Part I. Multiple Choice  (3 points each -- Total points = 45)

1. The “activation energy” for a chemical reaction is

1. the energy produced when bonds are formed in the reaction
2. highly dependent upon the temperature of the reaction
3. the form of the reactant-product “molecule” when it is in the transition state
4. generally not the same for both forward and reverse reactions
5. the same as the enthalpy change (ΔH) for the reaction

Answer: #4 none of other answers is true

2. An enzyme is a(an)

1. molecule that is acted on by a catalyst in a living system
2. organic or inorganic molecule or ion necessary for proper functioning of biological catalysts
3. catalyst for chemical reactions in a living system
4. biological molecule used for storage of energy
5. protein molecule whose primary function is transport of insoluble molecules in the bloodstream

Answer: #3 is the definition of an enzyme

3. Which statement is not correct regarding the function of a catalyst?

1. It lowers the activation energy.
2. It changes the mechanism of a reaction.
3. It affects the rate of a chemical reaction.
4. It lowers the energy of the product causing the reaction to be more exothermic.
5. It increases the energy of the product causing the reaction to be more endothermic.

Answer: either 4 or 5 is correct – the only energy affected by a catalyst is the activation energy, since the reaction proceeds by a different reaction “path” or sequence of molecular events (a different mechanism) and its rate is increased …
4. In the reaction, A \rightarrow \text{products}, the initial concentration of A is 1.60 M, and 45 s later it is 1.20 M. What is the initial rate of this reaction in M \cdot s^{-1}?

1. $8.0 \times 10^{-3}$
2. $3.1 \times 10^{-2}$
3. $8.9 \times 10^{-3}$
4. $2.7 \times 10^{-2}$
5. $3.5 \times 10^{-2}$

**Answer:** 3 \hspace{1em} \text{Rate} = \frac{(1.60 \text{ M} - 1.20 \text{ M})}{45 \text{ s}} = 8.9 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}

5. Which of the following statements would be correct regarding the following reaction?

$$2 \text{H}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{H}_2\text{O} (g)$$

1. The rate of O\(_2\) disappearance is twice the rate of H\(_2\) disappearance.
2. The rate of H\(_2\) disappearance is twice the rate of O\(_2\) disappearance.
3. The rate of H\(_2\)O disappearance is twice the rate of O\(_2\) disappearance.
4. The rate of H\(_2\)O appearance is equal to the rate of O\(_2\) disappearance.
5. The rate of H\(_2\) disappearance is equal to the rate of O\(_2\) disappearance.

**Answer:** 2 \hspace{1em} \text{here,} - \frac{1}{2} \Delta \text{[H}_2]/dt = - \Delta \text{[O}_2]/dt, \text{ so } - \Delta \text{[H}_2]/dt = - 2 \Delta \text{[O}_2]/dt

6. In the reaction $2 \text{A} + \text{B} \rightarrow 2 \text{C} + \text{D}$, \(-\frac{\Delta [\text{A}]}{\Delta t}\) is found to be 5.0 M·min\(^{-1}\). What is the rate of reaction of B in M·min\(^{-1}\)?

1. 2.5
2. 5.0
3. 10
4. 75
5. 4.0

**Answer:** 1 \hspace{1em} \text{here,} - \frac{1}{2} \Delta \text{[A])/dt} = - \Delta \text{[B]/dt, so } - \frac{1}{2} (5.0) = - \Delta \text{[B)/dt} = 2.5 \text{ M·min}^{-1}

7. Which statement is incorrect?

1. The rate equation for a reaction contains all the species in the balanced overall equation.
2. The rate equation for an elementary step contains the reactants raised to the exponent that is the coefficient of that species.
3. The slowest step of a mechanism controls the overall rate of the reaction.
4. The concentration of species involved in the mechanism after the slow step will not affect the reaction rate.
5. The sum of the elementary steps in a mechanism gives the net overall reaction.

**Answer:** 1 \hspace{1em} the only species that can be in the rate equation are the reactants
8. Which of the rate laws below is not a possible initial rate law for the reaction in which

$$2 \text{H}_2 + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_6$$

1. Rate = $$k \left[ \text{H}_2 \right] \left[ \text{C}_2\text{H}_2 \right]$$
2. Rate = $$k \left[ \text{H}_2 \right]^2 \left[ \text{C}_2\text{H}_2 \right]$$
3. Rate = $$k \left[ \text{H}_2 \right]^3$$
4. Rate = $$k \left[ \text{H}_2 \right]^2 \left[ \text{C}_2\text{H}_6 \right]$$
5. Rate = $$k \left[ \text{H}_2 \right]^3$$

**Answer:** 4 the only species that can be in the rate equation are the reactants .. C$_2$H$_6$ is a product

9. Which statement is incorrect?

1. The half-life of a zero order reaction is directly proportional to the initial concentration (i.e., the greater the concentration the longer the half-life).
2. The half-life of a first order reaction is directly proportional to the initial concentration.
3. The half-life of a second order reaction is inversely proportional to the initial concentration.
4. The half-life of a first order reaction is independent of the initial concentration.
5. The shorter the half-life, the faster is the reaction.

**Answer:** 2 (not true because $t_{1/2} = 0.693/k$ for first-order reactions ... independent of initial concentration

10. A chemical system is at equilibrium

1. when the concentration of reactants and products are equal.
2. when all of the reactants have been used up.
3. when the rate of the forward reaction becomes zero.
4. when the rates of the forward reaction and the reverse reaction are both zero.
5. when the rates of the forward reaction and the reverse reaction are equal.

**Answer:** 5 this is the definition of chemical equilibrium

11. The reaction: 2 NO (g) + Cl$_2$ (g) $\rightleftharpoons$ 2 NOCl (g) is allowed to reach equilibrium. Analysis of the equilibrium mixture shows [NO] = 0.0574, [Cl$_2$] = 0.126, and [NOCl] = 0.248. Based upon these data, $K_C$ for this reaction at this temperature is

1. $6.75 \times 10^{-3}$
2. $2.92 \times 10^{-3}$
3. 34.2

**Answer:** 5 $K_C = [\text{NOCl}] / ([\text{NO}][\text{Cl}_2]) = (0.248)^2 / (0.0574)(0.126) = 148$
12. For which one of the following values of $K_C$ will the equilibrium mixture consist almost entirely of products?

1. 0.030  
2. 1.00  
3. $4 \times 10^8$  
4. 30  
5. $1 \times 10^{-10}$

**Answer:** 3 The largest $K_C$ value corresponds to the *most product-favored* reaction.

13. For the system $\text{CaO (s) + CO}_2 (g) \rightleftharpoons \text{CaCO}_3 (s)$, the equilibrium constant expression is

1. $K_C = [\text{CaCO}_3] / [\text{CaO}] [\text{CO}]$  
2. $K_C = 1/ [\text{CaO}] [\text{CO}]$  
3. $K_C = [\text{CO}_2]$  
4. $K_C = [\text{CaO}] [\text{CO}_2] / [\text{CaCO}_3]$  
5. $K_C = 1/ [\text{CO}_2]$

**Answer:** 5 $K_C = [\text{products}] / [\text{reactants}]$ … no (s) species appear in equilibrium expressions.

14. The conjugate base of $\text{HPO}_4^{2-}$ is

1. $\text{PO}_4^{3-}$  
2. $\text{H}_2\text{PO}_4^{2-}$  
3. $\text{H}_2\text{PO}_4^-$  
4. $\text{H}_3\text{PO}_4$  
5. $\text{H}_2\text{PO}_4^{2-}$

**Answer:** 1 remove one H$^+$ from $\text{HPO}_4^{2-}$ to get its conjugate base.

15. The reason that HI is a stronger acid than HCl is that

1. bond dissociation energy decreases as you go down the periodic table.  
2. electronegativity increases as you go up the periodic table.  
3. anion radius decreases as you go down the periodic table.  
4. the difference in electronegativity gets larger as the atoms get farther apart on the periodic table.  
5. HI is an Arrhenius acid and HCl is not.

**Answer:** 1 acid strength is inversely proportional to bond strength for the X – H bond … #1 is *true* and applies to the H - I and H - Cl bonds. Lower bond dissociation energy means a weaker bond and a stronger acid.
1. (10 points) A chemist collected the data in the table below for the gas phase reaction between nitric oxide and hydrogen:

\[
2\text{NO} (g) + \text{H}_2 (g) \rightarrow \text{N}_2\text{O} (g) + \text{H}_2\text{O} (g)
\]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO], M</th>
<th>[H\textsubscript{2}], M</th>
<th>Rate, M s\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.4 \times 10^-3</td>
<td>2.2 \times 10^-3</td>
<td>2.6 \times 10^-5</td>
</tr>
<tr>
<td>2</td>
<td>12.8 \times 10^-3</td>
<td>2.2 \times 10^-3</td>
<td>1.0 \times 10^-4</td>
</tr>
<tr>
<td>3</td>
<td>6.4 \times 10^-3</td>
<td>4.5 \times 10^-3</td>
<td>5.1 \times 10^-5</td>
</tr>
</tbody>
</table>

(a) (5 points) Determine and write the complete rate law, including exponents, for this reaction.

\[
\text{Rate} = k[\text{NO}]^x [\text{H}_2]^y = k[\text{NO}]^2 [\text{H}_2]^1
\]

[NO] 6.4 \times 10^{-3} to 12.8 \times 10^{-3}: concentration doubles; 2.6 \times 10^{-5} to 1.0 \times 10^{-4}: rate quadruples

so, \( 2^x = 4 \quad \Rightarrow \quad x = 2 \)

[\text{H}_2] 2.2 \times 10^{-3} to 4.5 \times 10^{-3}: concentration doubles; 2.6 \times 10^{-5} to 5.1 \times 10^{-5}: rate doubles

so, \( 2^y = 2 \quad \Rightarrow \quad y = 1 \)

(b) (3 points) Calculate the value of the rate constant, \( k \) (you must include the appropriate units!)

Exp. #1 \[\text{rate} = k[\text{NO}]^2 [\text{H}_2]^1 \quad \Rightarrow \quad 2.6 \times 10^{-5} \quad \text{M} \text{s}^{-1} = k (6.4 \times 10^{-3} \text{ M})^2 (2.2 \times 10^{-3} \text{ M}) \]

\[
k = (2.6 \times 10^{-5} \text{ M} \text{s}^{-1}) / (9.01 \times 10^{-8} \text{ M}^3) = 2.9 \times 10^2 \text{ M}^{-2} \text{ s}^{-1}
\]

(c) (2 points) Is the mechanism shown below consistent with the observed rate law data above? You must briefly justify and explain your answer.

\[
\text{step 1 - } 2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \quad \text{(fast)} \quad \text{rate} = k_1 [\text{NO}]^2
\]

\[
\text{step 2 - } \text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \quad \text{(slow)} \quad \text{rate} = k_2 [\text{N}_2\text{O}_2][\text{H}_2]
\]

\[
\text{step 3 - } \text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad \text{(fast)} \quad \text{rate} = k_3 [\text{N}_2\text{O}][\text{H}_2]
\]

The rate equation for the slow (rate-determining) step does not agree with the experimentally observed rate law, \( \text{rate} = k[\text{NO}]^2 [\text{H}_2]^1 \), so the mechanism is not consistent.
2. (10 points) Consider the following reaction, where

\[ \text{H}_2 (g) + \text{I}_2 (g) \rightleftharpoons 2 \text{HI} (g) \quad K_C = 49.0 \]

If 0.080 moles of \( \text{H}_2 \), 0.080 moles of \( \text{I}_2 \) and 0.64 moles of \( \text{HI} \) are placed in a 4.0 L flask and allowed to reach equilibrium, what are the concentrations of \( \text{H}_2 \) and \( \text{HI} \), respectively, in the flask after equilibrium is reached? **You must show work, including the appropriate ICE table, for credit!**

\[
\begin{align*}
\text{C(H}_2) &= \text{C(I}_2) = 0.080 \text{ mol/4.0 L} = 0.020 \text{ M}; \text{C(HI)} = 0.64 \text{ mol/4.0 L} = 0.16 \text{ M} \\
Q_C &= (0.16 \text{ M})^2 / (0.020 \text{ M})(0.020 \text{ M}) = 64. > K_C (49.0) \\
\text{Since } Q_C > K_C, \text{ equilibrium must shift to the left, decreasing product concentrations and increasing reactant concentrations until equilibrium is re-established.}
\end{align*}
\]

ICE Table:

<table>
<thead>
<tr>
<th></th>
<th>( \text{H}_2(g) )</th>
<th>( \text{I}_2(g) )</th>
<th>( \text{HI(g)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.020</td>
<td>0.020</td>
<td>0.16</td>
</tr>
<tr>
<td>C</td>
<td>+ x</td>
<td>+ x</td>
<td>- 2x</td>
</tr>
<tr>
<td>E</td>
<td>0.020 + x</td>
<td>0.020 + x</td>
<td>0.16 - 2x</td>
</tr>
</tbody>
</table>

So, \( K_C = 49.0 = \frac{[\text{HI(g)}]^2}{[\text{H}_2(g)][\text{I}_2(g)]]} = \frac{(0.16 - 2x)^2}{(0.020 + x)^2} \)

Taking square roots: \((49.0)^{1/2} = 7.0 = (0.16 - 2x) / (0.020 + x)\)

\[ 7.0(0.020 + x) = (0.16 - 2x) \]
\[ 0.140 + 7.0x = 0.16 - 2x \]
\[ 9.0x = 0.16 - 0.140 = 0.020 \]
\[ x = 0.022 \text{ M} \]

\[ \text{[H}_2(g)] = \text{[I}_2(g)] = 0.020 + 0.0022 = 0.0222 \text{ M} \]

\[ \text{[HI(g)]} = 0.16 - 2(0.0022) = 0.1556 = 0.16 \text{ M} \]
3. (15 points) Many highly-chlorinated insecticides were introduced during the 1950s. One of these was Mirex, used as a pesticide to control the imported fire ant (*Solenopsis invicta*), which infested large portions of the southeastern United States.

(a) Calculate the half-life \( t_{1/2} \) of Mirex in soils, if at normal environmental temperatures, \( k = 0.0693 \text{ yr}^{-1} \). *You must show all work for credit or partial credit!*

\[
t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0693} = 10.0 \text{ yr}
\]

(b) If the initial concentration of Mirex in a sample of soil near a Mirex manufacturing plant in Hopewell, Virginia was \( 1.3 \times 10^3 \text{ mg/kg} \) soil, what would its concentration be after 2 years, assuming that no additional Mirex entered the soil during this time? *You must show all work for credit or partial credit!*

\[
\ln \left( \frac{[A_0]}{[A_t]} \right) = kt
\]

\[
\ln (1.3 \times 10^3 \text{ mg/kg})/ [A_t] = (2 \text{ yr})(0.0693 \text{ yr}^{-1})
\]

\[
\ln (1.3 \times 10^3 \text{ mg/kg})/ [A_t] = 0.1386, \text{ or } (1.3 \times 10^3 \text{ mg/kg})/ [A_t] = \exp(0.1386)
\]

\[
(1.3 \times 10^3 \text{ mg/kg})/ [A_t] = 1.149
\]

\[
[A_t] = 1.13 \times 10^3 \text{ mg/kg}
\]

(c) Assuming that no more Mirex entered the soil, how long would it take for the concentration of Mirex to drop to 5.0% of its initial value? *You must show all work for credit or partial credit!*

\[
\ln \left( \frac{[A_0]}{[A_t]} \right) = kt
\]

\[
\ln (1.00/0.05) = (0.0693 \text{ yr}^{-1}) \cdot t
\]

\[
2.996 = (0.0693 \text{ yr}^{-1}) \cdot t
\]

\[
t = 43.2 \text{ yr}
\]
4. (10 points) Consider the reaction in which \( 2 \text{NOBr} \, (g) \rightleftharpoons 2 \text{NO} \, (g) + \text{Br}_2 \, (g) \) \( \Delta H = +16.1 \text{kJ} \)

If NOBr (g), NO (g) and Br\(_2\) (g) are initially in equilibrium in a reaction vessel, how will each of the following changes affect the quantities shown below? Assume constant volume except for the next to last case. Answer the question by writing I (increase), D (decrease) or NC (no change) in each of the blanks provided.

\[
\text{Heat} + 2 \text{NOBr} \, (g) \rightleftharpoons 2 \text{NO} \, (g) + \text{Br}_2 \, (g)
\]

<table>
<thead>
<tr>
<th>Change</th>
<th>([\text{NOBr}])</th>
<th>([\text{NO}])</th>
<th>(K_C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Some NOBr is removed from the container (equilibrium shifts to LEFT)</td>
<td>(\text{D})</td>
<td>(\text{D})</td>
<td>(\text{NC})</td>
</tr>
<tr>
<td>The temperature is decreased (equilibrium shifts to LEFT)</td>
<td>(\text{I})</td>
<td>(\text{D})</td>
<td>(\text{D})</td>
</tr>
<tr>
<td>The pressure is decreased by increasing volume (equilibrium shifts to RIGHT)</td>
<td>(\text{D})</td>
<td>(\text{I})</td>
<td>(\text{NC})</td>
</tr>
<tr>
<td>Some Br(_2) is added to the container (equilibrium shifts to LEFT)</td>
<td>(\text{I})</td>
<td>(\text{D})</td>
<td>(\text{NC})</td>
</tr>
</tbody>
</table>

5. (10 points) At 500 K, \( \text{N}_2 \, (g) + 3 \text{H}_2 \, (g) \rightleftharpoons 2 \text{NH}_3 \, (g) \), where \(K_C = 5.97 \times 10^{-2}\). If this reaction is carried out in a sealed reaction vessel at 500 K, and if the initial concentrations of the gaseous species are \([\text{N}_2] = 0.500 \text{ M}\), \([\text{H}_2] = 0.250 \text{ M}\), and \([\text{NH}_3] = 4.2 \times 10^{-3} \text{ M}\), will more \(\text{NH}_3\) be formed, will it decompose to make more \(\text{N}_2\) and \(\text{H}_2\) once the mixture achieves equilibrium at 500 K, or is the system already at equilibrium?

Make the appropriate calculations and then clearly discuss your results for credit on this question.

\[
Q_C = \frac{C(\text{NH}_3)^2}{[C(\text{N}_2) \cdot C(\text{H}_2)^3]} = \frac{(4.2 \times 10^{-3})^2}{[(0.500)(0.250)^3}] = 2.26 \times 10^{-3}
\]

Since \(QC < KC\) (2.26 \times 10^{-3} < 5.97 \times 10^{-2}\), the equilibrium will shift to make more product and less reactant, i.e. it will shift to the RIGHT, so it will form MORE \(\text{NH}_3\).