1)(15 pts) The formation of carbon tetrachloride (CCl₄): CHCl₃ + Cl₂ → CCl₄ + HCl
was found experimentally to be first order in CHCl₃ and ½ order in Cl₂ and 3/2 order overall.
Is the following mechanism consistent with the overall rate law and stoichiometry?

Step 1 – fast  Cl₂ → 2 Cl
Step 2 – slow  Cl + CHCl₃ → HCl + CCl₃
Step 3 – fast  Cl + CCl₃ → CCl₄

Step 2 is the rate-determining step. Rate = k₂*[Cl]*[CHCl₃]
Cl is an intermediate and cannot be in the overall rate law.
Use the steady state approximation to solve for [Cl] in terms of constants & [reactants].

\[ \frac{\Delta [Cl]}{\Delta \text{time}} = 0 = \text{rate}_1 - \text{rate}_2 - \text{rate}_3 \]
\[ 0 = k₁*[Cl₂] - k₁*[Cl]² - k₂*[Cl]*[CHCl₃] \]
\[ k₁*[Cl₂] = k₁*[Cl]² + k₂*[Cl]*[CHCl₃] \]

If we assume that k₂*[Cl]* [CHCl₃] is small as it is the RDS and ignore it then:
\[ k₁*[Cl₂] = k₁*[Cl]² \]
\[ [Cl]² = \left(\frac{k₁}{k₁ + k₂}\right)*[Cl₂] \]
\[ [Cl] = \left(\frac{k₁}{k₁ + k₂}\right)^{1/2}*[Cl₂]^{1/2} \]

Substitute this into the rate law
Rate₂ = k₂*[Cl]*[CHCl₃] = k₂*(k₁/k₁ + k₂)¹/₂*[Cl₂]¹/₂*[CHCl₃] agrees with experiment.

Summing up all three rxns: Cl₂ + Cl + CHCl₃ + Cl + CCl₃ → 2 Cl + HCl + CCl₃ + CCl₄
Canceling out when possible gives: Cl₂ + CHCl₃ → HCl + CCl₄
Which agrees with overall reaction stoichiometry.

2)(15 pts) The rate constant for the decomposition of acetaldehyde: CH₃CHO → CH₄ + CO
was measured at various temperatures. The data is shown below. Determine the
activation energy and collision frequency of this reaction. R = 8.314 J/mol-K.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>k(M⁻¹/²sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>0.011</td>
</tr>
<tr>
<td>730</td>
<td>0.035</td>
</tr>
<tr>
<td>760</td>
<td>0.105</td>
</tr>
<tr>
<td>790</td>
<td>0.343</td>
</tr>
<tr>
<td>810</td>
<td>0.789</td>
</tr>
</tbody>
</table>

Slope = Δln(k) / Δ(1/T) = (ln(0.011)-ln(0.789))/(1/700 – 1/810) = -4.3/1.9x10⁻４K = -22025 K
-22025 = - Eₐ/R
Eₐ = 183,113 J/mole = 183.1 kJ/mole

K = A*exp(-Eₐ/RT)
0.011 = A * exp(-183,113 J/mole / (8.314 J/mole-K * 700 K))
0.011 = A * exp(-31.5)
0.011 = A * 2.2x10⁻¹⁴
A = 5.1x10¹¹ collisions/sec

k (@ 850 K) = 5.1x10¹¹/sec *exp(-183,113 J/mole/(8.314 J/mole-K * 850 K))
k (@ 850 K) = 2.85 M⁻¹/²sec⁻¹