1. **(5 points each)** The following kinetic data were obtained for the reaction 2 ICl(g) + H_2(g) → I_2(g) + 2 HCl(g):

	Initial concentration, millimol•L^{-1}		
Experiment	**$[IC1]_0$**	**$[H2]_0$**	**Initial rate, mol•L^{-1}•s^{-1}**
1	1.5	1.5	3.7×10^{-7}
2	3.0	1.5	7.4×10^{-7}
3	3.0	4.5	22×10^{-7}

a) Write the rate law for the reaction.

Doubling [ICl] doubles the rate
Tripling [H_2] triples the rate $\Rightarrow$ $R = K[ICl]^1[H_2]^1$

b) From the data, determine the value of the rate constant.

$$R_0 = K[ICl]_0[H_2]_0$$

$$\Downarrow$$

$$3.7\times10^{-7}\ mol\ L^{-1}\ s^{-1} = K\left[1.5\times10^{-3}\ \frac{mol}{L}\right]\left[1.5\times10^{-3}\ \frac{mol}{L}\right]$$

$$\Rightarrow$$

$$K = 0.16\ L\ mol^{-1}\ s^{-1}$$

2. (10+5+5 points) The rate constant for the decomposition of N_2O_5 at 45°C is $k = 5.1 \times 10^{-4}\ s^{-1}$. The activation energy for the reaction is 103 kJ•mol^{-1}.

a) Determine the value of the rate constant at 50°C.

$$\frac{K_2}{K_1} = \frac{\cancel{A} \exp(-E_a/RT_2)}{\cancel{A} \exp(-E_a/RT_1)} = \exp\left(-E_a/R\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right)$$

$$\Rightarrow K_{50} = 5.1 \times 10^{-4}\ s^{-1} \exp\left(\frac{-103 \times 10^{3}\ J/mol}{8.314\ J/molK}\left(\frac{1}{273+50} - \frac{1}{273+45}\right)\right)$$

$$= 9.3 \times 10^{-4}\ s^{-1}$$

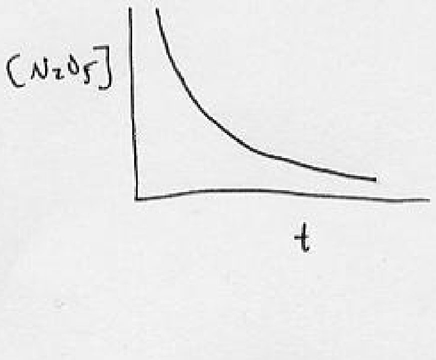
b) Calculate the half-life of N_2O_5 at 45°C.

$$t_{1/2} = \frac{\ln 2}{K}$$ since units of K => 1st order reaction

$$= \frac{\ln 2}{9.3 \times 10^{-4}\ s^{-1}}$$

$$= 1400\ s$$

c) Sketch a graph of $[N_2O_5]$ vs. time.



3. (10+5 points) The production of phosgene, $COCl_2$, from carbon monoxide and chlorine is believed to take place by the following mechanism:

Step 1 $Cl_2 \xrightarrow{k_1} Cl + Cl$

$Cl + Cl \xrightarrow{k_{-1}} Cl_2$ (both fast, equilibrium)

Step 2 $Cl + CO \xrightarrow{k_2} COCl$

$COCl \xrightarrow{k_{-2}} CO + Cl$ (both fast, equilibrium)

Step 3 $COCl + Cl_2 \xrightarrow{k_3} COCl_2 + Cl$ (slow)

a) Write the rate law implied by this mechanism (eliminate any intermediates).

- Use 2 fast pre-equilibrium assumptions

Step 1 => $K_1 = \frac{[Cl]^2}{[Cl_2]} = \frac{k_1}{k_{-1}}$ eq ① => $[Cl] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} [Cl_2]^{1/2}$

Step 2 => $K_2 = \frac{[COCl]}{[Cl][CO]} = \frac{k_2}{k_{-2}}$ eq ②

- Rate law comes from slow step, $R = k_3 [COCl][Cl_2]$
- Eliminate $[COCl]$ intermediate w/ ② => $R = k_3 \frac{k_2}{k_{-2}} [Cl][CO][Cl_2]$
- Eliminate $[Cl]$ intermediate w/ ① => $\boxed{R = k_3 \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_{-1}}\right)^{1/2} [CO][Cl_2]^{3/2}}$

b) What is the order of the reaction in chlorine?

3/2, from $[Cl_2]^{3/2}$ above in final rate expression

4. **(15 points)** The decomposition of ozone by light can be described by the mechanism.

$$O_3 + \text{light} \xrightarrow{k_1} O_2 + O$$

$$O + O_2 + M \xrightarrow{k_2} O_3 + M$$

$$O + O_3 \xrightarrow{k_3} 2\,O_2$$

with the overall reaction being

$$2\,O_3 + \text{light} \rightarrow 3\,O_2$$

The rate constant k_1 depends on the light intensity and the type of light source used. By making a steady-state approximation for the concentration oxygen atoms, express the rate of formation of O_2 in terms of the O_2, O_3, and M concentrations and the elementary rate constants.

First, write differential rate expression for $[O_2]$ =>

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_2[O][O_2][M] + 2k_3[O][O_3]$$

Next, eliminate $[O]$ through steady state approximation:

$$\frac{d[O]}{dt} \approx 0 = k_1[O_3] - k_2[O][O_2][M] - k_3[O][O_3] \Rightarrow$$

$$[O] = \frac{k_1[O_3]}{k_2[O_2][M] + k_3[O_3]}$$

Now, plug $[O]$ expression back into $\frac{d[O_2]}{dt}$ balance:

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_2\left[\frac{k_1[O_3]}{k_2[O_2][M] + k_3[O_3]}\right][O_2][M] + 2k_3\left[\frac{k_1[O_3]}{k_2[O_2][M] + k_3[O_3]}\right]$$

5. (10 points) The enzyme lysozyme kills certain bacteria by attacking a sugar called *N*-acetylglucosamine (NAG) in their cell walls. At an enzyme concentration of 2 x 10^{-6} M, the maximum rate for substrate (NAG) reaction, found at high substrate concentration, is 1 x 10^{-6} mol L^{-1} s^{-1}. The rate is reduced by a factor of 2 when the substrate concentration is reduced to 6 x 10^{-6} M. Determine the Michaelis-Menten constants K_m and k_2 for lysozyme.

The Michaelis-Menten rate law for enzyme catalysis is:

$$\text{Rate} = \frac{k_2\,[E]_0\,[S]}{[S] + K_m}$$

When [S] is large

$$\text{Rate} = \frac{k_2\,[E]_0\,\cancel{[S]}}{\cancel{[S]} + K_m \approx 0} = k_2\,[E]_0 \Rightarrow k_2 = \frac{\text{Rate},[S]\text{big}}{[E]_0}$$

$$= \frac{1\times10^{-6}\,\text{mol}\,L^{-1}s^{-1}}{2\times10^{-6}\,M}$$

$$\boxed{k_2 = 0.5\ s^{-1}}$$

$$\frac{1}{2}(R,[S]\text{big}) = \frac{k_2[E]_0[6\times10^{-6}\,M]}{K_m + [6\times10^{-6}\,M]}$$, solve for $\boxed{K_m = 6\times10^{-6}\,\frac{\text{mol}}{L}}$

6. (5 points each) Consider the collision theory result for the bimolecular reaction of H_2 with Cl_2 at 273 K.

a) Calculate the reduced molar mass (in kg).

$$\frac{2\cdot 71}{2+71}\,\frac{g}{mol} = 1.9\,g/mol = \boxed{1.9\times10^{-3}\,\frac{kg}{mol}}$$

b) Calculate the average relative speed $(8RT/\pi\mu)^{1/2}$.

$$\bar{c} = \left(\frac{8 \cdot 8.3145 \frac{J}{mol K} \cdot 273 K}{3.14 \cdot 1.9 \times 10^{-3} \frac{kg}{mol}} \right)^{1/2} = 1.7 \times 10^{3} \frac{m}{s}$$

c) Calculate A ($A = \sigma \bar{C}_{rel} N_0$) given that the collision cross section is 3.0×10^{-19} m².

$$A = (3 \times 10^{-19} m^2)(1.7 \times 10^{3} \tfrac{m}{s})(6.02 \times 10^{23} mol^{-1}) = \boxed{3.1 \times 10^{8} \frac{m^3}{mol\ s}}$$

$$= 3.1 \times 10^{11} \frac{L}{mol\ s}$$

d) The measured value of A is 1.2×10^{8} and E_a is 180 kJ/mol. Compute the steric factor for the reaction.

$$P = \frac{\sigma_{exp}}{\sigma_{theo}}$$

$$\frac{A_{exp}}{A_{theo}} = \frac{\sigma_{exp} \cancel{\bar{c}} \cancel{N_0}}{\sigma_{theo} \cancel{\bar{c}} \cancel{N_0}} = P = \frac{1.2 \times 10^{8} \frac{L}{mol\ s}}{3.1 \times 10^{11} \frac{L}{mol\ s}} = \boxed{3.8 \times 10^{-4} = P}$$

7. **(10 points)** A mechanism for reactions in liquids is:

$$A + B \underset{k_D}{\overset{k_D}{\leftrightarrow}} (AB) \xrightarrow{k_2} P$$

Using the steady-state approximation, derive the differential rate law appropriate for diffusion-controlled reactions.

$$\text{Rate} = k_2[AB]$$

$$\frac{d[AB]}{dt} \approx 0 = k_D[A][B] - k_D[AB] - k_2[AB] \quad \Rightarrow$$

$$[AB] = \frac{k_D[A][B]}{k_D + k_2} \quad \Rightarrow$$

$$\text{Rate} = \frac{k_2 k_D [A][B]}{k_D + k_2}$$

Diffusion controlled => $k_D \ll k_2$ =>

$$\text{Rate} \approx \frac{k_D \cancel{k_2} [A][B]}{\underset{0}{\cancel{k_D}} + \cancel{k_2}} \cong \boxed{k_D[A][B] = R}$$