1. Given the following:  \( A + B \rightarrow C \)

(intended for dividing the class into 4 groups and assigning one to each group)

and the rate law \( \text{Rate} = k[A]^2[B] \) answer the following true/false statements with justification?

a) This is an elementary step
b) The reaction is second order
c) 2 molecules of A collide with one molecule of B simultaneously to form C

Answer
a) This is definitely not an elementary step as a bimolecular reaction which was an elementary step should have the rate law \( \text{Rate} = k[A][B] \)
b) No, this is 3rd order
c) No, only if this was an elementary step

and the rate law \( \text{Rate} = k[A] \) answer the following true/false statements with justification?

d) This is an elementary step
e) The reaction is second order
f) A spontaneously becomes C in the presence of B

Answer
d) This is definitely not an elementary step as a bimolecular reaction which was an elementary step should have the rate law \( \text{Rate} = k[A][B] \)
e) No, this is 1st order
f) No, if B was not consumed (i.e., if in this case B catalyzed A), the reaction would be \( A + B \rightarrow C + B \)

and the rate law \( \text{Rate} = k[A][B] \) answer the following true/false statements with justification?

g) This is an elementary step
h) The reaction is second order
i) A and B, independently, each become a molecule of C

Answer
g) This is definitely not an elementary step as a bimolecular reaction which was an elementary step should have the rate law \( \text{Rate} = k[A][B] \)
h) No, this is 0th order
i) No. If that were the case, the reaction would be \( A + B \rightarrow 2C \)

and the rate law \( \text{Rate} = k[A][B] \) answer the following true/false statements with justification?

j) This is an elementary step
k) The reaction is second order
l) 1 molecule of A collides with one molecule of B simultaneously to form C

Answer
j) Maybe. One cannot prove a reaction mechanism with kinetics, only disprove one (Benson’s Rule), however, this rate does not disprove the reaction above being elementary
k) Yes
l) If indeed this rate is an elementary step

2. Label the graph below: reactants, activated complex, activation energy, \( \Delta E_{\text{rxn}} \), and products

Is this reaction endothermic or exothermic?

exothermic

Is the reverse reaction endo- or exo-thermic?

endothemic

\( A + B \rightarrow C \)

\( E_a = 25 \text{ kcal/mol} \)

\( \Delta E_{\text{rxn}} = -50 \text{ kcal/mol} \)

Is the sign of the \( \Delta E_{\text{rxn}} \) consistent with your determination about whether the reaction is endo- or exo-thermic? yes

\( C \rightarrow A + B \)

\( E_a = 75 \text{ kcal/mol} \)

\( \Delta E_{\text{rxn}} = +50 \text{ kcal/mol} \)

Is this reaction likely to proceed in the reverse direction at room temperature without a catalyst? no
3. The rate constant for the first-order reaction
\[ \text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + _2\text{O}_2 \]
is 1.20x $10^{-2}$ s$^{-1}$ at 45° C, and the initial concentration of N$_2$O$_5$ is 0.00500M.
   a. How long will it take for the concentration to decrease to 0.00110M?
   b. How much longer will it take for a further decrease to 0.000900M?

   $1/[A] = akt + 1/[A]_0$
   $[A] = -akt + [A]_0$
   $\ln[A] = -akt + \ln[A]_0$

   Answer: use $\ln[A] = -akt + \ln[A]_0$
   a. $t= 126$ s, b. $t=143$ s therefore it takes 17s longer.

4. In the first order reaction $\text{A} \rightarrow \text{products}$, $[\text{A}] = 0.724$M initially and 0.586M after 16.0 min.
   a. What is the value of the rate constant, $k$?
   b. What is the half-life of this reaction?
   c. At what time will $[\text{A}] = 0.185$M?
   d. What will $[\text{A}]$ be after 2.5 hours?

   Answer: a. 0.0132 min$^{-1}$, b. 53.5 min, c. 103 min, d. 0.10M

5. A famous mechanism, the Lindemann mechanism, is as follows

   \[ \text{A} + \text{M} \rightarrow \text{A}^* + \text{M} \]
   \[ \text{A}^* \rightarrow \text{products} \quad \text{(slow step)} \]

   a) Give the overall reaction \( \text{A} \rightarrow \text{products} \)
   b) What can be said about the first step in this mechanism? \text{It is reversible}
   c) Using the steady-state approximation, derive the differential rate law for this mechanism in terms of A, M, and individual step-wise rate constants only \( \text{(see worked out solution at the bottom)} \)
   d) Label all species in terms of reactants, intermediates, catalysts, etc. \( \text{(ignore M)} \)

   (\text{A-reactant} \quad \text{A*-intermediate})

6. Arrhenius Plot $k=A \exp(-E_a/RT)$ 25°C $R=0.001987$ kcal/mol*K  \( k \) is in units of cm$^3$/molecule*s

   \[ \text{C}_2\text{H}_4 + \cdot\text{OH} \rightarrow \text{C}_2\text{H}_4\text{OH} \]

   \begin{align*}
   \text{ln(K)} & \quad 0.0031 \quad 0.0032 \quad 0.0033 \quad 0.0034 \quad 0.0035 \quad 0.0036 \\
   1/T & \quad -2.69E+01 \quad -2.70E+01 \quad -2.71E+01 \quad -2.72E+01 \quad -2.73E+01
   \end{align*}

   \[ y = -444.04x - 25.515 \]

   What is the activation energy? 0.87 kcal/mol
   What is the A-factor? $8.30 \times 10^{-12}$ cm$^3$/molecule*s

   Rate of the second step = $k_2[A^*]$ This is the rate determining step, but you can’t use an
   intermediate in the overall rate law. The first step is reversible, so $k_1[A][M] = k_1[A^*][M] \rightarrow$
   $k_2/k_1 \quad [A] = [A^*]$ If you use this to sub in for $[A^*]$, then rate overall = $k_{\text{overall}}[A]$. 