

1. (6 pts) The mole fraction of NO<sub>2</sub> in Los Angeles in the spring time is 20 ppbv (parts per billion by volume) at sea level and 25°C. What is the concentration of NO<sub>2</sub> in moles/L?

$$20 \text{ ppbv (1 part/10}^9 \text{ ppbv)} = 2 \times 10^{-8} = \text{mole fraction of NO}_2$$

$$P_{\text{NO}_2} = X_{\text{NO}_2} \cdot P_{\text{atm}} \\ = (2 \times 10^{-8})(1 \text{ atm}) = 2 \times 10^{-8} \text{ atm}$$

$$PV = nRT \quad \text{and therefore } n/V = P/RT = \text{concentration in mol/L} \\ (n/V) = (2 \times 10^{-8} \text{ atm}) / [(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})] \\ = 8.2 \times 10^{-10} \text{ M}$$

2. (10 pts) As the temperature increases from 300 K to 400 K, the rate constant for a certain reaction increases 100 fold (that is  $k_{400} = 100 \cdot k_{300}$ ). What is the activation energy for this reaction?

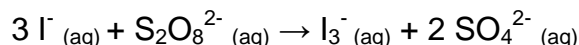
$$k_{400} / k_{300} = 100 = (A e^{-E_a/400R}) / (A e^{-E_a/300R})$$

$$\ln(100) = (-E_a / 400 R) - (-E_a / 300 R) \\ = -E_a/R [(1/400 \text{ K}) - (1/300 \text{ K})]$$

$$4.605 = (E_a / R) (8.3 \times 10^{-4})$$

$$E_a = 46.1 \text{ kJ/mol}$$

3. (6 pts) Consider the following (familiar) reaction:



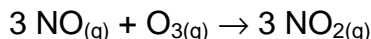
Triiodide has a molar absorptivity of 23500 M<sup>-1</sup>cm<sup>-1</sup> at 350 nm. Let's say you run a reaction in a 1.00 cm cuvette, and you see an absorbance change of 1.00 at 350 nm in 60 seconds. What is the rate of reaction?

$$\Delta \text{Abs} = a \cdot b \cdot \Delta c$$

$$(1/60 \text{ s}) = (23500 \text{ M}^{-1} \text{ cm}^{-1})(1 \text{ cm})(\Delta c)$$

$$\text{rate} = \Delta c \text{ per unit time} = 7.09 \times 10^{-7} \text{ M/s}$$

4. (6 pts) A sealed flask is charged with 6.00 atm of O<sub>3</sub> and 6.00 atm of NO. What will the final pressure in the flask be, assuming that the reaction goes to completion at a constant temperature. (Show your reasoning)



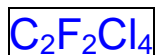
NO is the limiting reagent. No NO will remain at the end.

(1 O<sub>3</sub>/3 NO)(6 atm O<sub>3</sub>) = 2 atm O<sub>3</sub> will be used. 4.00 atm of O<sub>3</sub> remain

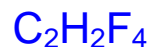
(3 NO<sub>2</sub>/3 NO)(6 atm NO<sub>2</sub>) = 6 atm NO<sub>2</sub> will be created. 6.00 atm of NO<sub>2</sub> produced.

10.00 atm final pressure (4 atm O<sub>3</sub> + 6 atm NO<sub>2</sub>)

5. (6 pts) Circle the molecule listed below that you believe would pose the greatest threat to stratospheric ozone depletion. Underline the molecule that you believe poses the least threat to ozone depletion.

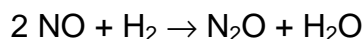


more atomic chlorine generated



no atomic chlorine

6. (22 pts) Consider the following data for the reaction:



Trial	[NO] (M)	[H <sub>2</sub> ] (M)	rate (M/s)
1	0.10	0.20	0.10
2	0.10	0.30	0.15
3	0.20	0.30	0.60

- a. What is the rate law for the reaction? Show or state your reasoning explicitly.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[\text{NO}]_1^x[\text{H}_2]_1^y}{k[\text{NO}]_2^x[\text{H}_2]_2^y} = \left(\frac{[\text{H}_2]_1}{[\text{H}_2]_2}\right)^y \quad \text{so } y = 1$$

$$\frac{0.10}{0.15} = \left(\frac{0.20}{0.30}\right)^y$$

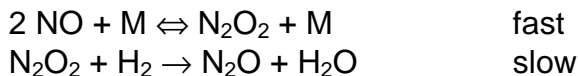
Similar analysis on NO, using trials 2 & 3 gives x = 2

$$\text{rate} = k[\text{NO}]^2[\text{H}_2]$$

- b. What is the rate constant for the reaction?

$$k = \text{rate}_1/[\text{NO}]^2[\text{H}_2] = (0.10 \text{ M/s})/(0.10 \text{ M})^2(0.20 \text{ M}) = 50 \text{ M}^{-2}\text{s}^{-1}$$

- c. What rate law is predicted by the following mechanism? Show your reasoning fully.



rate =  $k_2[\text{N}_2\text{O}_2][\text{H}_2]$  for slow second step. Need to replace  $[\text{N}_2\text{O}_2]$

rapid equil:  $k_1[\text{NO}]^2[\text{M}] = k_{-1}[\text{N}_2\text{O}_2][\text{M}]$   
 $[\text{N}_2\text{O}_2] = (k_1/k_{-1})[\text{NO}]^2$

rate =  $k_2(k_1/k_{-1})[\text{NO}]^2[\text{H}_2] = k[\text{NO}]^2[\text{H}_2]$

7. (14 points) The following reaction is first order in  $\text{CFCl}_3$ .



- a. The lifetime for  $\text{CFCl}_3$  in the atmosphere is 50 yr. What is the rate constant for this process?

$\tau = 1/k$ :  $k = 1/\tau = 1/(50 \text{ yr}) = 0.02 \text{ yr}^{-1}$

- b. In 1992, the concentration of  $\text{CFCl}_3$  in the atmosphere was  $1.1 \times 10^{-11} \text{ M}$ . What is the current concentration of  $\text{CFCl}_3$ , assuming no additional  $\text{CFCl}_3$  has been produced since then? (You will need the answer to part "a" to answer this. Assume a rate constant of  $1.0 \text{ yr}^{-1}$  if you were unable to answer "a").

$\ln[\text{CFCl}_3]_t = \ln[\text{CFCl}_3]_o - 1 \cdot kt$

$\ln[\text{CFCl}_3]_t = \ln(1.1 \times 10^{-11}) - (0.02 \text{ yr}^{-1})(16 \text{ yr}) = -25.6$

$[\text{CFCl}_3]_t = e^{-25.6} = 8.0 \times 10^{-12} \text{ M}$

8. (6 pts)  $\text{C}_2\text{H}_6$  reacts to produce two molecules of  $\text{CH}_3$  in a 2nd order process with a rate constant of  $0.010 \text{ M}^{-1}\text{s}^{-1}$ . What is the rate of reaction when  $[\text{C}_2\text{H}_6] = 2.0 \text{ M}$ ?

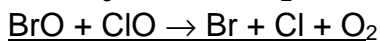
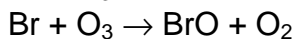
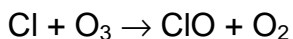
rate =  $k[\text{C}_2\text{H}_6]^2 = (0.010 \text{ M}^{-1}\text{s}^{-1})(2.0 \text{ M})^2 = 0.040 \text{ M/s}$

9. (6 pts) A 10.0 L sample of gas is heated from  $25^\circ\text{C}$  to  $100^\circ\text{C}$ . If the pressure is constant at 1.00 atm, what will the final volume be?

$V_1/T_1 = V_2/T_2$

$V_2 = T_2(V_1/T_1) = (373 \text{ K})(10.0 \text{ L}/298 \text{ K}) = 12.5 \text{ L}$

10. (18 pts) Consider the following “Cl/Br mechanism”, which is postulated to take place in the polar stratosphere during the formation of the “ozone hole”. Bromine is produced in the stratosphere by the break down of organic bromine compounds produced by marine organisms and humans.



- a. Write the net, balanced reaction described in the Cl/Br mechanism:



- b. Identify each of the following in the Cl/Br mechanism:

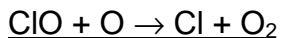
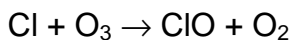
reactant(s) O<sub>3</sub>

product(s) O<sub>2</sub>

catalyst(s) Cl, Br

intermediate(s) ClO, BrO

- c. The standard mechanism for chlorine-only ozone depletion is shown below. What is the net reaction taking place in the chlorine-only mechanism?



- d. Explain why the “Cl/Br mechanism” might be a more important contributor to ozone depletion than the chlorine-only mechanism at lower altitudes in the stratosphere and in the springtime polar stratosphere.

The Cl-only mechanism requires atomic oxygen, O, which is a rare species in the polar stratosphere during the spring, or in the lower stratosphere in general, since O is made by the action of high energy UV light on O<sub>2</sub>.