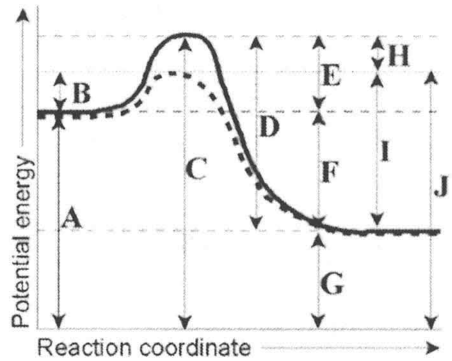
PLI 28
Monday July 11, 2016
Chapter 14 - Kinetics

1. Answer the following questions based on the reaction coordinate diagram below:



The reaction shown above is exothermic / endothermic.

Which letter represents the total energy of the reactants? A

Which letter represents the total energy of the products? G

Which letter represents ΔH for the catalyzed reaction? F

Which letter represents ΔH for the uncatalyzed reaction? F

these are the same!

Which letter represents the activation energy for the catalyzed reaction? B

Which letter represents the activation energy for the uncatalyzed reaction? E

Which letter represents the total energy of the transition state for the catalyzed reaction? J

Which letter represents the total energy of the transition state for the uncatalyzed reaction? C

2. The decomposition of ethanol (C_2H_5OH) on an alumina (Al_2O_3) surface was studied at 600 K.

$$C_2H_5OH\ (g) \rightarrow C_2H_4\ (g) + H_2O\ (g)$$

Concentration versus time data were collected for this reaction, and a plot of [A] versus time resulted in a straight line with a slope of −4.00 x 10^−5 M/s.

a) Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.

- because $[C_2H_5OH]$ vs. time is linear, this is a zero order rxn. The rate constant = − slope = 4.00×10^{-5} M/s

- rate law: rate = $k[C_2H_5OH]^0 = k = 4.00 \times 10^{-5}\ \frac{M}{s}$

integrated rate law:

$$[C_2H_5OH]_t = -4.00\times10^{-5}\,t + [C_2H_5OH]_0$$

b) If the initial concentration of ethanol is 1.25 x 10^−2 M, calculate the half-life for this reaction. for zero order rxn $t_{1/2} = \frac{[C_2H_5OH]_0}{2k}$

$$t_{1/2} = \frac{1.25\times10^{-2}M}{2(4.00\times10^{-5}M/s)} = 156 \text{ seconds}$$

c) How much time is required for all of the ethanol to decompose?

$$[C_2H_5OH]_t = -4.00\times10^{-5}\,t + [C_2H_5OH]_0$$

$$0 = -4.00\times10^{-5}\,t + 0.0125$$

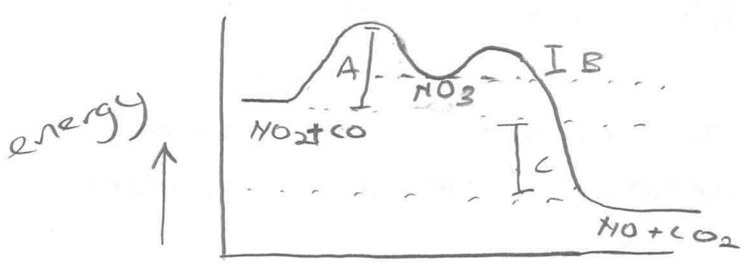
$$t = \frac{0.0125}{4.00\times10^{-5}} = 313 \text{ seconds}$$

3. Consider the following reaction: NO_2 (g) +CO (g) → NO (g) + CO_2 (g)

a) A proposed mechanism for the reaction is as follows:

Step1: Slow, endothermic	$2\,NO_2$ (g) → NO(g) + NO_3(g)
Step 2: Fast, exothermic	NO_3(g) + CO(g) → NO_2 (g) + CO_2 (g)
Overall: Exothermic	NO_2 (g) + CO(g) → NO(g) + CO_2 (g)

Draw a reaction coordinate diagram for this reaction. Indicate on this drawing the activation energy for each step, the overall reaction enthalpy, and where the reactants and products of the overall reactions are located. Also indicate where the products from step 1 are located. Label the y-axis.



A = step 1 activation energy
B = step 2 activation energy
C = overall rxn enthalpy.

rxn coordinate (also known as rxn progress)

b) What rate law does the proposed mechanism predict for the overall reaction? In a sentence, explain how you determined the rate law.

rate = $k[NO_2]^2$

use the slow step to determine the rate law. Since it is an elementary step, we use the stoichiometric co-efficients.

4. The gas-phase reaction $2N_2O_5$ (g) → $4NO_2$ (g) + O_2 (g) has an activation energy of 103 kJ/mol, and the rate constant is 0.0900 at 328.0 K. Find the rate constant at 308.9 K.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

T_1 = 328 K
T_2 = 308.9 K
E_a = 103 kJ/mol
R = 0.008314 kJ/mol·K

→

$\ln(k_2) - \ln(k_1) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln(k_2) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \ln(k_1) = \frac{103}{0.008314}\left(\frac{1}{328} - \frac{1}{308.9}\right) + \ln(0.0900)$

$\ln(k_2) = -4.74$ $\quad$ $\underline{k_2 = 0.00871}$ (rxn order not given, so no units)

5. The mechanism for the reaction of CH_3OH and HBr is believed to involve two steps. The overall reaction is exothermic.

Step 1: Fast, endothermic
$CH_3OH + H^+ \leftrightarrows \cancel{CH_3OH_2^+}$

Step 2: Slow
$\cancel{CH_3OH_2^+} + Br^- \rightarrow CH_3Br + H_2O$

Overall reaction equation (you solve): $CH_3OH + H^+ + Br^- \rightarrow CH_3Br + H_2O$

What is the overall rate law, given that intermediaries should not appear in the rate law?

1) since fast rxn is in equilibrium, its rate is:

$\text{rate} = K_1[CH_3OH][H^+] = k_{-1}[CH_3OH_2^+]$

$[CH_3OH_2^+] = \frac{k_1}{k_{-1}}[CH_3OH][H^+]$

2) plug into slow step:

$\text{rate} = k_2[Br^-][CH_3OH_2^+] = \frac{k_2 k_1}{k_{-1}}[Br^-][CH_3OH][H^+]$

6. If the rate constant for a reaction doubles when the temperature rises from 3.00×10^2 K to 3.16×10^2 K, what is the activation energy of the reaction?

$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln\left(\frac{2k_1}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$\ln(2) = \frac{E_a}{0.008314}\left(\frac{1}{300.} - \frac{1}{316}\right)$

$\underline{E_a = 34.1 \text{ kJ/mol rxn}}$

$T_1 = 300.$ K
$T_2 = 316$ K
$R = 0.008314$ kJ/mol·K
$K_2 = 2k_1$

7. Assume a bottle of wine is an 11% ethanol (CH_3CH_2OH) aqueous solution by mass. If the bottle is chilled to -4°C, will the solution freeze and break your wine bottle? Kfp for water is -1.86 °C/m.

11% ethanol by mass = 11 g C_2H_5OH and 89 g H_2O

$11 \text{ g } C_2H_5OH \left(\frac{1 \text{ mol}}{46.08 \text{ g}}\right) = 0.239 \text{ mol } C_2H_5OH$

$\text{molality} = \frac{0.239 \text{ mol } C_2H_5OH}{0.089 \text{ kg } H_2O} = 2.68 \text{ molal}$

$\Delta T = k_{fp} \times m = -1.86 \text{ C/m} \times 2.68 = -4.98$

new freezing point will be -5.0°C, so wine won't freeze.

ans: no