1) (10 points)

i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\quad K_1 = 4.4 \times 10^{-31}$ $\longrightarrow K_1 = \dfrac{[NO]^2}{[N_2][O_2]}$

ii) $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ $\quad K_2 = 1.0 \times 10^{-18}$ $\longrightarrow K_2 = \dfrac{[NO_2]^2}{[N_2][O_2]^2}$

iii) $2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$ $\quad K_3 = 2.8 \times 10^{-37}$ $\longrightarrow K_3 = \dfrac{[N_2O]^2}{[N_2]^2[O_2]}$

a) Write the equilibrium constant expression for each equilibrium equation, **i** and **ii** and **iii**.

b) From your work in part a, determine the equilibrium constant value (K_4) for the following equilibrium:

iv) $N_2O(g) + 3/2\ O_2(g) \rightleftharpoons 2NO_2(g)$

$N_2O \rightleftharpoons N_2 + \tfrac{1}{2}O_2 \quad \dfrac{1}{(K_3)^{1/2}}$

$N_2 + 2O_2 \rightleftharpoons 2NO_2 \quad K_2$

$N_2O + 3/2\,O_2 \rightleftharpoons 2NO_2$

$\longrightarrow \dfrac{1}{K_3^{1/2}} \cdot K_2 = K_4 = (2.8 \times 10^{-37})^{-1/2} \cdot (1.0 \times 10^{-18})$

$K_4 = 1.9$

c) What does the value of K_4 indicate about the reactants and products for the equilibrium **iv**?

Since $K_4 > 1$ products are favored, but only slightly

2) (4 points) For a particular reaction an increase in temperature (↑ T) increases the rate (↑ rate) and E_a does not change. For the same reaction adding a catalyst (+ Cat.) increases the rate (↑ rate) and E_a decreases. Explain these differences using collision theory.

If only temperature is changed, in this case increased, the energy of collisions will change, in this case increase, for more particles. An increase in E_k for more particles will increase the number of particles with $E_k \geq E_a$. A catalyst actually collides with substrate and in doing so creates a new, lower energy pathway to products ($E_a \downarrow$).

3) (5 points) Use the following initial rate results to determine the rate law for the reaction of X + Z + A.

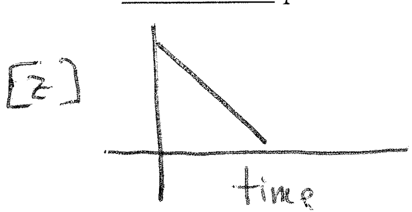
Doubling [X] while keeping [Z] and [A] constant decreases the rate 4 fold. $\quad 2x \rightarrow \tfrac{1}{4}x \quad -2$
Doubling [Z] while keeping [X] and [A] constant has no effect on the rate. $\quad 2x \rightarrow 1x \quad 0$
Doubling [A] while keeping [X] and [Z] constant increases the rate 2 fold. $\quad 2 \rightarrow 2x \quad 1$

a) Write the rate law in terms of X, Z, and A:

$rate = k[X]^{-2}[Z]^0[A]^1 = k[X]^{-2}[A]$

b) What is the overall order of the reaction? $\underline{-1}$

c) Sketch an axis-labeled plot showing linear behavior for Z.



4) (10 points) In the stratosphere, ozone (O_3) is converted to O_2 by the reaction $O_{(g)} + O_{3\,(g)}$ --------> $2\ O_{2\,(g)}$. The observed rate constant for this reaction at 220.K is $k_{obs} = 6.8 \times 10^{-16}$ cm^3 • molecule^{-1} • s^{-1}.

a) What is the overall order of this reaction?

$\frac{cm^3}{molecule \cdot s} \approx \frac{1}{M \cdot s}$ 2nd order

b) Calculate E_a in kilojoules for this reaction if the frequency factor is A = 8 x 10^{-12} cm^3 • molecule^{-1} • s^{-1}.

$$E_a = -\ln\left(\frac{k}{A}\right) \times RT$$

$$= -\ln\left(\frac{6.8\times10^{-16}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}}{8\times10^{-12}\ cm^3 \cdot molecule^{-1} \cdot s^{-1}}\right) \times 0.008314 \frac{kJ}{mol \cdot K} \times 220.\ K$$

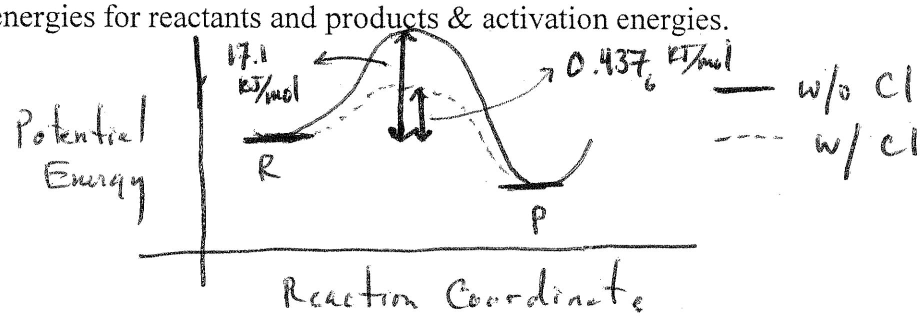
$17.1_4 \frac{kJ}{mol}$

c) If chlorine radicals (Cl) are present (the Arctic & Antarctic polar vortices contain Cl derived from chlorofluorocarbons, CFCs) the observed rate constant at 220.K is $k_{obs} = 3.7 \times 10^{-11}$ cm^3 • molecule^{-1} • s^{-1}. The frequency factor for this reaction is A = 4.7 x 10^{-11} cm^3 • molecule^{-1} • s^{-1}. Calculate E_a in kilojoules for the depletion of ozone in the presence of Cl.

$$E_a = -\ln\left(\frac{3.7\times10^{-11}}{4.7\times10^{-11}}\right) \times 0.008314 \frac{kJ}{mol \cdot K} \times 220.\ K$$

$= 0.437_6 \frac{kJ}{mol}$

d) Draw an axis-labeled reaction coordinate for both reactions (with and without Cl) showing the relative energies for reactants and products & activation energies.



e) What would you conclude about the effect of Cl on stratospheric ozone depletion based on this information?

The chlorine atom acts as a catalyst for accelerating ozone depletion in the stratosphere.

5) (15 points) **The following 3-step mechanism has been proposed for the reaction of chlorine and chloroform. The numerical values of the rate constants are given next to each elementary step.**

1) $Cl_{2\,(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Cl_{(g)}$ $\quad k_1 = 4.8 \times 10^3$ and $k_{-1} = 3.6 \times 10^3$

2) $Cl_{(g)} + CHCl_{3\,(g)} \xrightarrow{k_2} HCl_{(g)} + CCl_{3\,(g)}$ $\quad k_2 = 1.3 \times 10^{-2}$

3) $CCl_{3\,(g)} + Cl_{(g)} \xrightarrow{k_3} CCl_{4\,(g)}$ $\quad k_3 = 2.7 \times 10^2$

a) Write the overall reaction for this mechanism.

$Cl_2 + CHCl_3 \longrightarrow HCl + CCl_4$

b) What is the molecularity of each elementary step? 1) uni- -1) bi- 2) bi- 3) bi-

c) What are the units of k for each elementary step? 1) s^{-1} -1) $M^{-1} \cdot s^{-1}$ 2) $M^{-1} \cdot s^{-1}$ 3) $M^{-1} \cdot s^{-1}$

(time^{-1}) (conc^{-1} · time^{-1})

d) Calculate the forward reaction rate for step 1 given that the equilibrium concentration of chlorine gas is $[Cl_2]_{eq} = 2.0$ M.

$rate_1 = (4.8 \times 10^3\ s^{-1}) \times (2.0\ M) = 9.6 \times 10^3\ \frac{M}{s}$

e) Calculate $[Cl]_{eq}$.

$rate_1 = rate_{-1}$

$k_1 [Cl_2] = k_{-1} [Cl]^2$

$[Cl] = \left(\frac{k_1}{k_{-1}} [Cl_2]\right)^{1/2} = \left(\frac{4.8 \times 10^3\ s^{-1}}{3.6 \times 10^3\ M^{-1} s^{-1}} \cdot 2.0\ M\right)^{1/2} = 1.6\ M$

f) Using your result from part e calculate the reaction rate for step 2 if the $[CHCl_3]_o = 1.0$ M.

$rate_2 = k_2 [Cl][CHCl_3] = (1.3 \times 10^{-2}\ M^{-1} s^{-1})(1.6\ M)(1.0\ M) = 2.1 \times 10^{-2}\ \frac{M}{s}$

g) Which step is the rate determining or slow step, 1, -1, 2, or 3? 2

h) Derive the rate law for the overall reaction. Do not calculate the value of k_{obs} just show it symbolically.

$rate = k_2 [Cl][CHCl_3]$

↑ intermediate

from part e) $[Cl] = \left(\frac{k_1}{k_{-1}} [Cl_2]\right)^{1/2}$

$rate = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [Cl_2]^{1/2} [CHCl_3]$

i) Is the mechanism reasonable? Explain your answer by considering the molecularity of each elementary step and collision theory.

YES, each step is either 1st or 2nd order; these are the most common collision-based orders due to the greater probability of occurance.

6) (6 points) The following data is obtained for the reaction $2C_4H_6\,(g) \text{ --------> } C_8H_{12}\,(g)$ at a given temperature.

t = 0 s	[C_4H_6] =0.01000 M
1000	0.00625
1800	0.00476
2800	0.00370
3600	0.00313
4400	0.00270
5200	0.00241
6200	0.00208

1st $t_{1/2}$ = 1800 s

2nd $t_{1/2}$ = 5200 - 1800 s = 3400 s ~ 2x

a) Determine the order of this reaction.

$t_{1/2}$ is not constant, not 1st order

rate is not constant, $\frac{-(0.00476-0.01000)}{1800}\frac{M}{s} \neq \frac{-(0.00241-0.01000)}{5200}\frac{M}{s}$, not 0th order

$(2.911\times10^{-6}\ \frac{M}{s}) \neq (1.460\times10^{-6}\ \frac{M}{s})$

Check 2nd order:

$k_1 = \left(\frac{1}{0.00625} - \frac{1}{0.01000}\right)/1000$ → $6.000\times10^{-2}\ M^{-1}s^{-1}$

$k_2 = \left(\frac{1}{0.00313} - \frac{1}{0.01000}\right)/3600$ → $6.100\times10^{-2}\ M^{-1}s^{-1}$

$k_3 = \frac{\frac{1}{0.00208} - \frac{1}{0.01000}}{6200}$ → $6.141\times10^{-2}\ M^{-1}s^{-1}$

b) What is the rate of reaction when [C_4H_6] = 0.00333 M? In the interest of time one value of k is sufficient for the calculation rather than an average value.

$$rate = k\,[C_4H_6]^2 = (6.080\times10^{-2}\ M^{-1}\cdot s^{-1})(0.00333\ M)^2$$

$$= 6.74\times10^{-7}\ \frac{M}{s}$$

Extra Credit: Refer to question 5. Write a 3-step mechanism with the rate law being rate = k[$CHCl_3$]. Assume the overall reaction is the same as in question 5a.

$CHCl_3 \xrightarrow{k_1} H + CCl_3$ slow

$CCl_3 + Cl_2 \rightarrow CCl_4 + Cl$ fast

$Cl + H \rightarrow HCl$ fast

$rate = k_1[CHCl_3]$

$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4$