Chem 106 Lecture 5 Kinetics

According to the *collision model*, for a reaction to occur, three criteria must be satisfied.

Criterion	How this relates to Rate Law: Rate = $k[A]^x[B]^y$	How this relates to temperature effect: Rate = $Ae^{-Ea/RT}$
1. Collisions must occur between molecules. Increasing the rate of collision increases the rate of reaction.	Increasing the concentration of reactants increases the frequency of collisions and therefore the rate of reaction.	Only very slightly by a slight increase in molecular velocity
2. The orientation of molecules in the collision must be correct.	none	none
3. The energy of the collision must be large enough to allow reactant bonds to break. i.e., The collision energy must be > the activation energy, E_a.	Through k. Rate varies directly with k.	Very large dependence. The fraction of collision with $E > E_a = f$. $$f = e^{-Ea/RT}$$

$$\mathbf{k = p \times Z \times f}$$

p = the fraction of collisions with correct orientation
Z = the collision frequency
f = the fraction of collisions with $E>E_a$

The third criterion is especially interesting, as it addresses the strong, nonlinear relationship between temperature and rate constant (and therefore rate). The explanation is in the kinetic-molecular theory of matter. We remember from Chem 105 that molecular velocity of gases increases with temperature. The relationship between velocity and temperature is not very strong—average velocity is proportional to the square root of temperature ($v \propto T^{0.5}$)—see figure 1 at top of next page. So velocity, *per se*, is not the answer to the question of why rate is such a strong function of temperature.

The key is to examine how the fraction of very high energy collisions changes with temperature. It turns out that there is a very strong relationship between the fraction of collisions with energy greater than a given value (Ea) and temperature. Figure 2 on the bottom of the next page illustrates this. In fact, if we call the fraction of collision with $E > E_a = f$, then

$$f = e^{-Ea/RT}$$

Figure 1. The relatively weak temperature-velocity relationship.

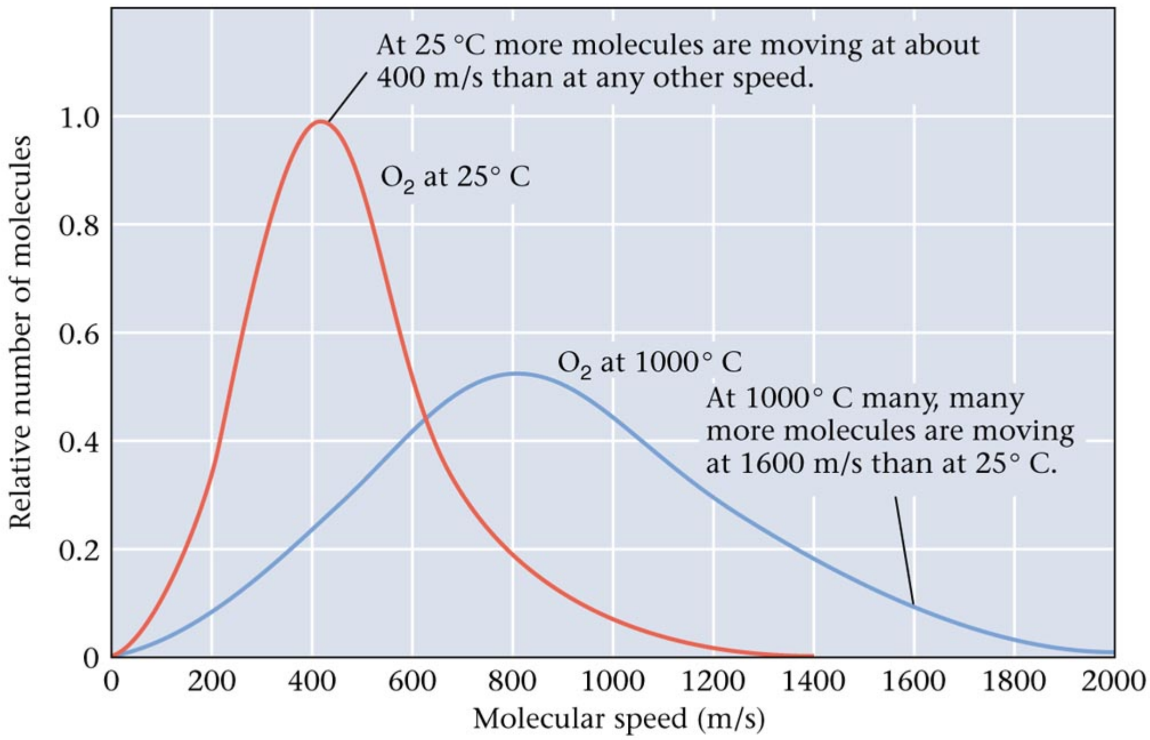
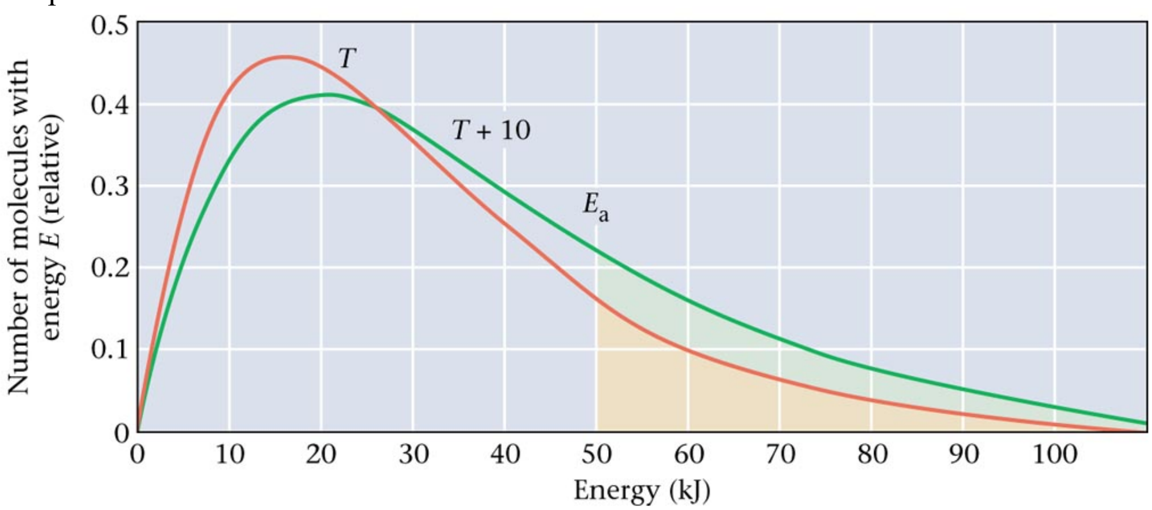


Figure 2. The strong relationship between (fraction of collision with E > Ea) and temperature.



The magnitude of the temperature effect on rate depends on the value of Ea for the reaction and the base temperature.

$$f = e^{-Ea/RT}$$

Let's look at the effect of a 10 K change in temperature, from $T_1 = 293$ K to $T_2 = 303$ K

Ea (kJ/mol)	f_1	f_2	f_2/f_1
30	4.5×10^{-6}	6.7×10^{-6}	1.5
50	1.2×10^{-9}	2.4×10^{-9}	2.0
80	5.4×10^{-15}	1.6×10^{-14}	3.0

Let's look at the effect of a 10 K change in temperature, from $T_1 = 500$ K to $T_2 = 510$ K and Ea = 80 kJ/mol

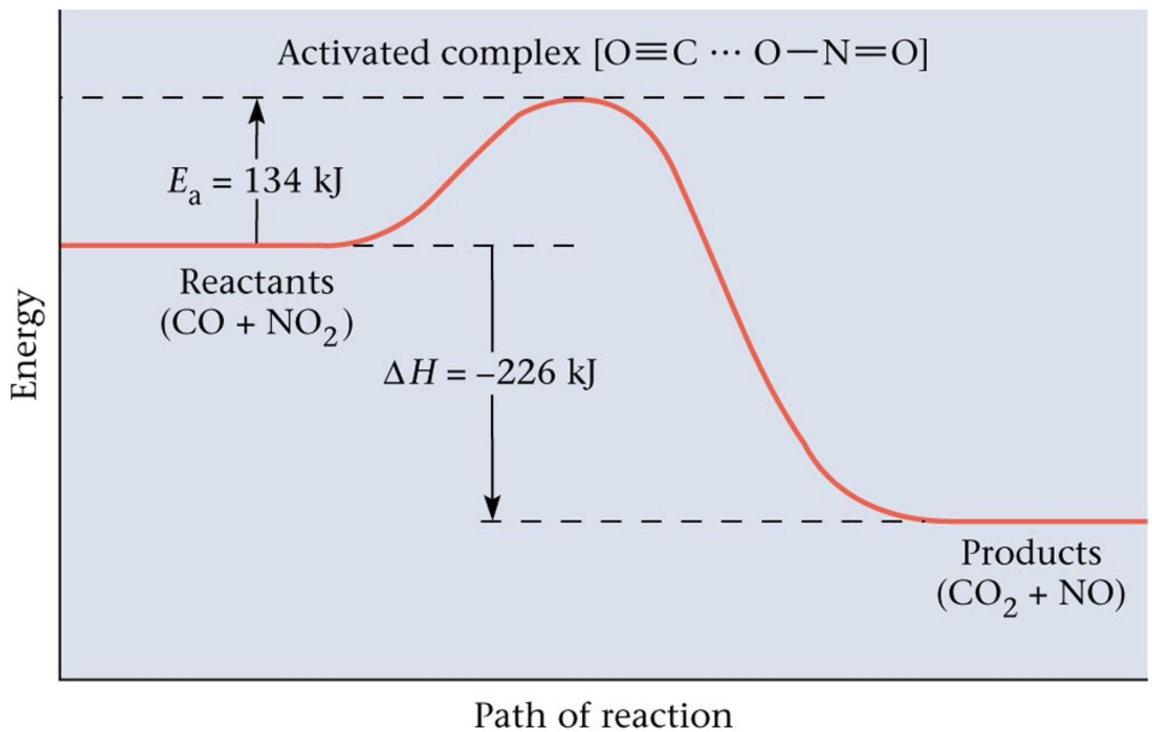
Ea (kJ/mol)	f_1	f_2	f_2/f_1
80	4.32×10^{-9}	6.34×10^{-9}	1.5

This accounts for the general rule of thumb that the rate of many reactions changes by a factor of 2 as the temperature increases by 10 K (or 10°C).

The transition state model also invokes activation energy.

The path of the reaction includes a reactive, unstable intermediate (activated complex, transition state) which represents a species where some of the reactant bonds have started to weaken and some of the product molecules bonds have started to form. In figure 3, the activated complex shows the start of the formation of the C=O bond of carbon dioxide as a dotted line. The difference in energy between the activated complex and the reactants is the activation energy, Ea. The value of Ea is always positive.

Figure 3. Reaction energy diagram for CO (g) + NO_2 (g) -----> CO_2 (g) + NO (g)



The transition state model is especially useful in explaining the energetics of catalysts. A catalyst speeds up a particular reaction by allowing the reaction to proceed by a different path, with an intermediate of lower energy.