Chemistry 4000 Fall 2012 Test 1 Solutions

1. There are four atoms, so the number of non-reactive normal modes is $3(4) - 7 = 5$.

2. (a) Simple collision theory predicts a temperature-dependent preexponential factor due to the temperature dependence of $\bar{v}_r$. In reactive scattering theory, the situation is less clear (due to the integral over either v_r or K_r), but since this theory is equivalent to simple collision theory, as seen in class, in fact it also predicts temperature-dependent preexponential factors. The transition-state theory expression for the preexponential factor is explicitly temperature-dependent, even if we ignore the temperature dependence of $\Delta^{\ddagger}S_m^{\circ}$. Accordingly, we expect a temperature-independent preexponential factor to be an approximation.

   (b)

$$\begin{aligned}
\frac{1}{\mu_m} &= \frac{1}{m_{\mathrm{O_2}}} + \frac{1}{m_{\mathrm{CO}}} \\
&= \frac{1}{32.00} + \frac{1}{28.01\,\mathrm{g\,mol^{-1}}} \\
&= 0.06696\,\mathrm{mol\,g^{-1}} \\
\therefore \mu_m &= 14.94\,\mathrm{g\,mol^{-1}} \equiv 14.94 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}.
\end{aligned}$$

   I'm going to take a temperature in the middle of the experimental range, i.e. 2700 K.

$$\begin{aligned}
\bar{v}_r &= \sqrt{\frac{8RT}{\pi\mu_m}} \\
&= \sqrt{\frac{8(8.314\,4621\,\mathrm{J\,K^{-1}mol^{-1}})(2700\,\mathrm{K})}{\pi(14.94 \times 10^{-3}\,\mathrm{kg\,mol^{-1}})}} \\
&= 1956\,\mathrm{m\,s^{-1}}. \\
R_{AB} &= R_{\mathrm{O_2}} + R_{\mathrm{CO}} \\
&= 1.8 + 1.9\,\text{Å} \\
&= 3.7\,\text{Å} \equiv 3.7 \times 10^{-10}\,\mathrm{m}. \\
\sigma &= \pi R_{AB}^2 = \pi(3.7 \times 10^{-10}\,\mathrm{m})^2 \\
&= 4.3 \times 10^{-19}\,\mathrm{m^2} \\
\therefore A &= \sigma\bar{v}_r L \\
&= (4.3 \times 10^{-19}\,\mathrm{m^2})(1956\,\mathrm{m\,s^{-1}})(6.022\,141\,29 \times 10^{23}\,\mathrm{mol^{-1}}) \\
&= 5.1 \times 10^{8}\,\mathrm{m^3s^{-1}mol^{-1}} \\
&\equiv (5.1 \times 10^{8}\,\mathrm{m^3s^{-1}mol^{-1}})(1000\,\mathrm{L\,m^{-3}}) = 5.1 \times 10^{11}\,\mathrm{L\,mol^{-1}s^{-1}}.
\end{aligned}$$

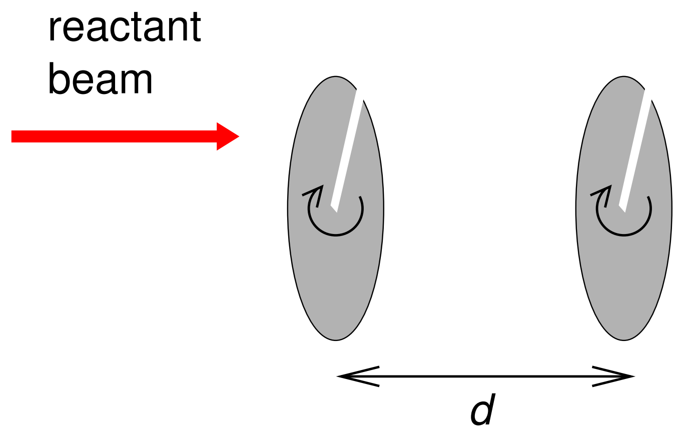

Figure 1: Velocity selector

The collision-theory preexponential factor is larger than the experimental value by a factor of about 145. This tells us that only one in 145 collisions actually results in a reaction.

3. Tunneling is the passage of a particle through a region that is classically forbidden. For example, in a chemical reaction, a particle lacking the energy to go over a potential energy barrier could go through it instead. This is a problem in transition state theory because this theory is based on calculating rates of passage over the barrier.

4. **Velocity selection:** See figure 1 for a diagram of the apparatus. The molecules in the incident beam will only pass through the first slit when it is in the vertical position. The second disc has to rotate a whole number of turns in the time it takes for a molecule to get from one disc to the other in order for the second slit to be in the vertical position when the molecule arrives. This time is $t = d/v$. If the frequency of rotation (in Hertz) of the discs is ν, then one turn takes ν^{-1} seconds. Thus, the condition which must be met is $d/v = n\nu^{-1}$, where n is a whole number, or $v = d\nu/n$. In principle, particles of many different velocities could make it through, corresponding to the different values of n, but in practice, we can usually pick a value of ν such that only one value of n (usually $n = 1$) corresponds to a significant number of particles for the particular velocity distribution of the molecular beam.

   Infrared chemiluminescence: Products in reaction dynamics experiments are often generated in excited vibrational states. The products then radiate in the infrared as they return to their ground states. This emission tells us what vibrational states the products were in when they were formed.

   Laser induced fluorescence: We use a laser to excite the products from a known energy level (1) to another known energy level (2). Return to the ground state will be accompanied by emission, which can be detected. The intensity of this emission is proportional to the original population of level 1. By tuning our laser to different gaps, we can therefore probe the distribution of the product among its energy levels following the reaction.

5. See table on next page.

Simple collision theory	**Reactive scattering theory**	**Transition-state theory**
• Activation energy not predicted	• Activation energy implicit in dependence of cross-section on kinetic energy (or speed)	• Activation energy predicted by theory
• Predicts preexponential factor	• Predicts preexponential factor	• Predicts preexponential factor
• Requires knowledge of molecular size	• Requires knowledge of energy dependence of cross-section	• Requires vibrational energies of reactants and transition state, and information about geometries of reactants and transition state
• Typically gives an upper bound to the rate constant (or preexponential factor)	• Can be very accurate if the dependence of the reactive cross-section on the kinetic energy is known	• In many reactions, gives an upper bound to the rate constant, but in reactions with tunneling, may underestimate the rate constant
• Assumes no forces between reactants	• Forces can be incorporated into cross-section	• Forces affect shape of potential energy surface and therefore the value of the partition function of the transition state
• Neglects any orientational effects	• A version of the theory includes orientational effects explicitly, but even in the version averaged over orientations, the averaging includes orientational effects in the magnitude of the cross-section	• Takes full account of the geometry needed to reach the transition state

Simple collision theory	Reactive scattering theory	Transition-state theory
• Based strictly on classical mechanics	• Formalism can accommodate quantum mechanical effects	• Some quantum mechanical effects (quantized energy levels, zero-point energy) taken into account, others (tunneling) not