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

1.

$$\begin{aligned} G^* &= \frac{(j+s-1)!}{j!(s-1)!} \\ &= \frac{(1000+22-1)!}{1000!(22-1)!} \\ &= 2.46 \times 10^{43} \end{aligned}$$

2.

$$\begin{aligned} G^\ddagger &= \frac{(j-m+s-1)!}{(j-m)!(s-1)!} \\ &= \frac{(1000-100+22-1)!}{(1000-100)!(22-1)!} \\ &= 2.76 \times 10^{42} \end{aligned}$$

3. For propane,

$$\begin{aligned} p^\ddagger &= \left(\frac{E-E^\ddagger}{E}\right)^{s-1} \\ &= \left(\frac{500-350\,\mathrm{kJ\,mol^{-1}}}{500\,\mathrm{kJ\,mol^{-1}}}\right)^{13-1} \\ &= 5.31 \times 10^{-7}. \end{aligned}$$

We want to find the E for which we would get this $p^\ddagger$ with $s = 22$.

$$\begin{aligned} p^\ddagger &= \left(\frac{E-E^\ddagger}{E}\right)^{s-1} \\ \therefore (p^\ddagger)^{\frac{1}{s-1}} &= \frac{E-E^\ddagger}{E} \\ \therefore E^\ddagger &= E\left[1-(p^\ddagger)^{\frac{1}{s-1}}\right] \end{aligned}$$

$$
\begin{aligned}
\therefore E &= \frac{E^\ddagger}{1-(p^\ddagger)^{\frac{1}{s-1}}} \\
&= \frac{350\,\mathrm{kJ\,mol^{-1}}}{1-(5.31\times10^{-7})^{\frac{1}{22-1}}} \\
&= 704\,\mathrm{kJ\,mol^{-1}}.
\end{aligned}
$$

Bonus: If we treat the reactive mode as a harmonic vibration, we have $\nu^\ddagger \propto \sqrt{k/\mu}$. The bond strength k should be similar between different molecules containing a terminal methyl group. What will change is the reduced mass along the reaction coordinate. Thus,

$$
\frac{\nu^\ddagger_{\mathrm{C_4H_{12}}}}{\nu^\ddagger_{\mathrm{C_3H_8}}} = \sqrt{\frac{\mu_{\mathrm{C_3H_8}}}{\mu_{\mathrm{C_4H_{12}}}}}
$$

In the case of 2,2-dimethylpropane, the two fragments created by the bond breaking event are a t-butyl group and a methyl group. The t-butyl group has a molar mass of $57.1143\,\mathrm{g\,mol^{-1}}$ while the methyl radical has a molar mass of $15.0345\,\mathrm{g\,mol^{-1}}$ The reduced molar mass is therefore

$$
\begin{aligned}
\mu^{-1}_{\mathrm{C_4H_{12}}} &= (57.1143)^{-1} + (15.0345\,\mathrm{g\,mol^{-1}})^{-1} = 8.402\,24\times10^{-2} \\
\therefore \mu_{\mathrm{C_4H_{12}}} &= 11.9016\,\mathrm{g\,mol^{-1}}
\end{aligned}
$$

Similarly, the ethyl radical made in the dissociation of propane has a molar mass of $29.0611\,\mathrm{g\,mol^{-1}}$ so the reduced mass is

$$
\begin{aligned}
\mu^{-1}_{\mathrm{C_3H_8}} &= (29.0611)^{-1} + (15.0345\,\mathrm{g\,mol^{-1}})^{-1} = 0.100\,924\,\mathrm{mol\,g^{-1}} \\
\therefore \mu_{\mathrm{C_3H_8}} &= 9.908\,45\,\mathrm{g\,mol^{-1}}
\end{aligned}
$$

Even without putting the numbers into our formula, we see that the effect will be very small since the reduced masses are very similar. The following calculation confirms this:

$$
\frac{\nu^\ddagger_{\mathrm{C_4H_{12}}}}{\nu^\ddagger_{\mathrm{C_3H_8}}} = \sqrt{\frac{9.908\,45\,\mathrm{g\,mol^{-1}}}{11.9016\,\mathrm{g\,mol^{-1}}}} = 0.912\,432.
$$

This is an extremely minor factor in determining the size of the rate constant.