Chemical Kinetics

Practice Exam Chemical Kinetics

Name (last) __________________________ (First) __________________________

Read all questions before you start. Show all work and explain your answers to receive full credit. Report all numerical answers to the proper number of significant figures. By signing your signature above you agree that you have worked alone and neither give nor received help from any source. Keep your eyes on your own paper at all times.

<table>
<thead>
<tr>
<th>System</th>
<th>LENGTH:</th>
<th>VOLUME</th>
<th>MASS</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>English:</td>
<td>1 ft = 12 in</td>
<td>1 gal = 4 qt</td>
<td>1 lb = 16 oz</td>
<td>(T_F = 1.8T_C + 32)</td>
</tr>
<tr>
<td>1 mile = 5280 ft</td>
<td>1 qt = 57.75 in³</td>
<td>1 ton = 2000 lb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 yd = 3 ft</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SI-</td>
<td>1 in = 2.54 cm</td>
<td>1 L = 1.057 qt</td>
<td>1 lb = 453.6 g</td>
<td>(T_C = \frac{(T_F - 32)}{1.8})</td>
</tr>
<tr>
<td>English:</td>
<td>1 mi = 1.609 km</td>
<td>1 qt = 0.946 L</td>
<td>1 oz = 28.35 g</td>
<td></td>
</tr>
<tr>
<td>Misc. info</td>
<td>1 mole = 6.02•10²³</td>
<td></td>
<td></td>
<td>(R = 8.314 \text{ J/mol}\cdot\text{K} \text{ or } 0.08206 \text{ L}\cdot\text{atm/mol}\cdot\text{K})</td>
</tr>
</tbody>
</table>

Rates of Reaction

rate = \(\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[\text{react}]}{\Delta t} = \frac{\Delta[\text{prod}]}{\Delta t}\)

Rate laws (Order of reaction)

<table>
<thead>
<tr>
<th>Conc. vs. Time dependence</th>
<th>initial rate = (k [A]^x [B]^y [C]^z \ldots)</th>
<th>Overall order = (x + y + z + \ldots)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeroth Order</td>
<td>([A] = [A]_0 - kt)</td>
<td>Conc. vs. Time (\rightarrow) straight line.</td>
</tr>
<tr>
<td>rate = (k)</td>
<td></td>
<td>Half life: (t_{1/2} = \frac{[A]_0}{2k})</td>
</tr>
<tr>
<td>First Order</td>
<td>([A] = [A]_0 \exp(-kt))</td>
<td>(\ln[\text{conc.}]) vs. Time (\rightarrow) straight line</td>
</tr>
<tr>
<td>rate = (k[A])</td>
<td>(\ln[A] = \ln[A]_0 - kt)</td>
<td>Half life: (t_{1/2} = 0.693 / k)</td>
</tr>
<tr>
<td>Second Order</td>
<td>(1/[A] = 1/[A]_0 + kt)</td>
<td>(1/[\text{conc.}]) vs. Time (\rightarrow) straight line</td>
</tr>
<tr>
<td>rate = (k[A]^2) or (k[A][B])</td>
<td></td>
<td>Half life: (t_{1/2} = 1 / k[A]_0)</td>
</tr>
<tr>
<td>Temperature vs. Rate dependence</td>
<td>(k = A \exp\left(-\frac{E_a}{RT}\right))</td>
<td>(\ln(k)) vs. (1/T) (\rightarrow) straight line.</td>
</tr>
<tr>
<td></td>
<td>(\ln k = \ln A - (E_a / R)\cdot1/T)</td>
<td>(\ln(k_1/k_2) = (E_a / R) \cdot (1/T_1 - 1/T_2))</td>
</tr>
</tbody>
</table>
Multiple-choice. Show work for partial credit.

1. Which of the following statement is true?
   a) The activation energy of a reaction increases with increasing temperature.
   b) The slowest step in a mechanism will always determine the rate of a reaction.
   c) A catalyst not only changes the activation energy of a reaction, it also changes $\Delta H_{rxn}$.
   d) All of these statements are true.

2. A plot of $\ln [A]$ vs. time is most likely what order kinetics?
   a) Arrhenius equation  
   b) second order reaction  
   c) first order reaction  
   d) zeroth order reaction

3. If the heat of reaction is endothermic, which of the following is always true?
   a) the reaction is fast  
   b) the reaction is slow  
   c) the energy of the reactants is greater than the products  
   d) the energy of the reactants is lower than the products

4. The rate of a reaction is not influenced by:
   a) concentration of reactant  
   b) Catalyst  
   c) Energy of Reactant  
   d) stirring of chemicals

5. The pre-exponential factor in the Arrhenius equation takes in to account:
   a) The steric factor 
   b) The activation energy  
   c) The energy of the reaction  
   d) The Maxwell-Boltzmann distribution

6. The reaction: $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$ was studied at 25°C. The following results were obtained

<table>
<thead>
<tr>
<th></th>
<th>$[I^-]_0$ (M)</th>
<th>$[S_2O_8^{2-}]$ (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.040</td>
<td>0.080</td>
<td>$12.50\cdot10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>0.040</td>
<td>0.040</td>
<td>$3.125\cdot10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.080</td>
<td>$12.50\cdot10^{-6}$</td>
</tr>
</tbody>
</table>

i) Determine the rate law.

ii) What is the rate constant using experiment # 2

iii) What is the molecularity of this reaction?

iv) Calculate the half-life using the data from Experiment 2
Most reaction occurs by a series of steps. The energy profile shown below follows a three-step mechanism for the reaction of NO with H₂:

i) \( 2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \) fast \( \Delta H_1 = +20 \text{ kJ} \) \( E_{\text{act}1} = 50 \text{ kJ} \) \( E_1^\ddagger = 50 \text{ kJ} \) (Transition state)

ii) \( \text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \) slow \( \Delta H_2 = +30 \text{ kJ} \) \( E_{\text{act}2} = ? \) \( E_2^\ddagger = 100 \text{ kJ} \)

iii) \( \text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \) fast \( \Delta H_3 = -10 \text{ kJ} \) \( E_{\text{act}3} = 30 \text{ kJ} \) \( E_3^\ddagger = ? \)

Place answers to questions ii, iii, iv, & vi.

\( E(\text{NO}) = ____ \)

\( E(\text{N}_2\text{O}_2) = ____ \)

\( E_{\text{act}2} = ____ \)

\( E_3^\ddagger = ____ \)

\( \Delta H_{\text{rxn}} = ____ \)

\( E_{\text{act}(f)} = ____ \)

\( E_{\text{act}(r)} = ____ \)

Label the graph above placing the chemical species along the reaction profile diagram and then answer the following:

i) What is the overall stoichiometry and what are the intermediate and the catalyst (if any)?

ii) What are the energies of NO and N₂O₂ according to the graph above?

iii) What are the energies of \( E_{\text{act}2} \) and \( E_3^\ddagger \)?

iv) What is the energy of the overall reaction, \( \Delta H_{\text{rxn}} \)?

v) Is the reaction endothermic or exothermic?

vi) What are the activation energies for the overall forward \( E_{\text{act}(f)} \), and overall reverse \( E_{\text{act}(r)} \), reactions?

vii) What are the rate law and the molecularity for this reaction?

viii) If the pre-exponential factor is \( 1.27 \cdot 10^{10} \), what is the rate constant (include units) for this reaction at 600K?

ix) What temperature is required to raise the rate constant to 250? (units are not shown here)

x) If the catalyzed reaction is ten times faster than the uncatalyzed reaction, what is the rate of disappearance of the reactant for the catalyzed reaction? You may assume that you are using the methods of initial rates in which the concentration of all chemicals are 1.0 M. \( T = 600 \text{ K} \)

Explain using a Maxwell-Boltzmann Distribution curve why an exothermic reaction favors an increase of the reverse reaction at higher temperature even though according to the Kinetic Molecular Theory, the rate of a reaction increases with increasing temperature.
Determine if the statements below are true or false then write a convincing statement to justify your answer.

a) At a given temperature, all molecules possess the same kinetic energy

b) Reactant molecules must collide with greater energy than the activation energy in order to change to product molecules.

c) The activation energy of a reaction is not dependent on the temperature.

d) A catalyst increases the rate by increasing collision frequency.

The reaction of hydrogen with iodine has the following accepted mechanism:

(1) \( \text{I}_2 (g) \rightarrow 2 \text{I} (g) \) fast
(2) \( \text{H}_2 \text{(g) + I} (g) \rightarrow \text{H}_2 \text{I} (g) \) fast
(3) \( \text{H}_2 \text{I} (g) + \text{I} (g) \rightarrow 2 \text{HI} (g) \) slow

What is the rate law for this reaction?

Consider the following reaction energy diagram:

i) How many elementary steps in the reaction mechanism?

ii) Which step is rate limiting? i.e. 1st, 2nd, 3rd, 4th...

iii) Is the overall reaction exothermic or endothermic?

iv) What is the energy of the reaction (kJ)?

v) What is the activation energy (kJ) for the reverse reaction?

vi) What is the \( E_{\text{Act}} \) (kJ) for the rate determining step?

A theoretical reaction: \( \text{A} + \text{B} \rightarrow \text{C} \), has the following initial rate data shown below.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (300K)</td>
<td>0.012</td>
<td>0.035</td>
<td>(1.0 \times 10^{-5})</td>
</tr>
<tr>
<td>2 (300K)</td>
<td>0.024</td>
<td>0.070</td>
<td>(8.0 \times 10^{-5})</td>
</tr>
<tr>
<td>3 (300K)</td>
<td>0.024</td>
<td>0.035</td>
<td>(1.0 \times 10^{-5})</td>
</tr>
<tr>
<td>4 (300K)</td>
<td>0.012</td>
<td>0.070</td>
<td>(8.0 \times 10^{-5})</td>
</tr>
<tr>
<td>5 (600K)</td>
<td>0.012</td>
<td>0.070</td>
<td>1.8</td>
</tr>
</tbody>
</table>

i) Determine the complete rate law for the reaction including the rate constant with proper units.

ii) What is the activation energy \( (E_a \text{ in kJ}) \) for this reaction and the frequency factor \( (A) \).

A slightly bruised apple will rot extensively in about 4 days at room temperature (20°C). If it is kept in the refrigerator at 0°C, the same extent of rotting takes about 16 days. What is the \( E_{\text{Act}} \) (kJ) for the rotting reaction?
Determine if the statements are true or false. Give a reasonable explanation to support or refute these statements.

i) At a given temperature, all molecules possess the same kinetic energy.

ii) The higher the activation energy of a reaction, the slower the rate of the reaction.

iii) If reactant molecules collide with greater energy than the activation energy, products are formed automatically.

iv) Exothermic reactions have faster rates than endothermic reactions.

v) The activation energy of a reaction is lowered by a catalyst.

vi) The enthalpy change for a reaction is lowered by a catalyst.