KINETICS

1. For the equation

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

How is the rate of formation of \( \text{H}_2\text{O} \) mathematically related to the rate of disappearance of \( \text{O}_2 \)?

\[ \frac{1}{2} \frac{\Delta [\text{H}_2\text{O}]}{\Delta t} = - \frac{\Delta [\text{O}_2]}{\Delta t} \]

2. Determine the relative reaction rates of the four substances involved in the following chemical reaction. Place the appropriate numbers in the boxes.

\[ 2 \text{C}_2\text{H}_2\text{(g)} + 5 \text{O}_2\text{(g)} \rightarrow 4 \text{CO}_2\text{(g)} + 2 \text{H}_2\text{O(l)} \]

\[ \frac{1}{2} \left( \frac{-\Delta [\text{C}_2\text{H}_2]}{\Delta t} \right) = \frac{1}{5} \left( \frac{-\Delta [\text{O}_2]}{\Delta t} \right) = \frac{1}{4} \left( \frac{\Delta [\text{CO}_2]}{\Delta t} \right) = \frac{1}{2} \left( \frac{\Delta [\text{H}_2\text{O}]}{\Delta t} \right) \]

3. For the following reaction, the rate of disappearance of \( \text{A} \) is equal to -0.084 M/s at the start of the reaction. What are the rates of change for \( \text{B} \), \( \text{C} \), and \( \text{D} \) at this time?

\[ 2\text{A} + \text{B} \rightarrow 3\text{C} + \text{D} \]

Rate of Change of \( \text{B} \) = _________ M/s \hspace{1cm} \text{Ans: -0.042} \\
Rate of Change of \( \text{C} \) = _________ M/s \hspace{1cm} \text{Ans: +0.126} \\
Rate of Change of \( \text{D} \) = _________ M/s \hspace{1cm} \text{Ans: +0.042} \\

4. Based on the graph below, determine the instantaneous rate of change of \([x]\) at 10 seconds.

Instantaneous Rate of Change of \( \text{X} \)

\[ = \frac{\text{rise}}{\text{run}} \]

\[ \text{Ans: rise} = (0.11\text{M} - 0.07\text{M}) = 0.04\text{M} \]

\[ \text{Run} = (15\text{s} - 5\text{s}) = 10\text{s} \]

\[ \text{Slope} = 0.04/10 = \boxed{0.004\text{M/s}} \]
5. Based on the data below, what are the average rates of change of $[O_2]$ and $[NO_2]$ over the interval 0 to 660 seconds?

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$[NO]$ M</th>
<th>$[O_2]$ M</th>
<th>$[NO_2]$ M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1000</td>
<td>0.01000</td>
<td>0.0000</td>
</tr>
<tr>
<td>285</td>
<td>0.0090</td>
<td>0.0095</td>
<td>0.0010</td>
</tr>
<tr>
<td>660</td>
<td>0.0080</td>
<td>0.0090</td>
<td>0.0020</td>
</tr>
<tr>
<td>1175</td>
<td>0.00070</td>
<td>0.0085</td>
<td>0.0030</td>
</tr>
</tbody>
</table>

Average Rate of Change of $O_2 = \frac{0.0090 - 0.0100}{(660 - 0)} = \frac{-1.5 \times 10^{-6}}{M/s}$

Average Rate of Change of $NO_2 = \frac{0.0020 - 0.0000}{(660 - 0)} = \frac{3.0 \times 10^{-6}}{M/s}$

6. If the rate constant, $k = 350 \text{ s}^{-1}$ for a certain reaction, what is the overall order for that reaction?  
   ___________________  First Order

8. The following reaction occurs in the gaseous state.

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

The following rate data were obtained.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Initial $[\text{NO}]$</th>
<th>Initial $[\text{H}_2]$</th>
<th>Initial rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20 M</td>
<td>0.20 M</td>
<td>0.060</td>
</tr>
<tr>
<td>2</td>
<td>0.20M</td>
<td>0.30 M</td>
<td>0.090</td>
</tr>
<tr>
<td>3</td>
<td>0.40M</td>
<td>0.20 M</td>
<td>0.240</td>
</tr>
</tbody>
</table>

(a) Determine the rate law for this reaction (including all exponents & rate constant).

Trial 2/Trial 1  conc ratio = 1.5  rate ration = 1.5  H$_2$ coefficient = 1
Trial 3/Trial 1  conc ratio = 2.0  rate ratio = 4  NO coefficient = 2

Using trial 3 data to get $k$, $0.240 = k(0.40)^2(0.20)$

$$k = \frac{0.240}{(0.40)^2(0.20)} = 7.5 \text{ M}^{-2}\text{s}^{-1}$$

Rate Law: ___________________  rate = $7.5 \text{ M}^{-2}\text{s}^{-1}[\text{NO}]^2[\text{H}_2]$

(b) What is the order or the reaction with respect to:
   NO? ______  2  H$_2$? ______  1  Overall? ______  3

(c) What would the initial rate of the reaction be if the initial concentrations were:
   $[\text{NO}] = 0.10\text{M}$  $[\text{H}_2] = 0.30\text{M}$

$$\text{Rate} = 7.5 \text{ M}^{-2}\text{s}^{-1}(0.10\text{M})^2(0.30\text{M}) = 0.022 \text{ M/s}$$
9. Determine the rate constant of the following reaction at 298K, where
A (the Arrhenius pre-exponent factor)=1.2x10^{12}, and Ea=11.6kJ/mol

\[
\text{NO}_\text{(g)} + \text{O}_3\text{(g)} \rightarrow \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}
\]

\[
k = \text{A}e^{-\frac{\text{Ea}}{\text{RT}}}
\]

\[
k = (1.2\times10^{12})e^{[-11600J/(8.314J/K \text{ mol})(298K)]} = 1.1 \times 10^{10}
\]

10. Complete the data table below for the reaction A + B \rightarrow C. Then calculate the slope of the plot of ln k vs 1/T (Arrhenius Plot) and the activation energy of the reaction. Be sure to use unrounded values in your calculations.

<table>
<thead>
<tr>
<th>K (M⁻¹s⁻¹)</th>
<th>T (K)</th>
<th>Ln k</th>
<th>1/T (K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6255</td>
<td>288</td>
<td>8.74114</td>
<td>0.003472</td>
</tr>
<tr>
<td>8831</td>
<td>323</td>
<td>9.08602</td>
<td>0.003096</td>
</tr>
</tbody>
</table>

Slope = \frac{(9.08602 - 8.74114)}{(0.003096 K⁻¹ - 0.003472 K⁻¹)} = 0.34488 = 0.9172K

Ea = (-R)(slope) = (-8.314 J/K mol)(-0.9172K) = 7.63kJ/mol

11. From the following graph, determine the activation energy and the enthalpy of the reaction.

Ea = \underline{25} kJ/mol

\[\Delta H = \underline{-150} kJ/mol\]

12. According to the graph below, about what percentage of the collisions will have sufficient kinetic energy to form products?

\[\underline{50\%}\]

13. In order for a reaction to occur reactant molecules must:
   A) \underline{collide}
   B) \underline{with sufficient energy}
   C) \underline{in the correct orientation}
14. The mechanism for the reaction \(3 \text{ClO}^- \rightarrow \text{ClO}_3^- + 2 \text{Cl}^-\) is

\[
\begin{align*}
\text{ClO}^- + \text{ClO}^- & \rightarrow \text{ClO}_2^- + \text{Cl}^- \quad \text{(slow)} \\
\text{ClO}^- + \text{ClO}_2^- & \rightarrow \text{ClO}_3^- + \text{Cl}^- \quad \text{(fast)}
\end{align*}
\]

Derive the rate law for this reaction: \(\text{Rate} = k[\text{ClO}^-]^2\)

15. Identify the catalyst(s) and/or reaction intermediate(s) in the following reaction mechanism.

| Step 1: O(g) + NO(g) \(\rightarrow\) O(g) + NO(g) |
| Step 2: NO(g) \(\rightarrow\) NO(g) + O(g) |
| Step 3: O(g) + O(g) \(\rightarrow\) 2 O(g) |

catalyst(s): __________________________

reaction intermediate(s): __________________________

16. At a certain temperature, the reaction \(2B \rightarrow C + D\) obeys the rate law:

\[
\text{rate} = 1.14 \times 10^{-3} \text{M}^{-1} \text{s}^{-1} [B]^2
\]

If 5.00 mol of B is initially present in a 1.00 L container at that temperature, how much B is left after 117 seconds?

We need to start by recognizing the fact that this reaction follows second order kinetics.

From our equation sheet: \(1/[A]_t = kt + 1/[A]_o\) for 2nd order

\[
\frac{1}{[B]_t} = (1.14 \times 10^{-3})(117) + \frac{1}{5.00} = 0.133 + 0.200 = 0.333
\]

\[
[B]_t = \frac{1}{0.333} = 3.00 \text{M} = 3.00 \text{ mol/L}
\]

\[
3.00 \text{ mol/molL} \times 1.00 \text{ L} = 3.00 \text{ mol B}
\]

17. Write a rate equation for the following elementary step:

\[
\text{BeO}_3^- + 2 \text{H}^+ \rightarrow \text{H}_2\text{BrO}_3^+
\]

\[
\text{Rate} = k [\text{BeO}_3^-][\text{H}^+]^2 \quad \text{Coefficients match exponents for elementary steps and elementary reactions.}
\]

18. For a given reaction, the concentration of reactant “A” was doubled and the rate of reaction remained the same. We can conclude that the reaction is what order with respect to “A”?

___________________________ zero order
THERMODYNAMICS

1. Predict the sign for the following reaction and then calculate the value of \( \Delta S^\circ \) using the information below and compare to your prediction for \( \Delta S^\circ \).

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

Predicted sign: _____ (-) fewer moles of substance

<table>
<thead>
<tr>
<th>compound</th>
<th>( S^\circ ) J/mol K</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{O}_2(\text{g})</td>
<td>205.0</td>
</tr>
<tr>
<td>\text{H}_2(\text{g})</td>
<td>130.6</td>
</tr>
<tr>
<td>\text{H}_2\text{O}(\text{g})</td>
<td>188.7</td>
</tr>
</tbody>
</table>

\( \Delta S^\circ = 2(188.7) - [(205.0)+2(130.6)] = 377.4 - 466.2 = -88.8 \text{ J/mol K} \)

2. Predict the value of \( \Delta G \) under the following conditions:

- **A)** \( \Delta H \) negative and \( \Delta S \) positive
  - \( \boxed{\times} \) \( \Delta G < 0 \)
  - \( \boxed{\times} \) \( \Delta G > 0 \)
  - Cannot predict the sign of \( \Delta G \)
- **B)** \( \Delta H \) positive and \( \Delta S \) positive
  - \( \boxed{\times} \) \( \Delta G < 0 \)
  - \( \boxed{\times} \) \( \Delta G > 0 \)
  - Cannot predict the sign of \( \Delta G \)
- **C)** \( \Delta H \) positive and \( \Delta S \) negative
  - \( \boxed{\times} \) \( \Delta G < 0 \)
  - \( \boxed{\times} \) \( \Delta G > 0 \)
  - Cannot predict the sign of \( \Delta G \)
- **D)** \( \Delta H \) negative and \( \Delta S \) negative
  - \( \boxed{\times} \) \( \Delta G < 0 \)
  - \( \boxed{\times} \) \( \Delta G > 0 \)
  - Cannot predict the sign of \( \Delta G \)

3. Determine the value of \( \Delta G \) in kJ at 25°C for the following reaction given that \( \Delta S^\circ = 326.4 \text{ J/K} \) and \( \Delta H^\circ = 571.6 \text{ kJ} \).

\[
2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{H}_2(\text{g}) + \text{O}_2(\text{g})
\]

**Step 1:** Convert the temperature to Kelvins:

\[
T_K = T_C + 273.15 = 25 \degree C + 273.15 = 298 \text{ K}
\]

**Step 2:** Convert the entropy change to kJ/K:

\[
\Delta S = \frac{326.4 \text{ J/K} - \frac{1 \text{ kJ}}{1000 \text{ J}} = 0.3264 \text{ kJ/K}}
\]

**Step 3:** Substitute the values of \( \Delta H, T, \) and \( \Delta S \) into the equation for \( \Delta G \):

\[
\Delta G = \Delta H - T \Delta S
\]

\[
\Delta G = (571.6 \text{ kJ}) - (298 \text{ K}) \times (0.3264 \text{ kJ/K})
\]

\[
\Delta G = (571.6 \text{ kJ}) - (97.3 \text{ kJ})
\]

\[
\Delta G = 474.3 \text{ kJ}
\]

4. Calculate the change in entropy for the following reaction.
   (Hint use your appendix data / green sheet.)

\[
\text{Ca}^{2+} \text{(aq)} + 2 \text{OH}^- \text{(aq)} \rightarrow \text{Ca(OH)}_2(\text{s})
\]

\[
-53.1 \quad -10.90 \quad 83.4
\]

\[
\Delta S^\circ = 83.4 - [-53.1 + 2(-10.90)] = 83.4 - (-74.9) = 158.3 \text{ J/K mol}
\]
5. Will the decomposition of potassium chlorate be spontaneous at low temperatures, high temperatures, or all temperatures? Use values from your appendix/handout.

Reaction: \(2 \text{KClO}_3(s) \rightarrow 2 \text{KCl}(s) + 3 \text{O}_2(g)\)

\[\Delta H^\circ_f = -397.7 \quad -436.5 \quad 0 \quad \Delta H^\circ_{\text{rxn}} = 2(-436.5) - 2(-397.7) = -77.6 \text{kJ/mol}\]

\[S^\circ = 143.1 \quad 82.6 \quad 205.2 \quad \Delta S^\circ_{\text{rxn}} = [3(205.2) + 2(82.6)] - 2(143.1) = +494.6 \text{J/mol K}\]

Since \(\Delta H^\circ_{\text{rxn}}\) is (-), it supports spontaneity.

Since \(\Delta S^\circ_{\text{rxn}}\) is (+), it supports spontaneity.

The reaction is spontaneous at all temperatures!

6. True or False

- ______ F A) Gases have less entropy than liquids.
- ______ T B) When solids dissolve they tend to increase in entropy.
- ______ F C) The greater the moles of solid, the greater the entropy.
- ______ F D) \(\text{CH}_4(g)\) has greater entropy than \(\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3(g)\).
- ______ T E) An endergonic reaction is always non-spontaneous.