- 1. Experimental data for the one-step reaction  $A \rightarrow B + C$  have been plotted in three different ways:
  - (i)  $\frac{1}{|A|}$  vs. time, which gives a straight line with a positive slope
  - (ii) [A] vs. time, which gives a curved line
  - (iii) ln[A] vs. time, which gives a curved line

Based on this information, write the rate law for this reaction and determine the units of *k*.

2. The decomposition of ethanol (C<sub>2</sub>H<sub>5</sub>OH) on an alumina (Al<sub>2</sub>O<sub>3</sub>) surface was studied at 400 K.

$$C_2H_5OH(g) \rightarrow C_2H_4(g) + H_2O(g)$$

You plot the [C<sub>2</sub>H<sub>5</sub>OH] vs. time and obtain a straight-line relationship (shown to the right) with a slope of  $-4.00 \times 10^{-5}$  M/s.

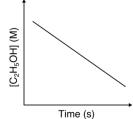
A) What is the half-life if the initial concentration of  $C_2H_5OH$  is  $1.25 \times 10^{-2}$  M?

B) Determine the time required for  $1.25 \times 10^{-2}$  M C<sub>2</sub>H<sub>5</sub>OH to *completely* decompose?

3. The activation energy for the following reaction is  $E_a = 32 \text{ kJ/mol}$  and  $\Delta E = -17 \text{ kJ/mol}$ .

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Assuming this is a single-step reaction, draw and label an energy diagram for this reaction and calculate the activation energy for the reverse reaction ( $E_a$ ').



4. Consider the following reaction again:

 $2 \text{ NO}(g) + O_2(g) \rightarrow 2 \text{ NO}_2(g)$ 

A) Determine the rate law for the reaction using the initial rates data collected at 298 K.

Experiment	[NO] <sub>0</sub> (M)	$[O_2]_0(M)$	Initial Rate (M/s)
1	0.10	0.20	$4.1 \times 10^{2}$
2	0.20	0.10	$8.2  imes 10^2$
3	0.10	0.30	$6.15 \times 10^2$

B) Which of the following are valid mechanisms for the reaction above?

Mechanism 1:	step 1) step 2)	$\begin{array}{l} \mathrm{NO}\left(\mathrm{g}\right) + \mathrm{O}_{2}\left(\mathrm{g}\right) \rightarrow \mathrm{NO}_{2}\left(\mathrm{g}\right) + \mathrm{O}\left(\mathrm{g}\right) \\ \mathrm{NO}\left(\mathrm{g}\right) + \mathrm{O}\left(\mathrm{g}\right) \rightarrow \mathrm{NO}_{2}\left(\mathrm{g}\right) \end{array}$	(slow) (fast)
Mechanism 2:	step 1) step 2)	$\begin{array}{l} 2 \text{ NO } (g) \rightarrow \mathrm{N_2O_2}  (g) \\ \mathrm{N_2O_2}  (g) + \mathrm{O_2}  (g) \rightarrow 2 \text{ NO_2}  (g) \end{array}$	(fast) (slow)
Mechanism 3:	step 1) step 2)	$\begin{array}{l} 2 \ \mathrm{NO} \ (\mathrm{g}) \rightarrow \mathrm{N}_2 \ (\mathrm{g}) + \mathrm{O}_2 \ (\mathrm{g}) \\ \mathrm{N}_2 \ (\mathrm{g}) + 2 \ \mathrm{O}_2 \ (\mathrm{g}) \rightarrow 2 \ \mathrm{NO}_2 \ (\mathrm{g}) \end{array}$	(fast) (slow)
Mechanism 4:	step 1) step 2)	$\begin{array}{l} \mathrm{NO}\left(\mathrm{g}\right) + \mathrm{O}_{2}\left(\mathrm{g}\right) \rightleftharpoons \mathrm{NO}_{3}\left(\mathrm{g}\right) \\ \mathrm{NO}_{3}\left(\mathrm{g}\right) + \mathrm{NO}\left(\mathrm{g}\right) \rightarrow 2 \mathrm{NO}_{2}\left(\mathrm{g}\right) \end{array}$	(fast) (slow)
Mechanism 5:	step 1) step 2) step 3)	$\begin{array}{l} 2 \ \mathrm{NO} \ (\mathrm{g}) \to \mathrm{N}_2 \mathrm{O}_2 \ (\mathrm{g}) \\ \mathrm{N}_2 \mathrm{O}_2 \ (\mathrm{g}) \to \mathrm{NO}_2 \ (\mathrm{g}) + \mathrm{N} \ (\mathrm{g}) \\ \mathrm{N} \ (\mathrm{g}) + \mathrm{O}_2 \ (\mathrm{g}) \to \mathrm{NO}_2 \ (\mathrm{g}) \end{array}$	(fast) (slow) (fast)

- 5. Consider the hydrolysis of urea (reaction below):  $H_2NCONH_2 (aq) + 3 H_2O (l) \rightarrow 2 NH_4^+ (aq) + OH^- (aq) + HCO_3^- (aq)$ 
  - A) You find the activation energy for the <u>uncatalyzed reaction</u> to be 138 kJ/mol. Calculate the rate constant ( $k_{uncat}$ ) for the uncatalyzed reaction at 37.0 °C assuming A = 8.66 × 10<sup>12</sup> s<sup>-1</sup>.

B) You find the activation energy for the <u>catalyzed reaction</u> to be 38.0 kJ/mol with the enzyme urease present. Calculate the rate constant ( $k_{cat}$ ) for the catalyzed reaction at 37.0 °C assuming A =  $8.66 \times 10^{12} \text{ s}^{-1}$ .

C) Calculate the temperature, theoretically, to which you would need to heat the <u>uncatalyzed</u> <u>reaction</u> to in order for the rate of the uncatalyzed reaction to be equal to the rate of the <u>catalyzed</u> reaction at 37.0 °C.

Assume the overall rate order, concentrations, and frequency factor (A) are constant between the catalyzed and uncatalyzed reactions.