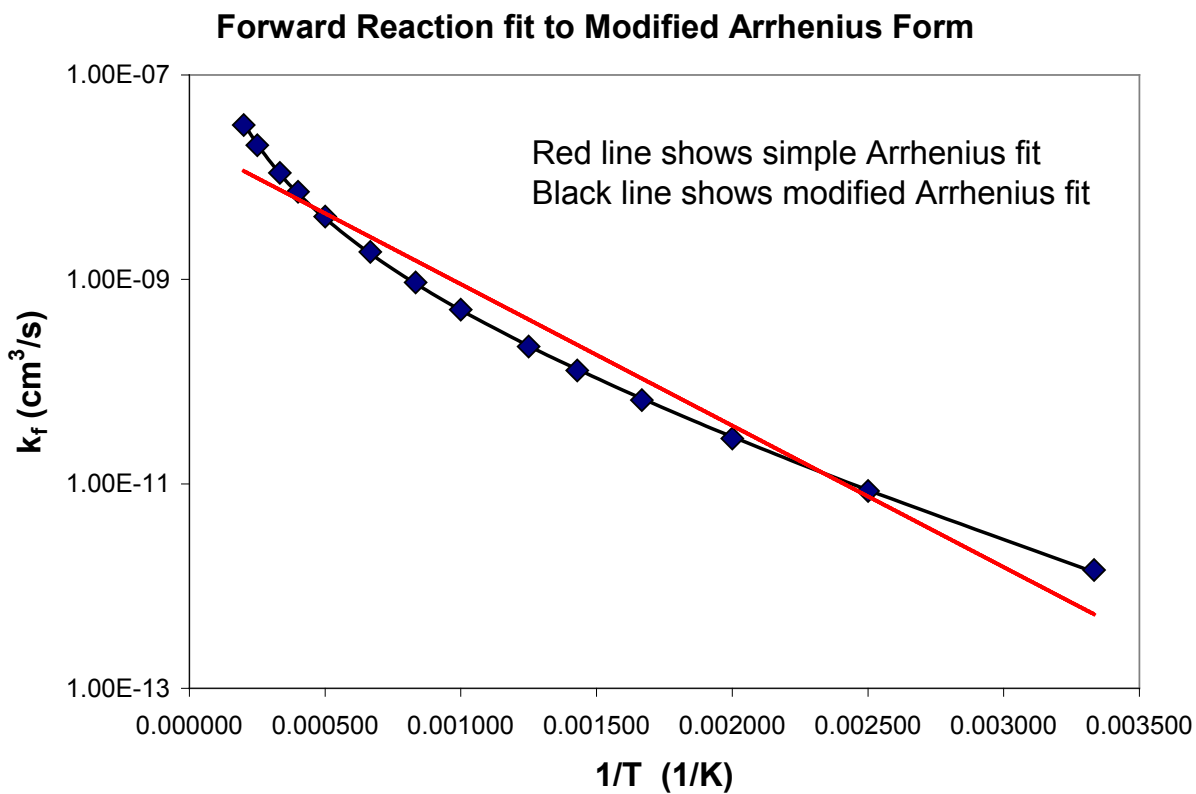
These were then used in the various expressions for the partition functions, which were, in turn, substituted into the transition state theory formulae for the forward and reverse rate constants.

Once a spreadsheet like that shown above, or a computer program that does the same thing, is set up, one can simply evaluate the rate constant at a number of temperatures and fit the modified Arrhenius expression through the data. The forward reaction part of a spreadsheet for doing this is shown below (sheet 2 of the one shown above):

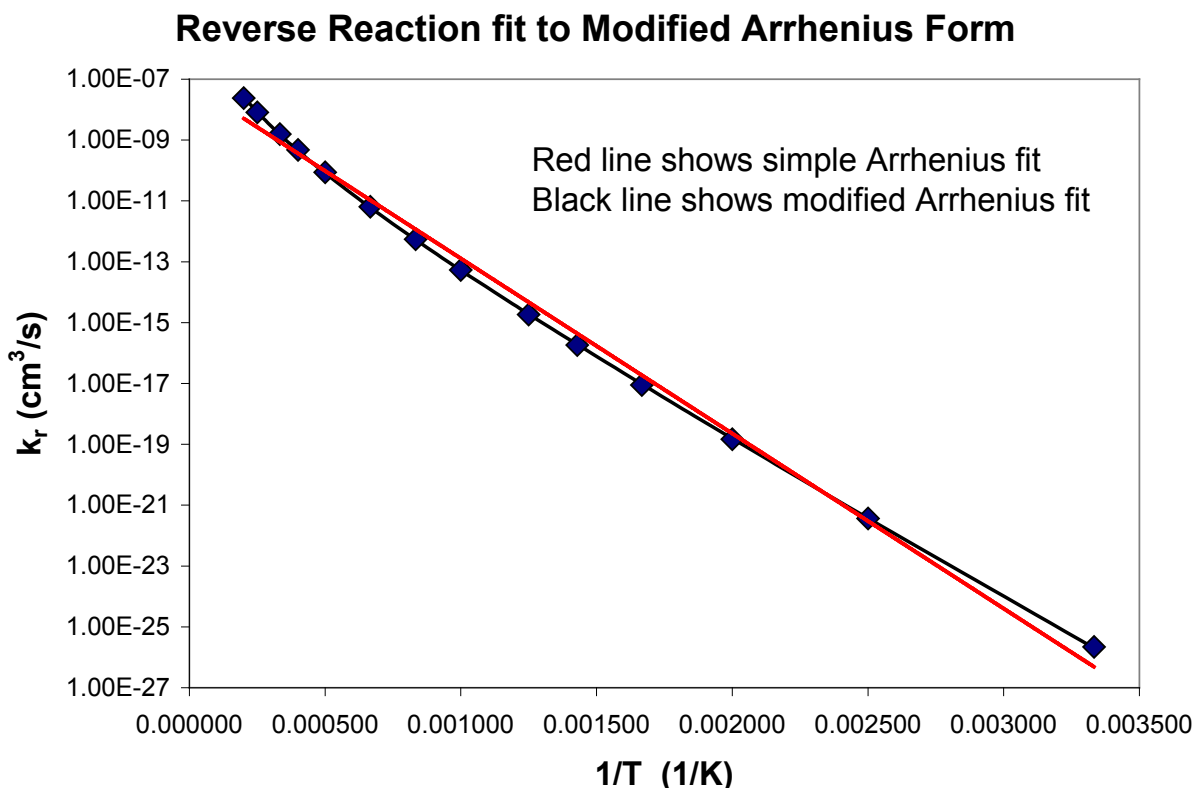
Forward Reaction

T (K)	k (m^3/s)	1/T (1/K)	k (cm^3/s)	ln(k)	ln(k _{fit})	Error ²	k _{fit} (cm^3/s)
300	1.43978E-18	0.003333	1.44E-12	-27.27	-27.32	0.002497	1.37E-12
400	8.52037E-18	0.002500	8.52E-12	-25.49	-25.47	0.000374	8.69E-12
500	2.78054E-17	0.002000	2.78E-11	-24.31	-24.27	0.001418	2.89E-11
600	6.60E-17	0.001667	6.60E-11	-23.44	-23.41	0.001282	6.84E-11
700	1.2884E-16	0.001429	1.29E-10	-22.77	-22.75	0.000697	1.32E-10
800	2.20928E-16	0.001250	2.21E-10	-22.23	-22.22	0.00022	2.24E-10
1000	5.05008E-16	0.001000	5.05E-10	-21.41	-21.41	4.46E-05	5.02E-10
1200	9.33372E-16	0.000833	9.33E-10	-20.79	-20.81	0.000508	9.13E-10
1500	1.85481E-15	0.000667	1.85E-09	-20.11	-20.14	0.001297	1.79E-09
2000	4.11012E-15	0.000500	4.11E-09	-19.31	-19.35	0.001602	3.95E-09
2500	7.1907E-15	0.000400	7.19E-09	-18.75	-18.78	0.001003	6.97E-09
3000	1.10084E-14	0.000333	1.10E-08	-18.32	-18.34	0.000307	1.08E-08
4000	2.05672E-14	0.000250	2.06E-08	-17.70	-17.68	0.000294	2.09E-08
5000	3.23352E-14	0.000200	3.23E-08	-17.25	-17.19	0.002831	3.41E-08
	ln(A)	-32.50			sum(Error ²)	0.014375	
	beta	1.83					
	E _a (kJ/mol)	13.17					
	A (cm^3/s)	7.67E-15					
	A ($\text{mol cm}^3/\text{s}$)	4.62E+09					

The best-fit set of parameters was obtained by using the 'Solver' function in Excel to vary $\ln(A)$, β , and E_a to minimize the sum of the squares of the difference between the fit and the actual value. The plot below shows this fit to the data, along with the simple Arrhenius fit:



The plot below shows the fit for the reverse reaction, done in the same way:



The non-Arrhenius behavior (curvature of this plot) is more obvious for the forward reaction, which has a small activation energy (relatively weak overall temperature dependence) than for the reverse reaction.

- (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_o to $3E_o$.
 - 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_{uni}/k_∞) 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.

Click [here](#) to download the Excel spreadsheet used for this problem

- (a) In QRRK theory (which assumes that a single frequency can be used to represent all vibrational modes), that frequency is simply equal to the high pressure pre-exponential factor. So, in this case, the frequency is $\nu = 2 \times 10^{14} \text{ s}^{-1} = 6667 \text{ cm}^{-1}$.
- (b) According to QRRK theory, the energy dependent rate constant for decomposition is

$$k(E = jh\nu) = \nu \frac{(j - m + s - 1)! j!}{(j - m)! (j + s - 1)!} \text{ for } j > m$$

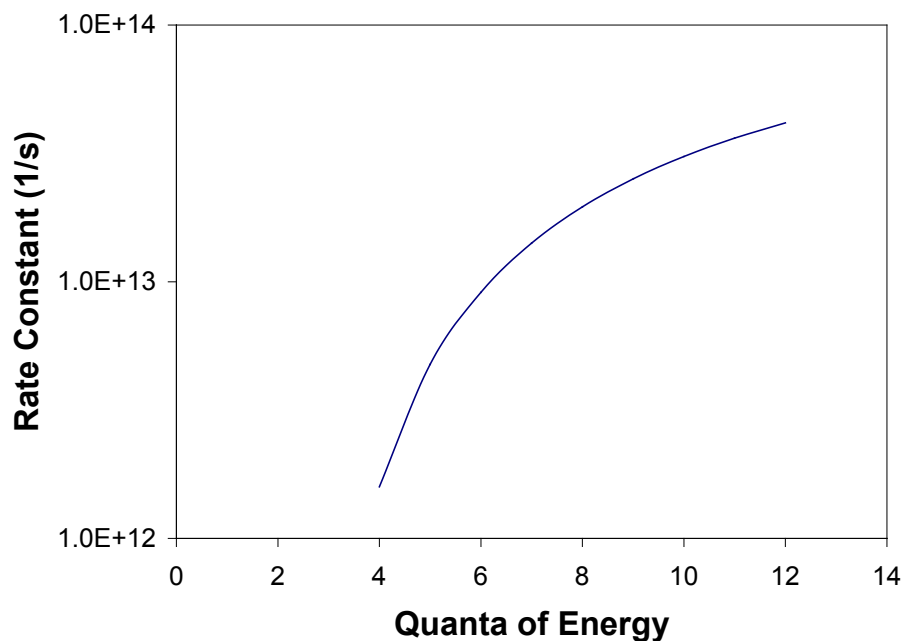
To match the high pressure pre-exponential factor, we use $\nu = 2 \times 10^{14} \text{ s}^{-1}$, so the energy quantum is $h\nu = 1.325 \times 10^{-19} \text{ J molecule}^{-1} = 79.8 \text{ kJ/mole}$. The activation energy, in kJ/mole is $32000 \text{ K} * 0.008314 \text{ kJ mol}^{-1} \text{ K} = 266 \text{ kJ/mol}$. The number of quanta equivalent to the critical energy is

$$266 \text{ kJ/mole} / 79.8 \text{ kJ/mole} = 3.33 \text{ so 4 quanta are required}$$

The total number of vibrational modes in AlH_2Cl is $s = 6$.

The above expression for $k(E)$ was evaluated for $j = 4$ to 12 in an Excel spreadsheet. The result is plotted below.

QRRK Energy-Dependent Rate Constant



The sharp rise in the rate constant just above the critical energy is typical of unimolecular decomposition reactions. In evaluating the QRRK expression for the rate constant at energies substantially above the critical energy, it is often useful to use Stirling's approximation to the factorial, which is valid for large values of n .

$$\ln(n!) \approx \frac{1}{2} \ln(2\pi n) + n \ln(n) - n$$

- (c) The collision rate for $\text{AlH}_2\text{Cl-N}_2$ collisions is given by the usual formula with a collision diameter of 3.0×10^{-10} m and a reduced mass of

$$\mu = \frac{64.45 * 28.02}{64.45 + 28.02} = 19.53 \text{ amu} = 3.24 \times 10^{-26} \text{ kg}$$

so

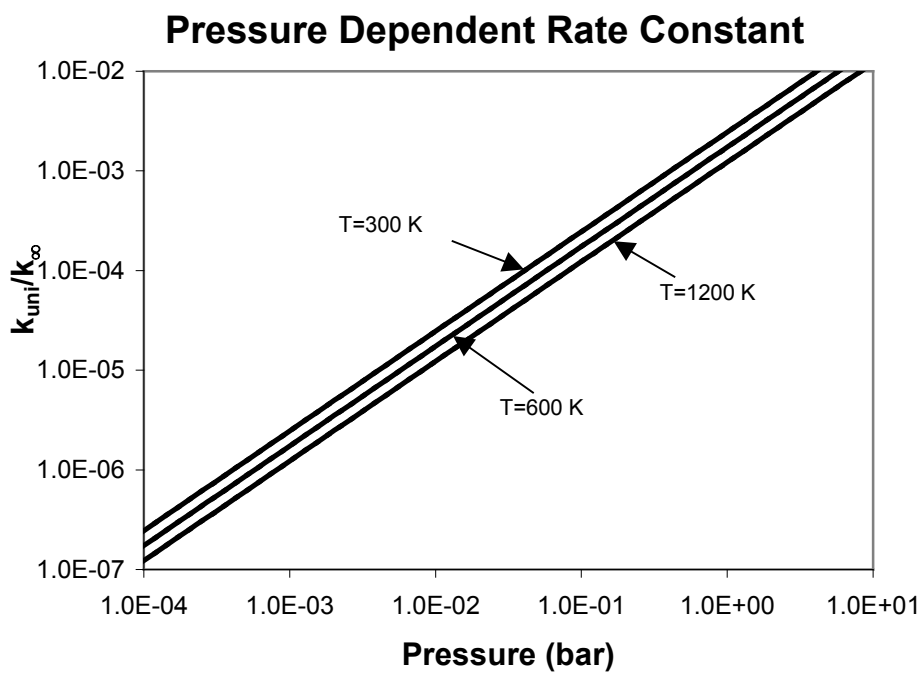
$$\begin{aligned} Z_{AB} &= \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A N_B \\ &= \pi (3.0 \times 10^{-10})^2 \left(\frac{8 \times 1.381 \times 10^{-23} T}{\pi (3.24 \times 10^{-26})} \right)^{1/2} \left(\frac{p(\text{bar}) \times 10^5 * 6.022 \times 10^{23}}{8.314 T} \right)^2 \end{aligned}$$

The collision rate of a given AlH_2Cl molecule with all other molecules is then

$$\begin{aligned} \omega &= \pi (3.0 \times 10^{-10})^2 \left(\frac{4 \times 1.38 \times 10^{-23} T}{\pi (1.07 \times 10^{-25})} \right)^{1/2} \left(\frac{p(\text{bar}) \times 10^5 * 6.022 \times 10^{23}}{8.314 T} \right) \\ &= 6.75 \times 10^{10} \frac{p(\text{bar})}{(T(\text{K}))^{1/2}} \text{ s}^{-1} \end{aligned}$$

The collision frequency is directly proportional to pressure and decreases weakly with temperature. At 300 K, it increases from $3.9 \times 10^5 \text{ s}^{-1}$ at 0.1 mbar to $3.9 \times 10^{10} \text{ s}^{-1}$ at 10 bar. At 600 K, it increases from $2.8 \times 10^5 \text{ s}^{-1}$ at 0.1 mbar to $2.9 \times 10^{10} \text{ s}^{-1}$ at 10 bar. At 1200 K, it increases from $1.9 \times 10^5 \text{ s}^{-1}$ at 0.1 mbar to $1.9 \times 10^5 \text{ s}^{-1}$ at 10 bar.

- (d) The rather bulky expression for k_{uni}/k_{∞} from QRRK theory is readily evaluated in a spreadsheet or short computer program. For this case, I used a large Excel spreadsheet, which is posted separately. The resulting plot of k_{uni}/k_{∞} is presented below.



For this pressure range, the reaction is essentially in the low pressure (bimolecular) limit for all three temperatures.