1. If $\Delta H = -138$ kJ for a certain process, then:
   
   a) it occurs rapidly  
   b) it does not need a catalyst  
   c) it does need a catalyst  
   d) it is exothermic  
   e) it is endothermic  

2. The reaction

$$2 \text{H}_2(g) + 2 \text{NO}(g) \rightarrow 2 \text{H}_2\text{O}(g) + \text{N}_2(g)$$

is first order in H$_2$ and second order in NO. Write out the Rate Law for this reaction.

3. Nitrosyl chloride is produced from the reaction of nitrogen(II)oxide and chlorine.

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

The following initial rates at a given temperature were obtained for the concentrations given below:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Rate (mol/L.hr)</th>
<th>NO (mol/L)</th>
<th>Cl$_2$(mol/L)</th>
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<tbody>
<tr>
<td>1</td>
<td>2.21</td>
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<tr>
<td>2</td>
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What is the experimental Rate Law?

4. At a given temperature, a first-order reaction has a rate constant of $2.5 \times 10^{-3}$ s$^{-1}$. Calculate the time required (in seconds) for the reaction to be 75% complete.

$$\text{______________ sec}$$

5. A first-order reaction is observed to have a rate constant of 35 min$^{-1}$. Calculate the corresponding half-life for the reaction.

$$t_{1/2} = \text{______________ min.}$$
6. $^{64}$Co decays by a first-order process via the emission of a beta particle. The $^{64}$Co isotope has a half-life of 7.8 min. How long (in min) will it take for $31/32$ of the cobalt to undergo decay?

________________min

7. A first-order reaction has a half-life of 11.6 minutes. Calculate the rate constant for this reaction in sec$^{-1}$.

$k = _______________{s}^{-1}$

8. Given the following reaction

$$\frac{1}{2} N_2O_4(g) \rightarrow NO_2(g) \quad \Delta H = 28.6 \text{ kJ}$$

at 30°C, $k = 5.1 \times 10^6 \text{ s}^{-1}$, and the activation energy is 54.0 kJ.

a) What is the rate constant of the same reaction at 45°C?

b) What is the activation energy for the reverse reaction?

9. A suggested mechanism for the decomposition of ozone is

$$ O_3 \rightarrow O_2 + O \quad \text{(fast, equilibrium)} $$

$$ O + O_3 \rightarrow 2 O_2 \quad \text{(slow)} $$

write out a rate law that is consistent with this mechanism.

10. Briefly explain why the half-life of a second-order reaction increases as the reaction proceeds.
CHEM 132
Problem Set Ch.13

1. If $\Delta H = -138$ kJ for a certain process, then:
   a) it occurs rapidly
   b) it does not need a catalyst
   c) it does need a catalyst
   d) it is exothermic
   e) it is endothermic

2. The reaction

$$2 \text{H}_2(g) + 2 \text{NO}_2(g) \rightarrow 2 \text{H}_2\text{O}_2(g) + \text{N}_2(g)$$

is first order in $\text{H}_2$ and second order in $\text{NO}$. Write out the Rate Law for this reaction.

$$\text{ RATE } = k \left[ \text{H}_2 \right] \left[ \text{NO} \right]^2$$

3. Nitrosyl chloride is produced from the reaction of nitrogen(II)oxide and chlorine.

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

The following initial rates at a given temperature were obtained for the concentrations given below:

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What is the experimental Rate Law?

$$\text{ RATE } = k \left[ \text{NO} \right]^2 \left[ \text{Cl}_2 \right]$$

4. At a given temperature, a first-order reaction has a rate constant of $2.5 \times 10^{-3}$ s$^{-1}$. Calculate the time required (in seconds) for the reaction to be 75% complete.

If 75% complete, then $\frac{[\text{A}_1]}{[\text{A}_0]} = 0.25$

$$\log (0.25) = \frac{-2.303 \log (0.25)}{2.303} \quad \text{or} \quad t = \frac{2.303 \log (0.25)}{-2.5 \times 10^{-3}} = 555 \text{ sec}$$

5. A first-order reaction is observed to have a rate constant of 35 min$^{-1}$. Calculate the corresponding half-life for the reaction.

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{35 \text{ min}^{-1}} = 1.98 \text{ min}^{-2} \quad t_{\frac{1}{2}} = \frac{1.98 \times 10^{-2}}{\text{min}}$$
6. $^{64}\text{Co}$ decays by a first-order process via the emission of a beta particle. The $^{64}\text{Co}$ isotope has a half-life of 7.3 min. How long (in min) will it take for 3/12 of the cobalt to undergo decay?

If only $\frac{1}{12}$ of the cobalt remains...then $5$ half-lives have passed.

$$\frac{1}{2} \rightarrow \frac{1}{4} \rightarrow \frac{1}{8} \rightarrow \frac{1}{16} \rightarrow \frac{1}{32} \rightarrow \frac{1}{64}$$

$5 \times 7.3 = 36.5$ min

$$3.9 \text{ min}$$

7. A first-order reaction has a half-life of 11.6 minutes. Calculate the rate constant for this reaction in sec$^{-1}$.

Since $t_{1/2} = \frac{0.693}{k}$

Then $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{11.6 \text{ sec}} = 9.46 \times 10^{-2}$ sec$^{-1}$

8. Given the following reaction

$$\frac{1}{2} \text{NO}_2^\circ \rightarrow \text{NO}_2 \quad \Delta H = -28.6 \text{ kJ}$$

at 30°C, $k = 5.1 \times 10^6$ s$^{-1}$, and the activation energy is 54.0 kJ/mol.

a) What is the rate constant of the same reaction at 45°C? From

$$\log k_2 = \frac{E_a}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \log k_1$$

$$\log k_2 = \frac{285.8}{2.303 \times 540} \left(\frac{1}{300} - \frac{1}{450}\right) + \log (5.1 \times 10^6)$$

$$k_2 = 1.40 \times 10^7 \text{ sec}^{-1}$$

b) What is the activation energy for the reverse reaction?

$$k_1 = \frac{1}{k_2} = \frac{5.1 \times 10^6}{1.40 \times 10^7} = 3.6 \times 10^{-1}$$

9. A suggested mechanism for the decomposition of ozone is

$$\text{O}_3 \xrightarrow{k_1} \text{O}_2 + \text{O} \quad \text{(fast, equilibrium)}$$

$$\text{O} + \text{O}_3 \xrightarrow{k_2} 2\text{O}_2 \quad \text{(slow)}$$

Write out a rate law that is consistent with this mechanism.

From the rate determining step (step 2) we get

$$\text{RATE} = k_2 [\text{O}_3][\text{O}]$$

But to get rid of $[\text{O}_3]$ we substitute...so...so

$$\text{RATE} = k_2 [\text{O}_3]^2 [\text{O}]^{-1}$$

10. Briefly explain why the half-life of a second-order reaction increases as the reaction proceeds.

Since $t_{1/2} = \frac{1}{[\text{A}]_0}$ after one half life has passed, you now have less "A" to lose as your new starting point for the next half-life. As "A" continues to decrease, $t_{1/2}$ increases.

A close examination shows that the second half life would be twice as long as the first...the third half life would be four times as long as the first...etc.