1. This problem illustrates how the differential rate law (DRL) can be simplified when the concentration of one or more of the participating species remains effectively constant during the course of the reaction.

(i) Since the initial concentration of CH$_3$COCl is 0.1 M, for convenience we will assume 1 liter of solution. Thus, we have 0.1 mols of CH$_3$COCl in 1000 mL of H$_2$O. Since the density of H$_2$O (assume that the reaction is run at room temperature) is ~1.0 g/ml, the weight of H$_2$O present initially is 1000 g.

∴ No. of mols H$_2$O present at time t (=0) = (1000 g)/(18 g mol$^{-1}$) = 55.6 mols

(ii) From the reaction stoichiometry, when the reaction is complete 0.1 mols CH$_3$COCl will have reacted with 0.1 mols H$_2$O.

∴ Final [H$_2$O] = 55.5 M

Thus, since H$_2$O is present in great excess, [H$_2$O] remains effectively constant during the course of the reaction. We will take the effective constant concentration of H$_2$O to be the average of the initial and final values; i.e. [H$_2$O] = 55.55 M. Therefore, under the conditions of the experiment, the DRL

\[-d[CH_3COCl]/dt = k[CH_3COCl][H_2O]\]  (1)

may be simplified to:

\[-d[CH_3COCl] / dt = k' [CH_3COCl]\]  (2)

where $k' = k [H_2O] = k (55.55 \text{ M})$  (3)

Thus, under these conditions, the overall order of the reaction has been effectively reduced from second to first -- we say that the reaction is **PSEUDO FIRST-ORDER**.

(iii) Rearranging equation (2) we may write that:

\[-d[CH_3COCl]/[CH_3COCl] = k'dt\]  (4)

Integrating equation (4) we obtain:

\[-\ln{[CH_3COCl]_t /[CH_3COCl]_0 } = k't\]
When \( [\text{CH}_3\text{COCl}]_t = 0.05 \text{ M}, \ t = t_{1/2} \ \text{i.e. the reaction half life} \)

Then \( t_{1/2} = (1/k') \{ - \ln (0.05 \text{ M} / 0.1 \text{ M}) \} = \{ \ln 2 \}/k' = 0.693/k' \)

From equation (3), \( k' = k \ (55.55 \text{ M}) = 1.16 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1} \) (55.55 M)
\[
= 6.44 \times 10^{-2} \text{ s}^{-1}
\]

\[ \therefore \ t_{1/2} = \{0.693 / 6.44 \times 10^{-2} \text{ s}^{-1}\} = 10.7 \text{ s} \]

2. The experimental rate law for the reaction \( 2 \text{ NO} + \text{Cl}_2 \rightarrow 2 \text{ NOCl} \) is:

\[
(1/2) \frac{d[\text{NOCl}]}{dt} = k \ [\text{NO}]^2[\text{Cl}_2]
\]

(the factor of \(1/2\) arises from the stoichiometric coefficient of NOCl)

Since step (ii) is the rate determining step (rds), we may write:

\[
\text{Reaction Rate} = (1/2) \frac{d[\text{NOCl}]}{dt} = k_2 \ [\text{N}_2\text{O}_2] \ [\text{Cl}_2] \quad (1)
\]

(Recall that the rate law for an \textbf{ELEMENTARY REACTION} may be written down by inspection)

Then, since Step(i) is a fast equilibrium step, we may use it to determine \([\text{N}_2\text{O}_2]\).

\textbf{Note} -- the final expression for the rate law must only contain concentrations of species appearing in the stoichiometric equation for the \textbf{overall} reaction.

From Step (i):
\[
K = \{[\text{N}_2\text{O}_2] / [\text{NO}]^2\} \quad (2)
\]

Thus,
\[
[\text{N}_2\text{O}_2] = K [\text{NO}]^2 \quad (3)
\]

Then, using the result of equation (3) in equation (1) we find:

\[
(1/2) \frac{d[\text{NOCl}]}{dt} = K k_2 \ [\text{NO}]^2 [\text{Cl}_2] \quad (4)
\]

Equation (4) agrees with the experimental rate law if \( k = K k_2 \). Thus the proposed mechanism is consistent with the experimental rate law.
3. An examination of the mechanism reveals that Step (ii) is the rds.

\[
\text{Reaction Rate} = \frac{1}{2} \frac{d [\text{NOCl}]}{dt} = k' \text{[NO-Cl]} \text{[NO]} \quad (1)
\]

Since NO•Cl\textsuperset{2} does not appear in the stoichiometric equation for the overall reaction we must use the fast equilibrium step to eliminate [NO•Cl\textsuperset{2}].

From Step(i): \[ [\text{NO-Cl]}] = K' \text{[NO]} \text{[Cl]} \quad (2) \]

Using the result of equation (2) in equation (1) we obtain:

\[
\frac{1}{2} \frac{d [\text{NOCl}]}{dt} = K' k' \text{[NO]}^2 \text{[Cl]} \quad (3)
\]

This agrees with the experimental rate law with \( k = K' k' \). Thus this mechanism and that proposed in Problem # 2 lead to the same rate law. Kinetic experiments such as varying initial reactant concentrations etc., cannot distinguish between these two mechanisms.

4. Since Step (ii) is the rds

\[
\text{Reaction Rate} = \frac{d [\text{Cl}] }{dt} = k \text{[NO-2Cl]} \text{[Cl]} \quad (1)
\]

Using the information in Step (i): \( K = \{ \frac{[\text{NO}][\text{Cl}]}{[\text{NO-2Cl}]} \} \quad (2) \]

or \[ [\text{Cl}] = K \frac{[\text{NO-2Cl}]}{[\text{NO}]} \quad (3) \]

Then Reaction Rate = \( k \text{[NO-2Cl]}^2 \text{[NO]}^{-1} \)

From the stoichiometric equation for the overall process, the Reaction Rate could be defined in any of the following equivalent ways:

\[
\text{Reaction Rate} = - \frac{1}{2} \frac{d [\text{NO-2Cl}]}{dt} = \frac{1}{2} \frac{d [\text{NO}]}{dt} = \frac{d [\text{Cl}]}{dt}
\]

i.e. 1 mol of Cl\textsuperset{2} is produced for every 2 mols of NO\textsuperset{2}Cl consumed. Thus,

\[
- \frac{1}{2} \frac{d [\text{NO-2Cl}]}{dt} = k \text{[NO-2Cl]}^2 \text{[NO]}^{-1} \quad \text{or rewriting}
\]

\[
- \frac{d [\text{NO-2Cl}]}{dt} = 2 k \text{[NO-2Cl]}^2 \text{[NO]}^{-1}
\]
5. The rate law for the reaction 2 NO (g) + H₂(g) → N₂O(g) + H₂O(g) is investigated under pseudo-first-order conditions. In this approach one attempts to determine the partial orders of each of the participating species by performing a series of kinetic experiments in which each of the participating species, in turn, is chosen to be the stoichiometrically limiting reagent, with all the other reagents taken to be present in such excess that their concentrations remain essentially unchanged during the course of the reaction.

For the above process we may write the rate law in the form:

\[- \left( \frac{1}{2} \right) \frac{d[NO]}{dt} = - \frac{d[H₂]}{dt} = k[NO]^a[H₂]^b\]  

where the goal is to determine values for a, b, and k. Now consider kinetic experiments where [NO] >> [H₂]. Then, [NO] will remain essentially unchanged during the consumption of H₂ -- i.e. it is present in such large excess that its concentration is effectively constant. Thus, we may rewrite equation (1) as:

\[- \left( \frac{1}{2} \right) \frac{d[NO]}{dt} = - \frac{d[H₂]}{dt} = k'[H₂]^b\]

where \(k' = k[NO]^a\)  

The partial order b can now be determined by measuring [H₂] at known times and then examining ln[H₂] vs. t, and \(1/[H₂]\) vs. t plots to establish first or second order kinetics. Once b is determined, NO is made the stoichiometrically limiting reagent, [H₂] remains effectively constant during the course of the reaction and we can determine the partial order a. With the values of a and b in hand we can then determine k.

In experiment (1), [NO] >> [H₂]. \([NO]_0 = 2.0 \text{ M}\) and from the stoichiometric equation 0.020 M NO will be consumed when 0.010 M H₂ have reacted. Thus, at the end of the reaction [NO] = 1.98 M which is ≈ 2.0 M and the conditions described above are satisfied. Using the conc.-time data given we can construct the following table:

<table>
<thead>
<tr>
<th>t (s)</th>
<th>[H₂] M</th>
<th>ln [H₂]</th>
<th>{1/[H₂]} M⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0e⁻²</td>
<td>-4.6052</td>
<td>1.0000e⁺²</td>
</tr>
<tr>
<td>10</td>
<td>6.2e⁻³</td>
<td>-5.0832</td>
<td>1.6129e⁺²</td>
</tr>
<tr>
<td>20</td>
<td>3.8e⁻³</td>
<td>-5.5728</td>
<td>2.6316e⁺²</td>
</tr>
<tr>
<td>30</td>
<td>2.4e⁻³</td>
<td>-6.0323</td>
<td>4.1667e⁺²</td>
</tr>
</tbody>
</table>

Using these data we plot ln [H₂] vs. t with the following result:
Clearly, we see that the reaction is first-order with respect to H₂ i.e. b = 1. (We could plot \{1/[H₂] vs. t and show that this plot is not linear).

From the slope of the plot we calculate \( k' = -\text{slope} = -(-0.0477\text{s}^{-1}) = 0.048\text{s}^{-1} \)

In Experiment (2), H₂ is present in large excess and NO is stoichiometrically limiting. Thus, \(-\frac{1}{2} \frac{d[NO]}{dt} = \frac{d[H₂]}{dt} = k'' [NO]^a\) where \( k'' = k[H₂] \). We can now plot the NO conc.-time data. From the data given in Experiment (2) we can construct the following table:

<table>
<thead>
<tr>
<th>t (s)</th>
<th>[NO] M</th>
<th>ln [NO]</th>
<th>{1/[NO]} M⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0e-2</td>
<td>-4.6052</td>
<td>1.0000e+2</td>
</tr>
<tr>
<td>1000</td>
<td>8.1e-3</td>
<td>-4.8159</td>
<td>1.2346e+2</td>
</tr>
<tr>
<td>2000</td>
<td>6.8e-3</td>
<td>-4.9908</td>
<td>1.4706e+2</td>
</tr>
<tr>
<td>3000</td>
<td>5.8e-3</td>
<td>-5.1499</td>
<td>1.7241e+2</td>
</tr>
</tbody>
</table>

The first step is to plot these data in the form ln [NO] vs. t. Since the plot is non-linear the reaction is not first-order in NO.
The next step is to construct the \(\frac{1}{[\text{NO}]}\) vs. \(t\) plot shown below:

The linearity of this plot indicates that the reaction is second-order in NO -- i.e. \(a = 2\). Thus, the DRL is

\[-\frac{1}{2} \frac{d [\text{NO}]}{dt} = - \frac{d [\text{H}_2]}{dt} = k [\text{NO}]^2 [\text{H}_2]^1\]

We can now use the values of \(a\) and \(b\) and \(k'\) from equation (3) -- i.e. \(k' = k [\text{NO}]^2\) to calculate a value for \(k\). Thus,

\[k = \frac{k'}{[\text{NO}]^2} = \frac{(0.048 \text{ s}^{-1})}{(2.0 \text{ M})^2} = 0.012 \text{ M}^{-2} \text{ s}^{-1}\]