

5.68J/10.652J Fall 2020
Quantum Chemistry Homework
Due Tuesday, Sept. 22, 9:30 a.m.

- 1) Using quantum chemistry, estimate the equilibrium constants of the gas phase reactions below at 300 K and 1000 K. For reaction 1, if the partial pressure of ethene is 0.3 bar, which radical (methyl or propyl) exists at higher concentration at equilibrium?
- 2) Estimate the forward reaction rate coefficient $k(T)$ at $T=300$ K and 1000 K in the gas phase if the reactant(s) were perfectly thermalized, using quantum chemistry and conventional transition state theory.
- 3) Estimate the reverse rate coefficients in each case.

In every case, make all your assumptions clear, and clearly show where all your numbers are coming from, and specify units. I suggest you try a couple of different theoretical methods and/or basis sets to get an idea of how reliable your results are. Start with very cheap methods (e.g. small basis sets) so you don't waste a lot of time waiting for an answer. Note that most people in the world use Density Functional Theory (DFT) to compute geometries and frequencies; the density functionals B3LYP and M06-2X are currently popular for kinetics calculations. I suggest you use psi4, but if you prefer to use another quantum chemistry program (e.g. GAUSSIAN, Q-Chem, or methods in the Materials Studio program) that is fine, too. Definitely visualize the input and computed geometries with a graphical user interface to make sure they make sense. There are many graphical interfaces that are convenient to use (e.g. ASE, webMO, AVOGADRO, MOLDEN, Materials Studio, GAUSSVIEW). I suggest you use the RRHO approximation to start with; if you have time/ambition you can improve on this by considering the effects of hindered rotations. Programs like Gaussian give quantities like ΔG or the RRHO partition function Q in their output (often reported as Q/V , in units of 'per volume'), or you can compute Q 's yourself using ARKANE or writing your own Matlab or python function. If you write your own Q or thermo calculator, be very careful with units! There is also some literature thermochemistry on these species that you can use to check if your calculations are sensible. Beware that experimental rate coefficients will probably not match the numbers you compute, that is fine, we can discuss the reasons why in class.

Reaction 1: $\text{CH}_3 + \text{CH}_2\text{CH}_2 \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2$

The reverse of this reaction is a critical reaction in both the combustion of propane and in the manufacture of ethylene (the largest volume petrochemical, and the basis of the plastics industry). Reactions analogous to the forward reaction are critical in the production of polymers such as polyethylene. Leo Radom has written important journal papers about this reaction. Note that one would expect the transition state to have a nearly-free internal rotor (the methyl group spinning about its axis), and the product will have two torsions which might be internal rotors, you could try replacing the partition functions for the lowest-frequency vibrations with free 1d-rotor partition functions to see how big the internal-rotor effect could be. Note this reaction has a change in number of moles, so K_c is not the same as K_{eq} , and k_{forward} has different units than k_{reverse} .

Reaction 2: $\text{NO}_2 + \text{NH}_2\text{OH} \rightleftharpoons \text{HONO} + \text{H}_2\text{NO}$

This reaction appears to be the rate-determining step in the autocatalytic reaction of NH_2OH with nitric acid, which has led to explosions in nuclear fuel processing facilities. The saddle point geometry calculated at B3LYP/6-311G(2d,d,p) level is given below. R.W. Ashcraft et al. have written journal papers about this reaction mechanism.

Geometry in Gaussian z-matrix format:

```
0 2
H
N      1      B1
H      2      B2  1      A1
O      2      B3  1      A2  3      D1
H      4      B4  2      A3  1      D2
O      4      B5  2      A4  1      D3
N      6      B6  4      A5  2      D4
O      7      B7  6      A6  4      D5
```

```
B1      1.01541356
B2      1.01519171
B3      1.32611711
B4      1.14767326
B5      2.37828677
B6      1.28385685
B7      1.19526442
A1      116.83168597
A2      115.84865508
A3      104.46799921
A4      96.56246045
A5      93.63185569
A6      120.44167161
D1      141.52391274
D2      106.04485208
D3      106.40918974
D4      0.50059229
D5      179.73890405
```

Geometry in Cartesian X-Y-Z matrix format:

```
H,0,-0.0898320657,-0.1694999973,0.0772147247
N,0,0.0355170496,0.0178391226,1.0672937415
H,0,0.9887712464,0.1449408024,1.3925113631
O,0,-0.8703209164,0.8095763082,1.6251439199
H,0,-1.5211405355,0.1028719453,2.2529626915
O,0,-2.0141738828,-0.8925163173,2.8296071614
N,0,-1.2364304731,-1.8245698339,2.4116618158
O,0,-1.402980334,-2.9550056116,2.7624216767
```