Assignment 14 A

1- Use the table of data shown below to calculate the average rate of the reaction between 10 sec and 20 sec.

\[ A \rightarrow B \]

<table>
<thead>
<tr>
<th>time (sec)</th>
<th>[A] mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.20</td>
</tr>
<tr>
<td>5</td>
<td>0.14</td>
</tr>
<tr>
<td>10</td>
<td>0.10</td>
</tr>
<tr>
<td>15</td>
<td>0.071</td>
</tr>
<tr>
<td>20</td>
<td>0.050</td>
</tr>
</tbody>
</table>

a) 0.05 M/s
b) 0.008 M/s
c) 200 M/s
d) 0.006 M/s
e) 0.005 M/s

(This is the \(-\Delta[A]/\Delta t\) over the range 10-20 sec.)

2- Consider the combustion of \(H_2(g)\):

\[ 2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \]

If hydrogen is burning at the rate of 4.6 mol s\(^{-1}\), what are the rates of consumption of oxygen and formation of water vapor?

a) \(-2.3\) mol s\(^{-1}\) (O\(_2\)) and +2.3 mol s\(^{-1}\) (H\(_2O\))
b) \(-2.3\) mol s\(^{-1}\) (O\(_2\)) and \(-4.6\) mol s\(^{-1}\) (H\(_2O\))
c) \(-4.6\) mol s\(^{-1}\) (O\(_2\)) and +4.6 mol s\(^{-1}\) (H\(_2O\))
d) \(-2.3\) mol s\(^{-1}\) (O\(_2\)) and +4.6 mol s\(^{-1}\) (H\(_2O\))
e) \(-4.6\) mol s\(^{-1}\) (O\(_2\)) and \(-4.6\) mol s\(^{-1}\) (H\(_2O\))

(O\(_2\) is consumed at 1/2 the rate of H\(_2\), and H\(_2O\) is produced at the same rate as the H\(_2\) is consumed.)

3- If the reaction \(2A + 3D \rightarrow \) products is first-order in A and second-order in D, then the rate law will have the form:

Rate =

a) \(k[A][D]\)
b) \(k[A]^2[D]^2\)
c) \(k[A][D]^3\)
d) \(k[A]^2[D]^3\)
e) \(k[A]^2[D]^4\)

(The rate is first order in A, and second order for D, as shown by the respective exponents in the rate expression.)

4- For a reaction of the type \(A + B + C\) going to products, the following observations are made: Doubling the concentration of A doubles the rate, doubling the concentration of B has no effect on the rate, and tripling the concentration of C increases the rate by a factor of 9. What is the rate law for the reaction?

a) Rate = \(k[A][B][C]\)
b) Rate = \(k[A][C]^2\)
c) Rate = \(k[A]^2[B][C]\)
d) Rate = \(k[A]^2[B][C]^2\)
e) Rate = \(k[A]^3[C]\)

(This reaction is first order in A, second order in C, and zero order in B, since changing the \([B]\) has no effect on the rate.)
5- The following data were collected for the rate of disappearance of NO in the reaction:

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

**Initial Rate Experiment**

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>[NO] (M)</th>
<th>[O(_2)] (M)</th>
<th>Initial rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0126</td>
<td>0.0125</td>
<td>1.41 × 10(^{-2})</td>
</tr>
<tr>
<td>2</td>
<td>0.0252</td>
<td>0.0250</td>
<td>1.13 × 10(^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>0.0252</td>
<td>0.0125</td>
<td>5.64 × 10(^{-2})</td>
</tr>
</tbody>
</table>

What is the rate law for the reaction and the value of the rate constant?

<table>
<thead>
<tr>
<th>Option</th>
<th>Rate Expression</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>Rate = (k[\text{NO}]^2[\text{O}_2]), (k = 7.11 \times 10^3 \text{ M}^{-2} \text{s}^{-1})</td>
<td></td>
</tr>
<tr>
<td>b)</td>
<td>Rate = (k[\text{NO}]^2), (k = 8.88 \times 10^1 \text{ M}^{-1} \text{s}^{-1})</td>
<td></td>
</tr>
<tr>
<td>c)</td>
<td>Rate = (k[\text{NO}][\text{O}_2]^2), (k = 7.16 \times 10^3 \text{ M}^{-2} \text{s}^{-1})</td>
<td></td>
</tr>
<tr>
<td>d)</td>
<td>Rate = (k[\text{O}_2]), (k = 1.12 \text{ M}^{-2} \text{s}^{-1})</td>
<td></td>
</tr>
<tr>
<td>e)</td>
<td>Rate = (k[\text{NO}][\text{O}_2]), (k = 8.95 \times 10^1 \text{ M}^{-1} \text{s}^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

(Using trials 2 & 3, the rate increases two times when the [\text{O}_2] is doubled, and using trials 1 & 3, the rate increases by a factor of four when the [\text{NO}] is doubled.)

6- In a second-order reaction the rate constant is 4.00 \(\times\) 10\(^{-4}\) M\(^{-1}\) s\(^{-1}\). What is the concentration of reactant after 10 min if the initial concentration is 0.800 M?

<table>
<thead>
<tr>
<th>Option</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>0.797 M</td>
</tr>
<tr>
<td>b)</td>
<td>1.49 M</td>
</tr>
<tr>
<td>c)</td>
<td>0.671 M</td>
</tr>
<tr>
<td>d)</td>
<td>0.629 M</td>
</tr>
<tr>
<td>e)</td>
<td>0.300 M</td>
</tr>
</tbody>
</table>

(The [A]_{\text{f}} equals the reciprocal of (kt + 1/[A]_{0}).)

7- The thermal decomposition of N\(_2\)O\(_5\)(g) to form NO\(_2\)(g) and O\(_2\)(g) is a first-order reaction. The rate constant for the reaction is 5.1 \(\times\) 10\(^{-4}\) s\(^{-1}\) at 318 K. What is the half-life of this process?

<table>
<thead>
<tr>
<th>Option</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>2.6 (\times) 10(^{-3}) s</td>
</tr>
<tr>
<td>b)</td>
<td>2.0 (\times) 10(^{3}) s</td>
</tr>
<tr>
<td>c)</td>
<td>1.0 (\times) 10(^{-3}) s</td>
</tr>
<tr>
<td>d)</td>
<td>3.9 (\times) 10(^{3}) s</td>
</tr>
<tr>
<td>e)</td>
<td>1.4 (\times) 10(^{3}) s</td>
</tr>
</tbody>
</table>

(The half-life is 0.693/k.)

8- In the diagram below, which measurement corresponds to the change in the enthalpy of the reaction? Is the reaction exothermic or endothermic?

![Reaction Coordinate Diagram](image)

<table>
<thead>
<tr>
<th>Option</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>Z; exothermic</td>
</tr>
<tr>
<td>b)</td>
<td>X; endothermic</td>
</tr>
<tr>
<td>c)</td>
<td>X; exothermic</td>
</tr>
<tr>
<td>d)</td>
<td>Y; exothermic</td>
</tr>
<tr>
<td>e)</td>
<td>Z; endothermic</td>
</tr>
</tbody>
</table>

(X represents the \(\Delta H^\circ_{\text{rxn}}\) and since P is at a lower energy than R, the reaction is exothermic.)
9- Write a rate law for the following elementary reaction:
\[ \text{NO} + \text{Cl}_2 \rightarrow \text{NOCl}_2 \]
and determine the molecularity of the elementary reaction.

a) rate = \( k[\text{NO}][\text{Cl}_2] \); unimolecular
b) rate = \( k[\text{NO}][\text{Cl}_2]^2 \); termolecular
c) rate = \( k[\text{NO}][\text{Cl}_2] \); bimolecular
d) rate = \( k[\text{NO}]^2[\text{Cl}_2] \); termolecular
e) rate = \( k[\text{NO}][\text{Cl}_2]^2 \); bimolecular

(This reaction is first order in each reactant.)

10- The decomposition of \( \text{N}_2\text{O}_5 \) in carbon tetrachloride proceeds as follows:
\[ 2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2 \]
The rate law is first-order in \( \text{N}_2\text{O}_5 \). At 45°C the rate constant is \( 6.08 \times 10^{-4} \text{ s}^{-1} \). What is the rate of the reaction when \( [\text{N}_2\text{O}_5] = 0.100 \text{ M} \), and what happens to the rate when the concentration of \( \text{N}_2\text{O}_5 \) is doubled to 0.200 \text{ M}?

a) \( 6.08 \times 10^{-3} \text{ M/s}; \) the rate will be halved at 0.200 \text{ M}
b) \( 6.08 \times 10^{-5} \text{ M/s}; \) the rate will double at 0.200 \text{ M}
c) \( 6.08 \times 10^{-4} \text{ M/s}; \) the rate will not change at 0.200 \text{ M}
d) \( 6.08 \times 10^{-5} \text{ M/s}; \) the rate will not change
e) \( 6.08 \times 10^{-4} \text{ M/s}; \) the rate will double when the concentration of \( \text{N}_2\text{O}_5 \) is doubled to 0.200 \text{ M}

(The rate = \( k[\text{N}_2\text{O}_5] \); doubling the \( [\text{N}_2\text{O}_5] \) will double the rate.)

11- A reaction has a rate law: rate = \( k[A]^2 \). What would you plot to have the concentration versus time data give a straight line?
a) plot ln (1/[A]) vs time
b) plot log[A] vs time
c) plot ln[A] vs time
d) plot [A] vs time
e) plot 1/[A] vs time

(This is the plot which will give a straight line for a second-order reaction.)

12- The decomposition of NOBr is second-order with respect to NOBr and second-order overall. If the initial concentration of NOBr is 0.102 \text{ M} and the rate constant is 25 \text{ M}^{-1} \text{ min}^{-1}, what is [NOBr] after 1.0 \text{ min}?

a) \( 1.4 \times 10^{-12} \text{ M} \)
b) \( 4.0 \times 10^{-7} \text{ M} \)
c) \( 9.8 \text{ M} \)
d) \( 2.9 \times 10^{-2} \text{ M} \)

(The [NOBr] equals the reciprocal of \( (kt + 1/[\text{NOBr}]_0) \).)

13- Which one of the following statements is incorrect?
a) The rate does not depend on the magnitude of the \( \Delta\text{E} \), the internal energy change for the overall reaction.
b) Activation energies of simple reactions can be negative.
c) The rates of two reactions can be equal at one temperature but differ at another.
d) The lower the activation energy, the faster the rate if equal numbers of orientation independent collisions are always involved.
e) More molecules in a gas have energies above some threshold value as the temperature is increased.

(Activation energies represent an endothermic process.)
14- A certain first-order reaction has a rate constant of $1.75 \times 10^{-1}$ s$^{-1}$ at 20.00°C. What is the value of $k$ at 60.00°C if $E_a = 121$ kJ/mol?
   a) $4.5 \times 10^{-4}$ s$^{-1}$
   b) 0.175 s$^{-1}$
   c) $6.82 \times 10^1$ s$^{-1}$
   d) 0.525 s$^{-1}$
   e) 2.8 s$^{-1}$
   (You used the equation $\ln(k_2/k_1)=(E_a/R)(1/T_1−1/T_2)$)

15- Given the following mechanism, which of the species below is a catalyst in the formation of XO$_2$ from X and O$_2$?
   $\text{X} + \text{YO}_2 \rightarrow \text{XO} + \text{YO}$
   $\text{XO} + \text{YO}_2 \rightarrow \text{XO}_2 + \text{YO}$
   $\text{YO} + \text{O}_2 \rightarrow \text{YO}_2 + \text{O}$
   $\text{YO} + \text{O} \rightarrow \text{YO}_2$
   a) XO$_2$
   b) XO
   c) O$_2$
   d) YO$_2$
   e) X
   (This is a catalyst. It is a reactant early in the mechanism, then regenerated as a product later in the mechanism.)

16- Which of the following will lower the activation energy for a reaction?
   a) increasing the concentrations of reactants
   b) adding a suitable catalyst
   c) raising the temperature of the reaction
   d) all of the above
   e) There is no way to lower the activation energy of a reaction.
   (A catalyst speeds up a chemical reaction by lowering the activation energy.)

17- Which statement is not correct regarding the function of a catalyst?
   a) A catalyst affects the rate of a chemical reaction.
   b) A catalyst lowers the activation energy.
   c) A catalyst changes the mechanism of a reaction.
   d) A catalyst lowers the energy of the product, causing the reaction to be more exothermic.
   e) none of these.
   (A catalyst has no effect on the overall energy change for a chemical reaction. The change in internal energy for the products compared with the reactants is primarily the result of the different bond energies associated with each.)

18- Which three factors directly affect the rate of a chemical reaction?
   a) temperature, reactant concentration, and catalyst
   b) catalyst, product concentration, and container volume
   c) temperature, product concentration, and container volume
   d) temperature, pressure, and humidity
   e) temperature, reactant concentration, and pressure
   (These are the major factors that influence the rate of a reaction.)
19- The reaction \(2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}\) is second-order in NO and first-order in \(\text{H}_2\). What happens to the rate when (i) [NO] is doubled, while [\(\text{H}_2\)] is fixed; (ii) [NO] is fixed, while [\(\text{H}_2\)] is doubled; (iii) both [NO] and [\(\text{H}_2\)] are doubled?

- **a**)
  - (i) increases by a factor of 4
  - (ii) doubles
  - (iii) increases by a factor of 6

- **b**)
  - (i) increases by a factor of 4
  - (ii) doubles
  - (iii) increases by a factor of 8

- **c**)
  - (i) doubles
  - (ii) doubles
  - (iii) increases by a factor of 4

- **d**)
  - (i) doubles
  - (ii) increases by a factor of 4
  - (iii) increases by a factor of 4

- **e**)
  - (i) increases by a factor of 4
  - (ii) doubles
  - (iii) increases by a factor of 4

*(The rate law is \(\text{Rate} = k[\text{NO}]^2[\text{H}_2]^1\). Thus, doubling the \([\text{NO}]\) quadruples the rate, doubling the \([\text{H}_2]\) doubles the rate, and doubling both increases it eight times.)*

20- A kinetic study of the reaction \(2\text{A} + 2\text{B} \rightarrow \text{products}\) was conducted yielding the following results:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A], (M)</th>
<th>[B], (M)</th>
<th>Initial Rate, M·s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.20</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.30</td>
<td>225</td>
</tr>
<tr>
<td>4</td>
<td>0.20</td>
<td>0.10</td>
<td>25</td>
</tr>
</tbody>
</table>

What is the rate law for the reaction?

- **a**) \(\text{Rate} = k[A]^2\)
- **b**) \(\text{Rate} = k[A]^2[B]\)
- **c**) \(\text{Rate} = k[A][B]\)
- **d**) \(\text{Rate} = k[A]^2[B]^2\)
- **e**) \(\text{Rate} = k[B]^2\)

*(Based on trials 1 & 4, this reaction is zero order in \(\text{A}\); using trials 1 & 3, this reaction is second-order in \(\text{B}\).)*

22- For the reaction:

\[2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)\]

the activation energy, \(E_a\), and overall \(\Delta E\) are 100 kJ/mol and −23 kJ/mol, respectively. What is the activation energy for the reverse reaction?

- **a**) 77 kJ/mol
- **b**) cannot estimate with data given
- **c**) 100 kJ/mol
- **d**) 123 kJ/mol

*(Since this is an exothermic reaction, the reverse process has a larger activation energy.)*

23- The decomposition of nitrogen dioxide to nitrogen and oxygen is second-order with a rate constant \(k = 12.5 \text{ M}^{-1}\cdot\text{s}^{-1}\). What is the half-life for the reaction if \([\text{NO}_2]_0 = 0.00260 \text{ M}\)?

- **a**) 0.0554 sec
- **b**) 30.8 sec
- **c**) 385 sec
- **d**) 61.5
- **e**) 0.0800 sec

*(The half-life for a second-order reaction equals \(1/k[\text{A}]_0\).)*

24- In a series of reactions, which is the rate-determining step?

- **a**) the slowest reaction
b) the simplest reaction
c) the main reaction involving the major reactant
d) the fastest reaction
e) the reaction with the highest order

(The rate-determining step is the slowest step in a reaction mechanism.)