WORKSHEET: KINETICS - SOLUTIONS

I. Rates of Reaction

1. a. Determine the order of the reaction with respect to ICl.

\[
\text{rate } 3 = 6.4 \times 10^{-3} = (0.2)^m [0.1]^n \\
\text{rate } 1 = 1.6 \times 10^{-3} = [0.1]^m [0.1]^n
\]

\[
4 = [2]^n \\
\log 4 = m \log 2 \\
m = 2
\]

This can actually be done by observation, but this is the way to set up more complicated order dependencies.

b. Determine the order with respect to H_2.

\[
\text{rate } 2 = 3.2 \times 10^{-3} = [0.1]^2 [0.2]^n \\
\text{rate } 1 = 1.6 \times 10^{-3} = [0.1]^2 [0.1]^n
\]

\[
2 = 2^n \\
n = 1
\]

Again, this can be done by observation in this case.

c. The rate equation is then:

\[
\text{rate } = k [\text{ICl}]^2 [\text{H}_2]
\]

d. The units are given by:

\[
\text{rate } = \text{M/s} = k (\text{M})^2 (\text{M}) \\
k = \text{M s}^{-1} \text{M}^2 = \text{M}^2 \text{s}^1
\]

e. In this case, the rate law happens to coincide with the overall stoichiometry of the reaction. This is not always the case. Rate laws must always be determined experimentally, they can not be deduced from the overall balanced equation.

f. \[\Delta [\text{I}_2]/\Delta t = 1/2 \Delta [\text{ICl}]/\Delta t = 6.4 \times 10^{-3} \text{ M s}^{-1}\] so, \[\Delta [\text{ICl}]/\Delta t = 1.28 \times 10^{-2} \text{ M s}^{-1}\]

2. a. From the rate equation, the order with respect to NO is 2.

b. From the rate equation, the order with respect to Cl_2 is 1.

c. The overall order is \(1 + 2 = 3\).

d. rate = Ms^{-1} = k (M)^2 (M), so k = M s^{-1} (M)^3 = M^2 s^{-1}

e. If [Cl_2] is doubled, the rate increases by a factor of \([2]^1 = 2\).

f. If [NO] is doubled, the rate increases by a factor of \([2]^1 = 4\).

g. If [NO] is doubled and [Cl_2] is halved, the rate increases by a factor of \((2)^2 \times (0.5)^1 = 2\).
3. a. First order in A rate = k[A] = 1.6 x 10^{-2}\text{ M s}^{-1} \text{ when } [A] = 0.35 \text{ M}
   1.6 \times 10^{-2} \text{ M s}^{-1} = k_1 (0.35 \text{ M}), \quad k = 4.6 \times 10^{-2} \text{ s}^{-1}

b. Second order in A rate = k_2 [A]^2 = 1.6 \times 10^{-2} \text{ M s}^{-1} \text{ when } [A] = 0.35 \text{ M}
   1.6 \times 10^{-2} \text{ M s}^{-1} = k_2 (0.35 \text{ M})^2, \quad k = 1.3 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}

4. \[ t_{1/2} = \frac{(\ln 2)}{k} \text{ for first-order processes and } \ln(N/N_0) = -kt, \text{ where } N = \text{ the current level of radioactivity (cpm)} \text{ and } N_0 = \text{ radioactivity level at the time the tree died.} \]

   \[ t_{1/2} = 5730 \text{ years} = \frac{(\ln 2)}{k} \text{ so, } k = 1.21 \times 10^{-4} \text{ year}^{-1} \]
   
   -1.21 \times 10^{-4} \text{ year}^{-1} (t) = \ln(10.8/15.3), \quad t = 2878 \text{ years.} 
   
   The tree died in (1996-2878) = 882 B.C.

5. The graphs show a linear relationship between ln[A] vs. t, making it a first order reaction in [A].

   a. Rate = k[A]
   
   b. \[ k = -\text{slope} = -\frac{[(5.40) - (4.80)]}{40 - 10 \text{ min}} = 0.02 = 2.0 \times 10^{-2} \text{ min}^{-1} \]

   c. \[ t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{2.0 \times 10^{-2} \text{ min}^{-1}} = 34.7 \text{ min} \]

   d. \[ y = mx + b \]
   
   \[ \ln[A] = -(2.0 \times 10^{-2})(t) + \ln[A]_0 \]

   -4.80 = -(2.0 \times 10^{-2})(10) + \ln[A]_0
   
   \[ [A]_0 = 1.00 \times 10^{-2} \]

   e. \[ \ln[A] = -kt + \ln[A]_0 \]

   = -2.0 \times 10^{-2} \times 70 \text{ min} + (-4.61)

   = -6.0

   \[ [A] = 2.5 \times 10^{-3} \text{ M} \]

II. Reaction Mechanisms

1. \[
   \begin{align*}
   \text{rate 1} & = 7.0 \times 10^{-3} = (0.20)^m (0.10)^n \\
   \text{rate 2} & = 1.4 \times 10^{-3} = (0.20)^m (0.20)^n \\
   \text{rate 3} & = 1.4 \times 10^{-3} = (0.40)^m (0.20)^n \\
   \text{rate 4} & = 1.4 \times 10^{-3} = (0.20)^m (0.20)^n
   \end{align*}
   \]

   \[ 2 = 2^n \quad n = 1 \]

   \[ 1 = 2^m \quad m = 0 \]

   a. \[ \text{rate} = k [Y] \quad 7.0 \times 10^{-4} \text{ M s}^{-1} = k (0.10 \text{ M}) \quad k = 7 \times 10^{-3} \text{ s}^{-1} \]
b. Rate law for:

*Mechanism I:* \( \text{rate} = k_1 [X] [Y] \)

*Mechanism II:* \( \text{rate} = k_2 [Y] [M] \)
\( [M] = k [X]^2 \)
\( \text{rate} = k_2 [Y] [X]^2 \)

*Mechanism III:* \( \text{rate} = k_3 [Y] \)

inconsistent with experimental rate law

inconsistent with experimental rate law

consistent with experimental rate law

2. a) \( 2\text{NO(g)} + 2\text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O(g)} \)
\( \text{N}_2\text{O}_2 \) and \( \text{N}_2\text{O}_3 \) are intermediates.

b) Based on the slowest step, the rate is determined by step 2.

\( \text{rate} = k [\text{N}_2\text{O}_2][\text{H}_2] \)

Since \( \text{N}_2\text{O}_2 \) is an intermediate, its concentration is given by the rapid equilibrium of step 1.

\( K = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \)

\( [\text{N}_2\text{O}_2] = K[\text{NO}]^2 \)

Substitute this value into the rate equation.

\( \text{rate} = k [\text{H}_2][\text{NO}]^2 \)

c) This is a **third-order** reaction overall.

d) The molecularity of the rate determining step is **bimolecular**.

III. **Arrhenius Equation and Catalysis**

1. \( \ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \)
\( \ln(7/1) = \left[ \frac{E_a}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \right] \cdot \left( \frac{1}{273} - \frac{1}{300} \right) \text{ K}^{-1} \)
\( 1.95 = \left[ \frac{E_a}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \right] \cdot (0.0036 - 0.0033) \text{ K}^{-1} \)
\( E_a = 53.4 \text{ kJ mol}^{-1} \)

2. \( t_{1/2} = \ln 2 / k \) at 50°C (323 K) \( k_{398} = \ln 2 / 120 \text{ s} = 5.78 \times 10^{-3} \text{ s}^{-1} \)
\( \ln (k_{398}/5.78 \times 10^{-3}) = (420 \times 10^{3} \text{ J} / 8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \cdot (1/323 - 1/310) \)
\( k_{398}/5.78 \times 10^{-3} = \exp (-6.56) \)
\( k_{398} = 8.19 \times 10^{6} \)
\( t_{1/2} = \ln 2/8.19 \times 10^{-6} \)
\( t_{1/2} = 8.46 \times 10^{4} \text{ s} \) or 23.4 hours

Regulation of body temperature is obviously very important in regulating genetic damage.
3. (a) The overall stoichiometry is given by the sum of the two steps:

\[ (\text{CH}_3)_2\text{C} = \text{CH}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{COH} \]

(b) The intermediate is the species:

\[ \overset{\oplus}{(\text{CH}_3)_2\text{C} = \text{CH}_3} \]

which is formed in step 1 and consumed in step 2. It is not present initially and is not present at the end of the reaction. It will not appear in the overall stoichiometry or in the experimental rate law.

(c) Yes. The reaction is catalyzed by H\(^+\). It is a reactant in step 1, where it is consumed, and a product in step 2, where it is regenerated. It is present before the reaction begins and after the reaction has finished, so it does not appear in the overall stoichiometry. It will appear in the experimental rate law, since it participates in the rate determining (slowest) step.

(d) *Step 1* is the rate determining step since it is the slowest step.

(e) The rate law would be derived from the rate determining step, *step 1*.

\[ \text{rate} = k [(\text{CH}_3)_2\text{C} = \text{CH}_2][\text{H}^+] \]

(f) *Step 1*