I. 60 pts.
Simultaneous reactions of hydrogenation and isomerization take place in a certain organic synthesis.
The normal isomer (N) isomerizes to the iso isomer (I) while N is also hydrogenated to N-H₂ by
hydrogen supplier S-H₂. This can be written short hand:

\[ \begin{align*}
N + S-H₂ & \rightarrow N-H₂ + S & r₁ &= k₁ C_N C_{S-H₂} \\
N & \rightarrow I & r₂ &= k₂ C_N
\end{align*} \]

For this particular case, we know that \( C_{N,O} = 1.8 \) moles/Lt, \( C_{S-H₂,O} = 2.0 \) moles/Lt, \( k₁ = 2.5 \) Lt/mole-min
and \( k₂ = 0.6 \) min⁻¹.

It is already known that we need to make 1.0 moles/Lt of N-H₂ (the hydrogenation product).

a) 40 pts.
Compute the concentration of I that would be formed when \( C_{N-H₂} = 1.0 \) moles/Lt.

b) 20 pts.
Set up a single integral which contains only time and one concentration (i.e., eliminate all
concentrations except one) to solve for the time required for \( C_{N-H₂} \) to reach 1.0 moles/Lt also starting
with \( C_{N,O} = 1.8 \) moles/Lt and \( C_{S-H₂,O} = 2.0 \) moles/Lt. (You do not need to solve the integral).

II. 40 pts.
The overall reaction for the thermal decomposition of acetaldehyde is:

\[ \text{CH}_3 \text{CHO} \rightarrow \text{CO} + \text{CH}_₄ \]

Given the mechanism:

Initiation:
\[ \text{CH}_3 \text{CHO} \rightarrow \text{CH}_₃⁺ + \text{CHO}⁺ \]

\[ k₁ \]

Propagation
\[ \text{CH}_₃⁺ + \text{CH}_₃\text{CHO} \rightarrow \text{CH}_₃\text{CO}⁺ + \text{CH}_₄ \]

\[ k₂ \]

\[ \text{CH}_₃\text{CO}⁺ \rightarrow \text{CH}_₃⁺ + \text{CO} \]

\[ k₃ \]

Termination:
\[ 2\text{CH}_₃⁺ \rightarrow \text{C}_₂\text{H}_₆ \]

\[ k₄ \]

\[ 2\text{CHO}⁺ \rightarrow \text{CHOCH} \]

\[ k₅ \]

What order do you expect to observe in \( \text{CH}_₃\text{CHO} \)?
Solution:

I. a) $r_1 = k_1 C_N C_{S-H_2}$

$r_2 = k_2 C_N$

$-\frac{dC_N}{dt} = k_1 C_N C_{S-H_2} + k_2 C_N$

$-\frac{dC_{S-H_2}}{dt} = k_1 C_N C_{S-H_2}$

$\frac{dC_N}{C_{S-H_2}} = 1 + \frac{k_2}{k_1} \frac{1}{C_{S-H_2}}$

$\int^{C_{S-H_2}}_{1.8} dC_N = \int^{C_{S-H_2}}_{2.0} \left(1 + \frac{k_2}{k_1} \frac{1}{C_{S-H_2}}\right) dC_{S-H_2}$

$C_N - 1.8 = C_{S-H_2} - 2.0 + \left(\frac{k_2}{k_1}\right) \ln \left(\frac{C_{S-H_2}}{2.0}\right)$

When one mole of $N-H_2$ is formed, 1 mole of $C_{S-H_2}$ has reacted, so $C_{S-H_2} = 1.0$.
\[ C_N = 1.8 - 1.0 + 0.24 \ln \left( \frac{1.0}{2.0} \right) = 0.6336 \]

\[ C_I = 1.8 - 0.6336 - 1.0 \]

\[ C_I = 0.1664 \]

b) \[- \frac{dC_N}{dt} = k_1 C_N C_{S-H_2} + k_2 C_N\]

If we could eliminate \( C_{S-H_2} \) using \( C_{S-H_2} = f(C_N) \), we could solve this integral for time. However, we know \( C_N = f(C_{S-H_2}) \) rather than the other way around, so it is easier to solve for the time required to react one mole of \( S-H_2 \) which is the same as the time required to form 1 mole of \( N-H_2 \).
\[- \frac{d [C_{5-H_2}]}{dt} = k_1 C_N [C_{5-H_2}] \]
\[- \frac{d [C_{5-H_2}]}{dt} = k_1 \left[ (C_{5-H_2} - 0.2) + \frac{k_2}{k_1} \ln \left( \frac{C_{5-H_2}}{2} \right) \right] C_{5-H_2} \]

\[
\int_{2.0}^{1.0} \frac{d [C_{5-H_2}]}{\left[ (C_{5-H_2} - 0.2) + \frac{k_2}{k_1} \ln \left( \frac{C_{5-H_2}}{2} \right) \right] C_{5-H_2}} = -k_1 \int_0^t dt
\]

II. for chain rxn, rate is equal to the rate of the propagation step:
\[- \frac{d [CH_3CHO]}{dt} = k_2 [CH_3^\cdot] [CH_3CHO] + k_3 [CH_3CHO] \]

Need to eliminate \([CH_3^\cdot]\)

Use S.S. approximation.
\[
\begin{align*}
\frac{d[CH_3\cdot]}{dt} &= 0 = k_1 [CH_3CHO] - k_2 [CH_3\cdot][CH_3CHO] + k_3 [CH_3CO\cdot] \\
&\quad - 2k_4 [CH_3\cdot]^2 \\
\frac{d[CH_3CO\cdot]}{dt} &= 0 = k_2 [CH_3\cdot][CH_3CHO] - k_3 [CH_3CO\cdot] \\
[CH_3CO\cdot] &= \frac{k_2 [CH_3\cdot][CH_3CHO]}{k_3} \\
0 &= k_1 [CH_3CHO] - k_2 [CH_3\cdot][CH_3CHO] + k_2 [CH_3\cdot][CH_3CHO] \\
&\quad - 2k_4 [CH_3\cdot]^2 \\
[CH_3\cdot] &= \sqrt{\frac{k_1}{2k_4}} [CH_3CHO]^{1/2} \\
t &= -\frac{d[CH_3CHO]}{dt} = k_2 - \sqrt{\frac{k_1}{2k_4}} [CH_3CHO]^{1/2} [CH_3CHO] + k_1 [CH_3CHO] \\
t &= k_{obs} [CH_3CHO]^{3/2} \\
N_{obs} &= 3/2
\end{align*}
\]
This exam comes from 1981 back when I used to give hard exams. It represents more difficult work than I would normally expect on your first exam. However, it does require students to perform many rudimentary calculations such as the concentration of ideal gases, and the fundamental definition of fractional conversion, and as such, should be workable by an average student.

Please try to work the exam before looking at the solution.
I. 70 points

The gas phase, irreversible, elementary reaction:

\[ A + 2B \rightarrow C \]

takes place at 2 atmospheres constant pressure. At 50°C, the rate constant (expressed in units containing g-moles, liters, and minutes) is 110. Initially, an equimolar mixture of A & B with no C or inerts is present. Assume ideal gases. The activation energy is 20 Kcal/mole.

a) Calculate \( r, r_A, r_B, \) and \( r_C \) initially.

b) Calculate \( r \) when one fourth of the A is reacted.

c) Calculate \( r \) initially if the temperature is changed to 60°C.

d) How long will it take to react one fourth the A at 60°C?

II. 30 points

The liquid phase, constant density, irreversible reaction:

\[ A \rightarrow B \]

has been studied in a batch reactor at constant temperature. The following data has been reported:

<table>
<thead>
<tr>
<th>( t (\text{min}) )</th>
<th>( C_A (\text{moles/lt}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>4.00</td>
</tr>
<tr>
<td>1.00</td>
<td>3.31</td>
</tr>
<tr>
<td>2.00</td>
<td>2.78</td>
</tr>
<tr>
<td>3.00</td>
<td>2.37</td>
</tr>
<tr>
<td>4.00</td>
<td>2.04</td>
</tr>
<tr>
<td>5.00</td>
<td>1.78</td>
</tr>
<tr>
<td>6.00</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Use the differential approach to calculate the reaction order and the rate constant. What are the units of the rate constant?
CHE 4190
EXAM I, FEBRUARY 1981 Solution

I)

a) start with calc. \( C_A + C_B \)

\[
P_A V = M_A RT \\
\frac{P_A}{RT} = C_A \\
P_{A0} = P_{B0} = 1 \text{ atm} \\
\frac{1 \text{ atm}}{\left( \frac{0.08205}{180+273} \right)} = C_{A0} = C_{B0} = 3.77 \times 10^{-2} \text{ mole/atm}
\]

calc. \( R \)

\[
r = k C_A C_B^2 \quad \text{(elementary, irreversible)} \\
\]

\[
r_0 = k (3.77 \times 10^{-2})^3 - 110 (3.77 \times 10^{-2})^3
\]

\[
r_0 = 5.89 \times 10^{-3} \text{ moles/at-min}
\]

\[
[ r_A = -V_A r = (-1)(5.89 \times 10^{-3}) = -5.89 \times 10^{-3} \text{ mole/at-min} \\
V_B r = -1.18 \times 10^{-3} \\
V_C r = V_C r = +5.89 \times 10^{-3}
\]

b) must use \( f_B \) since \( B \) is limiting

when \( y_A \) the \( A \) is used up, \( y_B \) the \( B \) is used up

\[
f_B = 0.5
\]

\[
r = k C_A C_B^2
\]
\[ C_A = \frac{C_{A0} - \frac{1}{2} C_{B0} f_B}{1 + S_B f_B} \]

\[ C_B = \frac{C_{B0} (1 - f_B)}{1 + S_B f_B} \]

\[ S_B = \frac{V}{f_{e=0}} - \frac{V}{f_{e=1}} \]

\[ V \mid f_{e=0} = 0 \quad V \mid f_{e=1} = 1 \]

\[ r = 110 \left( \frac{C_{A0} - Y_Z C_{B0} f_B}{C_{B0}} \right) \left( 1 - f_B \right) \]

\[ (1 - Y_Z f_B)^3 \]

\[ \text{With } f_B = 0.5, C_{A0} = C_{B0} = 3.77 \times 10^{-2} \]

\[ r = 2.62 \times 10^{-3} \]

\[ S_B = \frac{1 - \frac{2}{2}}{2} = -\frac{1}{2} \]

\[ \text{Initial Conditions:} \]

\[ A = 1 \quad Y_Z \]

\[ B = 1 \quad 0 \]

\[ C = 0 \quad Y_Z \]

\[ \frac{Z}{2} = 1 \]

\( c) \text{ Need to calc } k_{60}, \text{ Find } A \)

\[ 110 = A \exp\left( -\frac{20000}{1.987 (273 + 60)} \right) \]

\[ A = 3.70 \times 10^{15} \text{ mole}^{-2} \text{ min} \]

\[ k_{60} = 3.70 \times 10^{15} \exp\left( -\frac{20000}{1.987 (273 + 60)} \right) \]

\[ k_{60} = 280 \]

\[ C_{A0} = C_{B0} = \frac{1}{(0.08205)(273 + 60)} = 3.66 \times 10^{-2} \]

\[ r = 280 \left( 3.66 \times 10^{-2} \right)^3 = 1.37 \times 10^{-2} \]

\[ d) \quad r = k C_A C_B^2 \]

\[ \frac{C_{B0}}{(1 + S_B f_B)} \frac{d f_B}{d t} = 2k \left( \frac{C_{A0} - Y_Z C_{B0} f_B}{1 + S_B f_B} \right) \left( \frac{C_{B0} (1 - f_B)}{1 + S_B f_B} \right)^2 \]
Since \( C_{A0} = C_{B0} \) and \( S_B = -\frac{1}{2} \),

\[
\frac{C_{A0}}{1 - \frac{1}{2} f_B} \frac{df_B}{dt} = 2k \left( \frac{C_{A0} - f_B}{1 - \frac{1}{2} f_B} \right)^2 \left( \frac{C_{A0} (1 - f_B)}{1 - \frac{1}{2} f_B} \right)^2
\]

\[
df_B = 2k C_{A0} \left( 1 - \frac{1}{2} f_B \right) \left( 1 - f_B \right)^2
\]

\[
df_B = 2k C_{A0} \left( 1 - f_B \right)^2
\]

Separate variables:

\[
\int_{0}^{\frac{1}{2}} \frac{1}{(1 - f_B)^2} df_B - \frac{1}{2} \int_{0}^{\frac{1}{2}} \frac{f_B}{(1 - f_B)^2} df_B = 2k C_{A0} \int_{0}^{t} dt
\]

Integral Tables:

\[
- \frac{1}{(-1)^{1} f_B} \left[ \ln \left( \frac{1}{1-f_B} \right) + \frac{1}{1-f_B} \right]_{0}^{\frac{1}{2}} = 2k C_{A0} t
\]

\[
\left[ \left( \frac{1}{5} \right)^{-1} - 1 \right] - \frac{1}{2} \left[ \ln \left( \frac{1}{2} \right) - \ln(1) \right] + \frac{1}{1 - \frac{1}{2}} - 1 = 2k C_{A0} t
\]

\[
1 - \frac{1}{2} \left[ \ln \left( \frac{1}{2} \right) + 1 \right] = 2k C_{A0} t
\]

\[
\frac{1}{2} + \ln 2 = 2 \times 280 \times \left( 3.66 \times 10^{-2} \right)^2 t
\]

\[
t = 1.59 \text{ min}
\]
II) \[ A \rightarrow B \]

\[- \frac{dc_A}{dt} = k c_A^n \]

Approximate w/ diff. approach

\[- \frac{dc_A}{dt} = k c_A^n \]

\[
\ln \left( \frac{- dc_A}{dt} \right) = \ln k + n \ln c_A
\]

<table>
<thead>
<tr>
<th>(c_A )</th>
<th>( dc_A )</th>
<th>( \ln \left( \frac{- dc_A}{dt} \right) )</th>
<th>( \ln (c_A)_{AVG} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>0</td>
<td>(0.69)</td>
<td>(-0.371)</td>
</tr>
<tr>
<td>3.31</td>
<td>1</td>
<td>(0.53)</td>
<td>(-0.635)</td>
</tr>
<tr>
<td>2.78</td>
<td>2</td>
<td>(0.41)</td>
<td>(-0.192)</td>
</tr>
<tr>
<td>2.37</td>
<td>3</td>
<td>(0.33)</td>
<td>(-1.109)</td>
</tr>
<tr>
<td>2.04</td>
<td>4</td>
<td>(0.26)</td>
<td>(-1.347)</td>
</tr>
<tr>
<td>1.78</td>
<td>5</td>
<td>(0.22)</td>
<td>(-1.514)</td>
</tr>
<tr>
<td>1.52</td>
<td>6</td>
<td>(0.18)</td>
<td>(-1.681)</td>
</tr>
</tbody>
</table>

See graph

\[
\text{slope} = m = 1.514 - 0.317 = 1.45
\]

\[-0.635 = \ln k + 1.45 (1.11)\]

(Pick point)

\[
\ln k = -2.24
\]

\[
k = 0.106 \frac{dt}{\text{mole} \cdot 45 \text{ min}}
\]