Chemistry 4000/5000/7001, Fall 2012, Assignment 9 Solutions

1.

$$
\begin{aligned}
k_D &= 4\pi L D_{AB} R_{AB} \\
R_A &= \frac{k_B T}{6\pi D_A \eta} \\
&= \frac{(1.380\,6488 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}{6\pi(10^{-9}\,\mathrm{m^2 s^{-1}})(8.91 \times 10^{-4}\,\mathrm{Pa\,s})} \\
&= 2 \times 10^{-10}\,\mathrm{m} \\
k_D &= 4\pi(6.022\,141\,29 \times 10^{23}\,\mathrm{mol^{-1}})[(2)(10^{-9}\,\mathrm{m^2 s^{-1}})][(2)(2 \times 10^{-10}\,\mathrm{m})] \\
&= 7 \times 10^{6}\,\mathrm{m^3 mol^{-1} s^{-1}} \\
&\equiv 7 \times 10^{9}\,\mathrm{L\,mol^{-1} s^{-1}} \\
K_D &= \frac{\mathcal{N}}{[\mathrm{H_2O}]} \\
&= \frac{6}{55.33\,\mathrm{mol\,L^{-1}}} = 0.1084\,\mathrm{L\,mol^{-1}} \\
k_{-D} &= k_D / K_D \\
&= \frac{7 \times 10^{9}\,\mathrm{L\,mol^{-1} s^{-1}}}{0.1084\,\mathrm{L\,mol^{-1}}} = 7 \times 10^{10}\,\mathrm{s^{-1}} \\
\therefore t_{1/2} &= \ln 2 / k_{-D} \\
&= \frac{\ln 2}{7 \times 10^{10}\,\mathrm{s^{-1}}} = 1 \times 10^{-11}\,\mathrm{s} \equiv 10\,\mathrm{ps}
\end{aligned}
$$

2. This question amounts to asking whether $f/2m\omega^{\ddagger}$ is small or large.

$$
\begin{aligned}
f &= k_B T/D \\
&= \frac{(1.380\,6488 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}{10^{-9}\,\mathrm{m^2 s^{-1}}} = 4 \times 10^{-12}\,\mathrm{N\,s\,m^{-1}} \\
m &= \frac{100\,\mathrm{g\,mol^{-1}}}{6.022\,141\,29 \times 10^{23}\,\mathrm{mol^{-1}}} = 1.66 \times 10^{-22}\,\mathrm{g} \\
&\equiv 1.66 \times 10^{-25}\,\mathrm{kg} \\
\therefore \frac{f}{2m\omega^{\ddagger}} &= \frac{4 \times 10^{-12}\,\mathrm{N\,s\,m^{-1}}}{2(1.66 \times 10^{-25}\,\mathrm{kg})(10^{13}\,\mathrm{s^{-1}})} \\
&\approx 1
\end{aligned}
$$

This is actually a medium-friction regime where friction is comparable to the frequency at which the transition state is traversed.