Chemistry 4000/5000/7001, Fall 2012, Assignment 6

Due: Friday, November 2, 4:00 p.m.
Total marks: 10

Suppose that we have a molecule for which, in an RRK model, $s = 22$ (which might be appropriate, for example, for the decomposition of 2,2-dimethylpropane to a *t*-butyl radical and a methyl radical: $(CH_3)_4C \rightarrow (CH_3)_3C + CH_3$).

1. Suppose that the 22 active oscillators share 1000 quanta of vibrational energy. How many different ways are there of storing those quanta in the oscillators? Give your answer in scientific notation. [2 marks]

   Hints: You will almost certainly need to use Maple to do this question since calculators can't handle some of the large numbers generated in this calculation. Maple will do the calculation exactly. To get a number in scientific notation, use the `evalf()` command. One way you could use this is to type `{evalf(%)}` on the line immediately following your calculation. In Maple, `%` represents the last thing computed.

2. Suppose that reaching the transition state requires that at least 100 quanta are stored in the reactive mode. How many different configurations of the 1000 quanta include at least 100 of them in the reactive mode? [2 marks]

3. Cutting a terminal methyl group off from a hydrocarbon tends to have about the same energetic cost, i.e. a barrier height of about $350\,\mathrm{kJ\,mol^{-1}}$. There is a small effect on the frequency, but only a small one if the hydrocarbon is much heavier than a methyl group. Comparing the decomposition of 2,2-dimethylpropane ($s = 22$) to the decomposition of propane ($CH_3CH_2CH_3 \rightarrow CH_3CH_3 + CH_3$, $s = 13$), what energy would a 2,2-dimethylpropane molecule have to reach before it had the same probability of reaction as a molecule of propane with a total energy equivalent to $500\,\mathrm{kJ\,mol^{-1}}$? [6 marks]

Bonus: What relative effect would you predict the different masses of the radicals to have on the reactive mode frequency? Is this significant compared to the effect of the number of active modes?