INITIAL RATES PROBLEMS KEY

1. Given reaction rate data for: $H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$

Trial	$[H_2O_2]$ M	$[I^-]$ M	$[H^+]$ M	Rate (M/s)
1	0.010	0.010	0.00050	1.15×10^{-6}
2	0.020	0.010	0.00050	2.30×10^{-6}
3	0.010	0.020	0.00050	2.30×10^{-6}
4	0.010	0.010	0.00100	1.15×10^{-6}

A. Determine the order of each reactant and the overall reaction order.

From 1 → 2 $[H_2O_2]$ doubles and Rate doubles so **order = 1 for $[H_2O_2]$**

From 1 → 3 $[I^-]$ doubles and Rate doubles so **order = 1 for $[I^-]$**

From 1 → 4 $[H^+]$ doubles and Rate does not change so **order = 0 for $[H^+]$**

Overall Reaction Order: 2

B. Write the rate law for the reaction.

Rate = $k[H_2O_2][I^-]$

C. Calculate the rate constant, k.

$$k = \frac{Rate}{[H_2O_2][I^-]} = \frac{1.15x10^{-6}\ M/s}{(0.010\,M)(0.010\,M)} = \mathbf{1.2x10^{-2}\ M^{-1}s^{-1}}$$

2. Given the rate data for: $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

$[NO]\left(\frac{mol}{L}\right)$	$[H_2]\left(\frac{mol}{L}\right)$	Rate $\left(\frac{mol}{L{\cdot}s}\right)$
0.420	0.122	0.136
0.210	0.122	0.0339
0.210	0.244	0.0678
0.105	0.488	0.0339

A. What is the rate law for the reaction?

NO: order = 2 H_2: order = 1

Rate = $k[NO]^2[H_2]$

B. Calculate the rate constant, k.

$$k = \frac{Rate}{[NO]^2[H_2]} = \frac{0.136\frac{mol}{L\cdot s}}{\left(0.420\frac{mol}{L}\right)^2\left(0.122\frac{mol}{L}\right)} = 6.32\ \frac{L^2}{mol^2 s} = \mathbf{6.32\ M^{-2}s^{-1}}$$

C. What is the rate of reaction when [NO] = 0.550 M and $[H_2]$ = 0.199 M?

Rate = $k[NO]^2[H_2]$ = 6.32 $M^{-2}s^{-1}$(0.550 M)^2(0.199 M) = **0.380 Ms^{-1}**

FIRST-ORDER KINETICS PROBLEMS KEY

1. The rate law for the decomposition of N_2O_5 is Rate = k[N_2O_5], where k = 5.0 x 10^{-4} s^{-1}. What is the concentration of N_2O_5 after 1900 s, if the initial concentration is 0.56 M?

   $\ln \frac{[\mathbf{A}]_t}{[\mathbf{A}]_0} = -kt$ $\quad$ $[N_2O_5]_0 = 0.56$ M; k = 5.0 x 10^{-4} s^{-1}; t = 1900 s

   $\ln \frac{[N_2O_5]_t}{(0.56\,M)} = -(5.0 \times 10^{-4}\ s^{-1})(1900\ s) = -0.95$

   Take anti ln both sides: $\frac{[N_2O_5]_t}{(0.56\,M)} = e^{-0.95} = 0.387$

   $[N_2O_5]_t = 0.56 \times 0.387 =$ **0.22 M**

2. The first order reaction, $SO_2Cl_2 \rightarrow SO_2 + Cl_2$, has a rate constant of 0.17 h^{-1}. If the initial concentration of SO_2Cl_2 is 1.25 x 10^{-3} M, how many seconds does it take for the concentration to drop to 0.31 x 10^{-3} M?

   k = 0.17 h^{-1} $\quad$ $[SO_2Cl_2]_t = 0.31 \times 10^{-3}$ M $\quad$ $[SO_2Cl_2]_0 = 1.25 \times 10^{-3}$ M

   $$\ln \frac{[\mathbf{A}]_t}{[\mathbf{A}]_0} = -kt \quad \Rightarrow \quad t = \frac{-\ln\left(\frac{0.31x10^{-3}\,M}{1.25x10^{-3}\,M}\right)}{0.17\,h^{-1}} = -\left(\frac{-1.39}{0.17\,h^{-1}}\right) = \mathbf{8.18\ h}$$

   $$t = 8.18\ h\left(\frac{3600\,s}{1\,hr}\right) = \mathbf{2.9x10^4\ s}$$

3. Cobalt-60 is a radioisotope that decays by first-order kinetics and has a half-life of 5.26 years. The Cobalt-60 in a radiotherapy unit must be replaced when the concentration of Co decreases to 75.0% of its initial value. When does this occur?

   $t_{1/2} = 5.26$ yr $\quad$ $k\,t_{1/2} = 0.693$ $\quad$ $k = \frac{0.693}{5.26\,yr} = 0.132\ yr^{-1}$

   $\ln \frac{[\mathbf{A}]_t}{[\mathbf{A}]_0} = -kt$ $\quad$ $[Co]_t = 0.75[Co]_0$ $\quad$ $\ln \frac{0.750[Co]_0}{[Co]_0} = -(0.132\ yr^{-1})\,t$

   $\ln 0.750 = -(0.132\ yr^{-1})\,t \quad \Rightarrow \quad -0.288 = -(0.132\ yr^{-1})\,t \quad \Rightarrow$ **t = 2.18 yr**

4. The first order reaction, $CH_3NC \rightarrow CH_3CN$, has a rate constant of 6.3x10^{-4} s^{-1} at 230 °C.
   A. What is the half-life of the reaction?

   $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.3x10^{-4}\,s^{-1}} = \mathbf{1.1 \times 10^3\ s}$$

   B. How much of a 10.0 g sample of CH_3NC will remain after 5 half-lives?

   $$10.0\ g\left(\frac{1}{2}\right)^5 = \mathbf{0.313\ g}$$

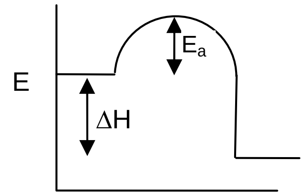
   C. How many seconds would be required for 75% of a CH_3NC sample to decompose?

   75% decomposed; 25% remains, so 2 half lives have passed.

   2×1.1 x 10^3 s = 2.2 x 10^3 s

ACTIVATION ENERGY AND REACTION MECHANISMS KEY

1. Draw the potential energy profile for a reaction with $\Delta H = -150$ kJ and $E_a = 100$ kJ.



2. A certain first order reaction has a rate constant of $1.75 \times 10^{-1}\ s^{-1}$ at 20.0 °C. What is the value of k at 60.0 °C if $E_a = 55.5$ kJ/mol?

$k_1 = 1.75 \times 10^{-1}\ s^{-1}$ $T_1 = 293$ K $E_a = 55.5$ kJ/mol

$k_2 = ?$ $T_2 = 333$ K $R = 8.314\ \frac{J}{Kmol}\left(\frac{1\,kJ}{1000\,J}\right) = 8.314 \times 10^{-3}$ kJ/(K×mol)

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\left(\frac{1.75x10^{-1}\,s^{-1}}{k_2}\right) = \frac{55.5\frac{kJ}{mol}}{8.314x10^{-3}\frac{kJ}{Kmol}}\left(\frac{1}{333\,K} - \frac{1}{293\,K}\right)$$

$$\ln\left(\frac{1.75x10^{-1}\,s^{-1}}{k_2}\right) = 6.68x10^{3}\ K(-0.000410\ K^{-1}) = -2.74$$

$$\frac{1.75x10^{-1}\,s^{-1}}{k_2} = e^{-2.74} = 0.0646 \qquad \Rightarrow k_2 = \frac{1.75x10^{-1}\,s^{-1}}{0.0646} = \mathbf{2.71\ s^{-1}}$$

3. The mechanism for the decomposition of ozone is:

Step 1: $O_3 \leftrightarrows O_2 + O$ fast

Step 2: $O_3 + O \rightarrow 2O_2$ slow

yielding the following overall reaction: $2O_3 \rightarrow 3O_2$

A. Which is the rate determining step? **step 2**

B. What is the molecularity of the rate determining step? **bimolecular**

C. Is O an intermediate or a catalyst? **intermediate**

D. Write the rate law predicted by this mechanism. Rate = $k_2[O_3][O]$

$$k_1[O_3] = k_{-1}[O_2][O] \Rightarrow [O] = \frac{k_1}{k_{-1}}\frac{[O_3]}{[O_2]} \quad \text{Rate} = \frac{k_2k_1}{k_{-1}}[O_3]\frac{[O_3]}{[O_2]} \text{ or } \textbf{Rate} = \frac{k_2k_1}{k_{-1}}\frac{[O_3]^2}{[O_2]}$$

4. The catalyzed reaction: $2SO_2 + O_2 \rightarrow 2SO_3$
is thought to occur by the following mechanism:

Step 1: $2NO + O_2 \rightarrow 2NO_2$ slow

Step 2: $2NO_2 + 2SO_2 \rightarrow 2NO + 2SO_3$ fast

A. Identify the catalyst. **NO**

B. Identify the intermediate. **NO_2**

C. Write the rate law for the reaction. **Rate = $k[NO]^2[O_2]$**