Chemistry 4000/5000/7000 Fall 2021
Assignment 2

Due: October 13th This assignment will be submitted electronically. As usual, I will accept neatly handwritten, scanned answers. However, any figures you generate should be included with your writing in a single document. In some questions, I will require additional files. The file names should be mentioned in your report so that I can make the correct associations between the written work and files. The report and any additional files should be sent as attachments to a single email.

Detailed solutions or answers are required. Little to no credit will be given for answers presented without your detailed reasoning. However, do look at the number of marks assigned to a question. As a rough rule of thumb, a 10-mark question might require about a page of math, or two to three substantial paragraphs.

For computational problems, you must provide sufficient detail of the calculation to enable replication. Typically, this would mean the method used and basis set.

In this assignment, you will carry out a set of calculations for a diatomic molecule. Each of you is assigned a different molecule, as follows:

HK: HF	DD: HCl	LD: LiF
MF: LiCl	MK: LiH	DM: ClF
SN: OH^-	CG: Li_2	NP: Cl_2
TP: F_2		

1. Choose a basis set that you consider to be reasonable for your molecule and for the task of computing both equilibrium properties and a potential energy curve. Explain briefly how you chose this basis set. [2 marks]

2. Carry out a geometry optimization. Report both the optimized geometry and corresponding energy. Include the `.log` file for this calculation in your final submission. [4 marks]

Note: The easiest way to find the energy after the geometry optimization is to open up the `.chk` or `.log` file, then click on `Results`→`Summary`. The '`Electronic Energy`' is misnamed. This is really the value of the effective potential (which includes nuclear-nuclear repulsion) at the computed geometry. The value given will be in hartree. The Wikipedia page for the hartree gives conversion factors to many other units of energy, which you may find useful in later parts of this assignment.

3. Obtain the effective potential energy curve for your diatomic molecule. Provide a graph of your potential energy curve. Ideally, this would look reasonably smooth. [4 marks]

4. Carry out a vibrational analysis (frequency calculation) using Gaussian. Use data from your geometry optimization and vibrational analysis to calculate the partition functions using formulas seen in class, and compare the values you obtain to those given in the `.log` file. Note that Gaussian uses a volume of $k_B T/p^\circ$ in the calculation of the translational partition function. Explain what this volume represents (based on the ideal-gas law). Does it make sense to you to use this volume to calculate a translational partition function? Explain briefly. [15 marks]

   (It will turn out that when we calculate equilibrium constants, this choice of volume has the right effect. The question is whether we should take the value of the translational partition function calculated by Gaussian seriously for any other purpose.)

   Additionally note that Gaussian uses the old standard pressure of 1 atm, instead of the modern value of 1 bar. Please use the latter in your calculations. This will result in a small discrepancy from Gaussian's value.

   Finally, note that $\hbar\omega_0 = hc\tilde{\nu}_0$, where $\tilde{\nu}_0$ is the wavenumber (usually in cm^{-1}).

5. In class, we derived the equation

$$K = \frac{\mathfrak{q}_\mathsf{C}^c \mathfrak{q}_\mathsf{D}^d}{\mathfrak{q}_\mathsf{A}^a \mathfrak{q}_\mathsf{B}^b} \left(\frac{p^\circ}{k_B T}\right)^{-\Delta n} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right)$$

   Show that if we use Gaussian's value of the volume to calculate the

translational partition functions, the latter equation is equivalent to

$$K = \frac{q_{\mathsf{C}}^c q_{\mathsf{D}}^d}{q_{\mathsf{A}}^a q_{\mathsf{B}}^b} \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right)$$

[3 marks]

6. Calculate the equilibrium constant at 25 °C for the dissociation of your molecule using the results of Gaussian calculations. [10 marks]

   Note: A table may be a good way to present the data extracted from Gaussian for each relevant species.