5.68J/10.652J Spring 2008
Homework
Due Thursday, April 3. I suggest you start early.

1) Estimate the equilibrium constants of the 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 transition state theory.
3) Estimate the reverse rate constants in each case.

In every case, make all your assumptions clear, and clearly show where all your numbers are coming from, and specify units. Estimated uncertainties are welcome, for example you could try different theoretical methods and basis sets. I suggest you use Gaussian (and the Gaussview interface) which is available on Athena:
http://web.mit.edu/acs/www/simulation.html#mol
If you have trouble accessing Gaussian, ask the students in the Green group for help.

Reaction 1: $CH_3 + CH_2CH_2 = CH_3CH_2CH_2$

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.

Reaction 2: $NO_2 + NH_2OH = HONO + H_2NO$

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

Reaction 2:
Gaussian z-matrix:

```
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
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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

Cartesian X-Y-Z matrix

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