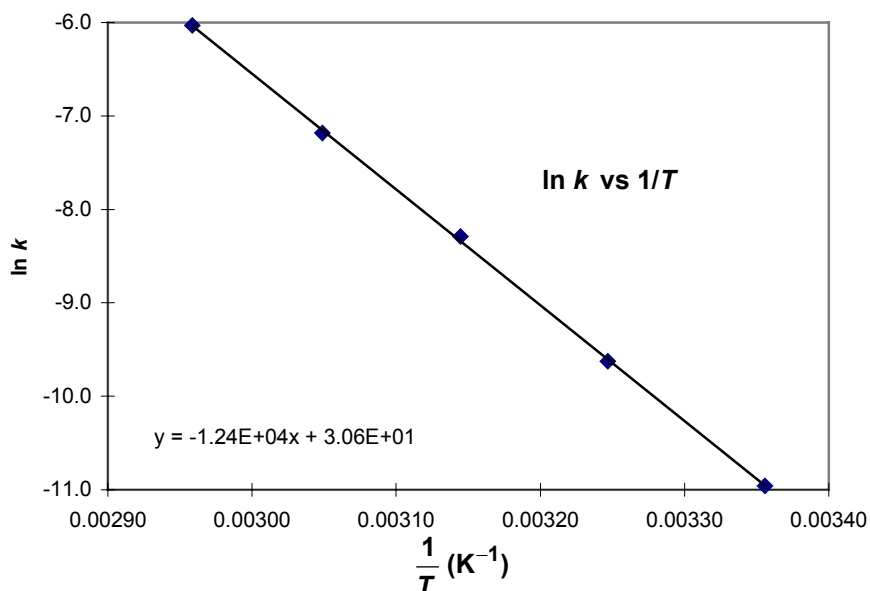


Solutions to Homework Assignment #4
CHM 152
Spring 2002

13.31 Activation energy is the minimum amount of energy required to initiate a chemical reaction. The magnitude of the activation energy will affect the reaction rate. The larger the activation energy, typically the slower the reaction.

13.37 Graphing Equation (13.10) of the text requires plotting $\ln k$ versus $1/T$. The graph is shown below.



The slope of the line is $-1.24 \times 10^4 \text{ K}$, which is $-E_a/R$. The activation energy is:

$$-E_a = \text{slope} \times R = (-1.24 \times 10^4 \text{ K}) \times (8.314 \text{ J/K}\cdot\text{mol})$$

$$E_a = 1.03 \times 10^5 \text{ J/mol} = 103 \text{ kJ/mol}$$

Do you need to know the order of the reaction to find the activation energy? Is it possible to have a negative activation energy? What would a potential energy versus reaction coordinate diagram look like in such a case?

13.38 The ratio of the rates at two different temperatures is equivalent to the ratio of the rate constants at the two temperatures.

Use the modified form of the Arrhenius equation shown below to calculate the energy of activation.

Let $T_1 = 250^\circ\text{C} = 523 \text{ K}$ and $T_2 = 150^\circ\text{C} = 423 \text{ K}$.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

$$\ln(1.50 \times 10^3) = \frac{E_a}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{523 \text{ K} - 423 \text{ K}}{(523 \text{ K})(423 \text{ K})} \right)$$

$$7.31 = \frac{E_a}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}} \left(4.52 \times 10^{-4} \frac{1}{\text{K}} \right)$$

$$E_a = 1.35 \times 10^5 \text{ J/mol} = 135 \text{ kJ/mol}$$

- 13.39** The appropriate value of R is 8.314 J/K mol, not 0.0821 L·atm/mol·K. You must also use the activation energy value of 63000 J/mol (why?). Once the temperature has been converted to Kelvin, the rate constant is:

$$k = Ae^{-E_a/RT} = (8.7 \times 10^{12} \text{ s}^{-1}) e^{-63000 \text{ J}/(8.314 \text{ J/mol}\cdot\text{K})(348 \text{ K})} = (8.7 \times 10^{12} \text{ s}^{-1})(3.5 \times 10^{-10})$$

$$k = 3.0 \times 10^3 \text{ s}^{-1}$$

Can you tell from the units of k what the order of the reaction is?

- 13.42** Since the ratio of rates is equal to the ratio of rate constants, we can write:

$$\ln \frac{\text{rate}_1}{\text{rate}_2} = \ln \frac{k_1}{k_2}$$

$$\ln \frac{k_1}{k_2} = \ln \left(\frac{2.0 \times 10^2}{39.6} \right) = \frac{E_a}{8.314 \text{ J/K}\cdot\text{mol}} \left(\frac{(300 \text{ K} - 278 \text{ K})}{(300 \text{ K})(278 \text{ K})} \right)$$

$$E_a = 5.10 \times 10^4 \text{ J/mol} = 51.0 \text{ kJ/mol}$$

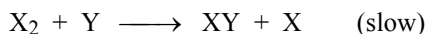
- 13.46** The rate-determining step is the slowest step in the sequence of steps leading to product formation. See p. 537, last paragraph, for an everyday analogy.

- 13.49** (a) The order of the reaction is simply the sum of the exponents in the rate law (Section 13.2 of the text). The order of this reaction is 2.
- (b) The rate law reveals the identity of the substances participating in the slow or rate-determining step of a reaction mechanism. This rate law implies that the slow step involves the reaction of a molecule of NO with a molecule of Cl₂. If this is the case, then the first reaction shown must be the rate-determining (slow) step, and the second reaction must be much faster.
- 13.50** (a) Since the reaction rate doubles when the X₂ concentration is doubled, the reaction is first-order in X. The reaction rate triples when the concentration of Y is tripled, so the reaction is also first-order in Y. The concentration of Z has no effect on the rate, so the reaction is zero-order in Z.

The rate law is:

$$\text{rate} = k[\text{X}_2][\text{Y}]$$

- (b) If a change in the concentration of Z has no effect on the rate, the concentration of Z is not a term in the rate law. This implies that Z does not participate in the rate-determining step of the reaction mechanism.
- (c) The rate law shows that the slow step involves reaction of a molecule of X₂ with a molecule of Y. Since Z is not present in the rate law, it does not take part in the slow step and must appear in a fast step at a later time. (If the fast step involving Z happened before the rate-determining step, the rate law would involve Z in a more complex way.) A mechanism that is consistent with the rate law could be:



The rate law only tells us about the slow step. Other mechanisms with different subsequent fast steps are possible. Try to invent one.

- 13.81** (a) A catalyst works by changing the reaction mechanism, thus lowering the activation energy.
 (b) A catalyst changes the reaction mechanism.
 (c) A catalyst does not change the enthalpy of reaction.
 (d) A catalyst increases the forward rate of reaction.
 (e) A catalyst increases the reverse rate of reaction.

- 13.84** In terms of the initial concentration of A, the concentration of A remaining after 4.90 min is $0.645[A]_0$.
 Using the first-order rate equation,

$$\ln \frac{[A]}{[A]_0} = -kt$$

or

$$\ln \frac{0.645[A]_0}{[A]_0} = -kt$$

$$0.439 = k(4.90 \text{ min})$$

$$k = \frac{0.439}{4.90 \text{ min}} = 0.0896 \text{ min}^{-1}$$

- 13.89** For a first order reaction: $t = \frac{1}{k} \ln \frac{\text{decay rate at } t = 0}{\text{decay rate at } t = t}$

$$t = \frac{1}{1.21 \times 10^{-4} \text{ yr}^{-1}} \ln \frac{0.260}{0.186} = 2.77 \times 10^3 \text{ yr}$$

- 13.94** During the first five minutes or so the engine is relatively cold, so the exhaust gases will not fully react with the components of the catalytic converter. Remember, for almost all reactions, the rate of reaction increases with temperature.

13.107

