#1 The reaction 2 NOCl → 2 NO + Cl_2 exhibits the differential rate law: rate = k[NOCl]^2. In an experiment, 0.100 *M* NOCl is present initially. After 12 minutes, 0.085 *M* remains.

A) Determine k for this reaction.

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$$\frac{1}{0.085\,M} = k(12\,min) + \frac{1}{0.100\,M}$$

$$k = 0.147\ M^{-1}\,min^{-1} = 0.00245\ M^{-1}s^{-1}$$

B) Determine $t_{1/2}$ for this reaction.

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$$\frac{1}{\frac{1}{2}[NOCl]_0} = (0.147\,M^{-1}\,min^{-1})\,t_{1/2} + \frac{1}{[NOCl]_0}$$

$$\frac{2}{[NOCl]_0} - \frac{1}{[NOCl]_0} = (0.147\,M^{-1}\,min^{-1})\,t_{1/2}$$

$$t_{1/2} = \frac{1}{[NOCl]_0(0.147\,M^{-1}\,min^{-1})} = \frac{1}{(0.100\,M)(0.147\,M^{-1}\,min^{-1})}$$

$$t_{1/2} = 68.0\,min = 4080\,s$$

#2 For the reaction: 2 B → products, a plot of ln [B] versus time yields a straight-line graph. In a separate experiment, the half-life is determined to be 3.2 hours. If you start with a sample that contains 3.87g of B, how long will it take to for only 0.25g of B to ~~remain~~ remain.

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.2\,h} = 0.217\ h^{-1}$$

$$\ln\left(\frac{[B]_t}{[B]_0}\right) = -kt$$

$$\ln\left(\frac{0.25\,g}{3.87\,g}\right) = -(0.217\,h^{-1})\,t$$

$$t = 12.6\,h = 13\,h$$

#3 For a given reaction, A + B → C, the rate constant triples when the temperature is increased from 25°C to 45°C. What is the activation energy for this reaction?

$k_2 = 3k_1$ $T_2 = 318\ K$ $T_1 = 298\ K$

$$\ln\left(\frac{3k_1}{k_1}\right) = \frac{-E_a}{8.3145\times10^{-3}\ kJ/mol\cdot K}\left(\frac{1}{318\,K} - \frac{1}{298\,K}\right)$$

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$$E_a = 43\ kJ/mol$$

#4

Consider the proposed reaction mechanism for phosphorus monoxide and hydrogen gas:

$2\,PO \rightleftharpoons P_2O_2$	rxn 1: fast, equilibrium
$P_2O_2 + H_2 \rightarrow P_2O + H_2O$	rxn 2: slow
$P_2O + H_2 \rightarrow P_2 + H_2O$	rxn 3: fast

A) Write the balanced equation for the overall reaction.

4 $2\,PO + 2H_2 \rightarrow P_2 + 2H_2O$

B) Which species serve as intermediates in the reaction mechanism?

4 P_2O_2 & P_2O

C) Write the differential rate law expression, excluding any intermediates.

7 $\text{rate} = k_2[P_2O_2][H_2]$

$$k_1[PO]^2 = k_{-1}[P_2O_2]$$

$$[P_2O_2] = \frac{k_1}{k_{-1}}[PO]^2$$

$$\text{rate} = k_2\frac{k_1}{k_{-1}}[PO]^2[H_2]$$

$$\text{rate} = k[PO]^2[H_2]$$

#5 Sketch in detail the Reaction-Energy Diagram for the ***endothermic*** overall reaction **A+B → 2C +D**. ***Assume that the reaction mechanism for this process involves three elementary steps, and the second step is the slow step (rate-determining step).***

- Label the axes.
- Label the relative energies of the reactants, products, transition state(s), and intermediate(s).
- Clearly indicate the Activation energy (E_a).
- Clearly indicate ΔE for the reaction.