

## CHEM 302 Assignment #1

*Provide solutions to the following questions in a neat and well organized manner, including dimensional analysis, where appropriate. Reference data sources for any constants and state assumptions, if any.*

Due: Thursday, September 28<sup>th</sup>, 2017

1. Each of the following gases are known atmospheric contaminants with both natural and anthropogenic sources. Identify gaseous species in lower oxidation that may act as sources and higher oxidation states that may act as sinks for each of the following.

Carbon monoxide, **CO**

Nitrogen dioxide, **NO<sub>2</sub>**

Chlorine monoxide, **ClO**

### Answers

Let's start by assigning oxidation states to the atoms involved. Since oxygen has an oxidation state of (-2) in all chemical combinations with other elements (except for peroxides), we can quickly assign the oxidation state of remaining elements as follows. See first year text and/or review sheet handouts for practice.

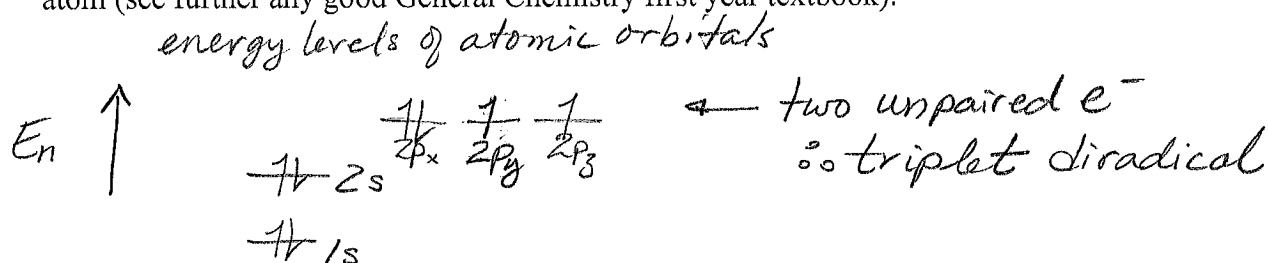
		oxidation state			
<b>CO</b>		<b>carbon (+2)</b>			
<b>NO<sub>2</sub></b>		<b>nitrogen (+4)</b>			
<b>ClO</b>		<b>chlorine (+2)</b>			
	Sources	→	X	→	Sinks
	(lower oxidation state)				(higher oxidation state)
	<b>CH<sub>4</sub> or CH<sub>2</sub>O</b>	→	<b>CO</b>	→	<b>CO<sub>2</sub></b>
	<b>NH<sub>3</sub> or N<sub>2</sub> or N<sub>2</sub>O or NO</b>	→	<b>NO<sub>2</sub></b>	→	<b>NO<sub>3</sub></b>
	<b>Cl</b>	→	<b>ClO</b>	→	<b>ClO<sub>2</sub></b>

(See further in-class handout on biogeochemical cycles for C and N)

2. The ground electronic state of both atomic and molecular oxygen are said to be diradical 'triplet' states. Use your knowledge of atomic and molecular orbital theory to explain why 'singlet' (spin paired) states are electronically excited.

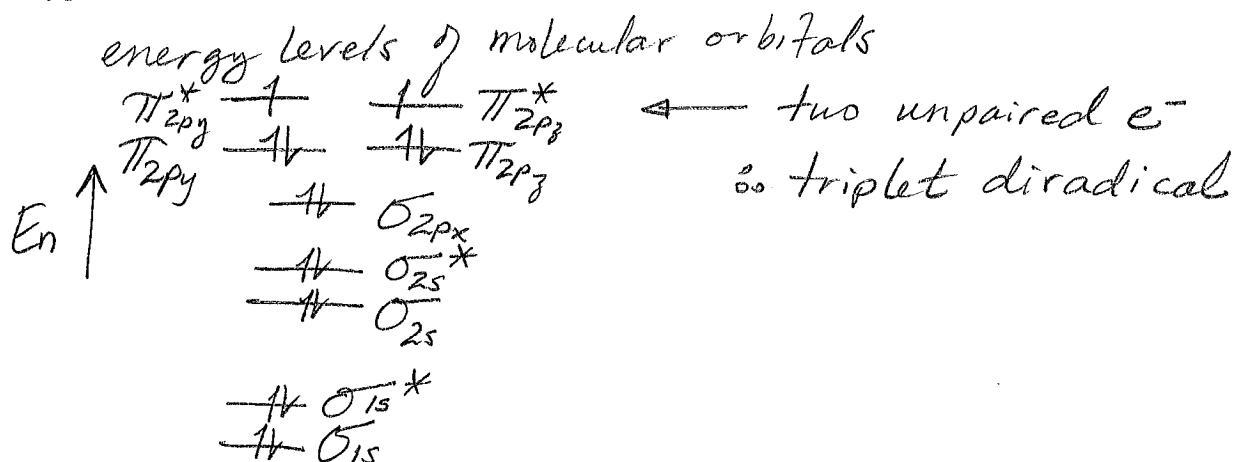
**Answer:** The ground electronic state corresponds to the lowest energy electronic configuration. Remembering that the energy levels of electrons are quantized and characterized by specific 'orbitals' (atomic orbitals or molecular orbitals), the lowest energy electron configuration is derived by placing electrons into the lowest energy orbitals up to a maximum of two per orbital. If a set of orbitals have identical energies, then Hund's rule is applied and the lowest energy configuration involves singly occupied orbitals first.

**Atomic oxygen** → use atomic orbital energy level diagram for the 8 electrons of oxygen atom (see further any good General Chemistry first year textbook).



The electron configuration is given by;  $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$  which has two unpaired electrons and hence is a ground state *triplet*. All other allowable electronic configurations are excited states. For instance,  $1s^2 2s^2 2p_x^2 2p_y^2$  is a *singlet* state (all electrons spin paired), but represents an excited state. The excitation energy  $E_e(\text{O})$  is  $190 \text{ kJ mol}^{-1}$ .

**Molecular oxygen** → use molecular orbital energy level diagram for the 16 electrons of oxygen molecule (see further any good General Chemistry first year textbook).



The electron configuration is given by;  $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2py}^2 \pi_{2pz}^2 \pi_{2py}^{*1} \pi_{2pz}^{*1}$  which has two unpaired electrons and hence is a ground state *triplet*. All other allowable electronic configurations are excited states. The excitation energy  $E_e(\text{O}_2)$  is  $90 \text{ kJ mol}^{-1}$ .

3. Exhaust gases from internal combustion engines can contain as much as 200 ppm<sub>v</sub> of nitric oxide (NO). Express this concentration in (a) mg m<sup>-3</sup> and (b) molecules per cm<sup>3</sup>.

**Answers**

a) mass per volume (mg m<sup>-3</sup>)

[270 mg m<sup>-3</sup>; STP]

$$200 \text{ ppm}_v = \frac{200 \text{ mols NO}}{10^6 \text{ mols air}}$$

← convert to mass in mg  
 ← convert to volume in m<sup>3</sup>

$$\frac{200 \text{ mols NO}}{10^6 \text{ mols air}} \times \frac{30 \text{ g}}{1 \text{ mol NO}} \times \frac{1 \text{ mol air}}{22.4 \text{ L}} \times \frac{10^3 \text{ L}}{1 \text{ m}^3} \times \frac{10^3 \text{ mg}}{1 \text{ g}}$$

$$= 270 \frac{\text{mg NO}}{\text{m}^3}$$

where molar volume of air at STP was assumed.

b) number density (molecules per cm<sup>3</sup>)

[5.4 × 10<sup>15</sup> molec cm<sup>-3</sup>; STP]

$$n_{\text{NO}}^* = X_{\text{NO}} n_{\text{air}}^*$$

where  $X_{\text{NO}} = \frac{200}{10^6}$

and  $n_{\text{air}}^* = \frac{P V}{RT} \times N_A$

$$= \frac{(1 \text{ atm})(1 \times 10^{-3} \text{ L})(6.023 \times 10^{23} \text{ mol}^{-1})}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol K}})(273 \text{ K})}$$

$$= 2.69 \times 10^{19} \text{ molec/cm}^3$$

at  $P = 1 \text{ atm}$ ,  $T = 273 \text{ K}$

$$\therefore n_{\text{NO}}^* = \frac{200}{10^6} (2.69 \times 10^{19} \frac{\text{molec}}{\text{cm}^3}) = 5.4 \times 10^{15} \frac{\text{molec}}{\text{cm}^3}$$

4. Acrolein (2-propenal) is a volatile organic compound with a disagreeable odour and physiological effects (lachymator). It has a reported vapour pressure of 200 torr at 17 °C. It is soluble in water, and photochemically active with an estimated outdoor half-life of 1 day. The 8 hour workplace exposure limit is 250 µg/m<sup>3</sup>.

- Identify at least one indoor and outdoor source of atmospheric acrolein, properly citing your reference/s.
- Determine the mixing ratio of acrolein in the air if a spill were to occur in a closed room at 17°C. How does this compare to the 8 hour workplace exposure limit?
- Assuming the loss of acrolein follows *psudeo* first order kinetics, show that the outdoor residence time residence time is around 35 hours.

### Answers

a) Sources generally include incomplete combustion of organic fuels. Indoor concentrations of acrolein generally exceed outdoor concentrations.

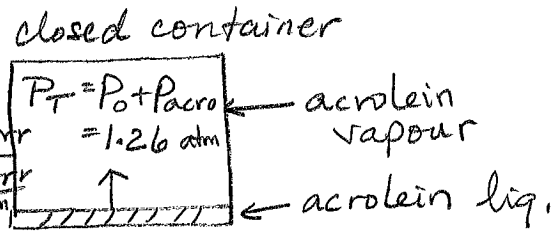
Indoor Source = Cigarette smoke, gas stoves, space heaters

Outdoor Source = Forest fires, open burning etc.

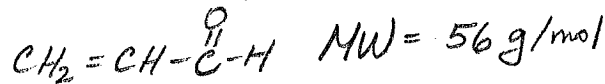
Source: Priority Substances List Assessment Report for Acrolein, Health Canada  
<https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/environmental-contaminants/canadian-environmental-protection-act-1999-priority-substances-list-assessment-report-acrolein.html#a222>  
 accessed September 29, 2017

b) Mixing ratio and mass concentration

$[X_{\text{acrolein}} = 0.21; 6.2 \times 10^8 \mu\text{g m}^{-3}]$   $P_{\text{acrolein}} = \frac{200 \text{ torr}}{760 \text{ torr atm}} = 0.26 \text{ atm}$



$\therefore X_{\text{acrolein}} = \frac{0.26 \text{ atm}}{1.26 \text{ atm}} = 0.21$



$\frac{0.21 \text{ mol acro}}{1.0 \text{ mol air}} \times \frac{56 \text{ g}}{1 \text{ mol acro}} \times \frac{1 \text{ mol air}}{18.9 \text{ L}} \times \frac{10^3 \text{ L}}{1 \text{ m}^3} \times \frac{10^6 \mu\text{g}}{1 \text{ g}} = 6.2 \times 10^8 \mu\text{g/m}^3$

volume of 1 mol of contaminated air at 290 K = 18.9 L

c) Outdoor residence time

For first order process,  
 $\ln \frac{[A]_t}{[A]_0} = -kt$  and at  $t = t_{1/2}$   
 $\therefore \ln(1/2) = -kt_{1/2}$   
 or  $t_{1/2} = \frac{0.693}{k}$

also,  $\tau = \frac{\text{amt}}{\text{flux}} = \frac{[A]}{k[A]} = \frac{1}{k}$   
 $\therefore k = \frac{1}{\tau}$   
 So,  $t_{1/2} = \frac{0.693}{(1/\tau)} = 0.693 \tau$

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 or  $\tau = t_{1/2} / 0.693 = \frac{24 \text{ hr}}{0.693} = 35 \text{ hr}$

5. The mass of the atmosphere is roughly  $5.2 \times 10^{15}$  tonnes. Carbonyl sulfide (COS) is present as a trace gas at a concentration of 0.51 ppb<sub>v</sub> and its major source is from the oceans;  $6 \times 10^8$  kg yr<sup>-1</sup>. Estimate the total mass and the residence time of COS in the atmosphere.

**Answer**

The total mass of COS in the atmosphere can be estimated from the mixing ratio and the mass of atmosphere. To do this, we need to estimate the total number of moles of air in the atmosphere using the total mass and the average molecular mass of air ( $MW_{\text{air}} = 28.96$  g/mol), since the mixing ratio is defined as a ratio of number of mols of COS to number moles of air.

$$[\text{mass COS} \approx 5.5 \times 10^9 \text{ kg}]$$

$$\text{mass COS} = n_{\text{COS}}^{\text{total}} \times MW_{\text{COS}}$$

$$n_{\text{COS}}^{\text{total}} = \frac{0.51}{10^9} \times n_{\text{air}}^{\text{total}}$$

$$n_{\text{air}}^{\text{total}} = \frac{\text{mass atmosphere} \leftarrow 5.2 \times 10^{18} \text{ kg}}{MW_{\text{air}} \leftarrow 0.0289 \text{ kg mol}^{-1}}$$

$$\begin{aligned} \therefore \text{mass of COS} &= \frac{0.060 \text{ kg}}{\text{mol}} \times \frac{0.51}{10^9} \times \frac{5.2 \times 10^{18} \text{ kg}}{0.0289 \text{ kg mol}^{-1}} \\ &= 5.5 \times 10^9 \text{ kg} \end{aligned}$$

The residence time of COS in the atmosphere can be estimated using the stock from part a) in kg and the flux given flux in kg yr<sup>-1</sup>.

$$[\tau_{\text{COS}} \approx 9 \text{ yrs}]$$

$$\begin{aligned} \tau_{\text{COS}} &= \frac{\text{amt COS}}{\text{rate influx}} \\ &= \frac{5.5 \times 10^9 \text{ kg}}{6 \times 10^8 \text{ kg yr}^{-1}} \\ &= 9.1 \text{ yr} \\ &\approx 9 \text{ yr} \end{aligned}$$

6. The average North American car is driven 20,000 km per year and travels ~ 500 km on a 60 L tank.
- a) Assuming gasoline has a composition of  $C_8H_{18}$  and a density of 0.8 kg/L, estimate the mass of carbon dioxide produced by the average NA vehicle per year.
- b) Assuming no atmospheric losses, estimate the number of car – years required to increase the mass of  $CO_2$  in the Earth's atmosphere by 100 ppm<sub>v</sub>.

**Answers**

- a) mass of  $CO_2$  produced by avg NA car per yr

[5900 kg]

$$\text{mass of } CO_2 \text{ per car per yr} = n_{CO_2} \times MW_{CO_2}$$

$$n_{CO_2} = 8 n_{C_8H_{18}} \quad \text{since } C_8H_{18} + \frac{25}{2} O_2 \rightarrow 8 CO_2 + 9 H_2O$$

$$n_{C_8H_{18}} = \frac{\text{mass } C_8H_{18}}{MW_{C_8H_{18}}}$$

$$\text{mass } C_8H_{18} = \frac{20000 \text{ km}}{\text{car} \cdot \text{yr}} \times \frac{\text{tank}}{500 \text{ km}} \times \frac{60 \text{ L}}{\text{tank}} \times \frac{0.8 \text{ kg}}{\text{L}} = 1920 \frac{\text{kg}}{\text{car yr}}$$

$$\begin{aligned} \% \text{ mass } CO_2 &= \frac{1920 \text{ kg car}^{-1} \text{ yr}^{-1}}{0.114 \text{ kg mol}^{-1}} \times \frac{8 \text{ mols } CO_2}{1 \text{ mol } C_8H_{18}} \times \frac{0.044 \text{ kg}}{\text{mol } CO_2} \\ &= 5900 \text{ kg } CO_2 / \text{car yr} \end{aligned}$$

- b) car – years for 100 ppm<sub>v</sub> increase

[~ 100 billion car yrs]

mass of  $CO_2$  corresponding to 100 ppm<sub>v</sub> increase

$$= \frac{100}{10^6} \times n_{\text{air}}^{\text{total}} \times MW_{CO_2}$$

$$\text{where } n_{\text{air}}^{\text{total}} = \frac{5.2 \times 10^{18} \text{ kg}}{0.0291 \text{ kg mol}^{-1}} \quad (\text{from Q5})$$

$$\% \text{ mass of } CO_2 \text{ increase} = 7.9 \times 10^{14} \text{ kg } CO_2$$

$$\begin{aligned} \text{Therefore } \frac{7.9 \times 10^{14} \text{ kg } CO_2}{5900 \text{ kg } CO_2 / \text{car} \cdot \text{yr}} &= 1.3 \times 10^{11} \text{ car yrs} \\ &\approx 100 \text{ billion car yrs} \end{aligned}$$

7. Consider the typical altitude number density profile for ozone (attached).

a) Calculate the mixing ratio of  $O_3$  at ground level ( $z = 0$  km,  $P = 101,300$  Pa,  $T = 300$  K) and 25 km ( $P = 3500$  Pa,  $T = 220$  K). Why does the mixing ratio fall off more dramatically than the number density?

b) The stratospheric ozone layer is actually a fairly diffuse distribution of  $O_3$  that spans ~20 – 60 km in altitude, peaking at about 8 ppmv around 35 km above sea-level. The total number of  $O_3$  molecules in a column above a unit area of the Earth's surface is measured often measured and reported in Dobson units (DU, where 1 DU corresponds to a layer of  $O_3$  that would be 10  $\mu\text{m}$  thick at STP). Estimate the number of  $O_3$  molecules in a  $1\text{m}^2$  column if there are 200 DU of ozone. Would this be considered 'ozone hole' conditions?

### Answers

a) From the attached Figure, the following number densities for ozone are apparent;

$$n^*_{O_3}(z=0 \text{ km}) = 1 \times 10^{12} \text{ molec/cm}^3$$

$$n^*_{O_3}(z=25 \text{ km}) = 5 \times 10^{12} \text{ molec/cm}^3$$

$$[\chi_{O_3}(z=0 \text{ km}) = 40 \text{ ppbv}; \chi_{O_3}(z=25 \text{ km}) = 4.2 \text{ ppmv}]$$

$$z=0 \text{ km}, \chi_{O_3} = \frac{n^*_{O_3}}{n^*_{air}(P=1 \text{ atm}, T=300 \text{ K})}$$

$$n^*_{air} = \frac{P \cdot V \cdot N_A}{R \cdot T} = 2.45 \times 10^{19} \text{ molec/cm}^3$$

$$\therefore \chi_{O_3} = \frac{1.0 \times 10^{12}}{2.5 \times 10^{19}} = 4.0 \times 10^{-8} \text{ or } 40 \text{ ppbv}$$

$$z=25 \text{ km}, \chi_{O_3} = \frac{n^*_{O_3}}{n^*_{air}(P=0.035 \text{ atm}, T=220 \text{ K})} = \frac{5 \times 10^{12}}{1.2 \times 10^{18}}$$

$$= 4.2 \times 10^{-6} \text{ or } 4.2 \text{ ppmv}$$

The number densities represent an absolute expression of the ozone molecules present, whereas the mixing ratios are expressed as a fraction of ozone molecules relative to all other atmospheric gas molecules. Since there are considerably more atmospheric gas molecules at sea level than there are at  $z = 25$  km, the mixing ratio of ozone is much lower at sea level. Recall that the barometric law indicates that the pressure (and hence the number of gas molecules) drops exponentially with altitude.  $P_z = P_0 e^{-\{z/H\}}$

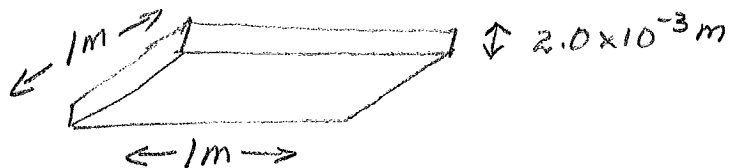
b) We can estimate the number of  $O_3$  molecules in a vertical column of air using the ideal gas law. Since 200 DU is equivalent to the number of ozone molecules in a volume of air that is  $1\text{ m}^2 \times 200 \times 10 \mu\text{m}$  of pure ozone at STP.

$$V = 1\text{ m} \times 1\text{ m} \times 200 (10 \times 10^{-6}\text{ m}) = 2.0 \times 10^{-3}\text{ m}^3$$

$$P = 101,300\text{ Pa}$$

$$T = 273\text{ K}$$

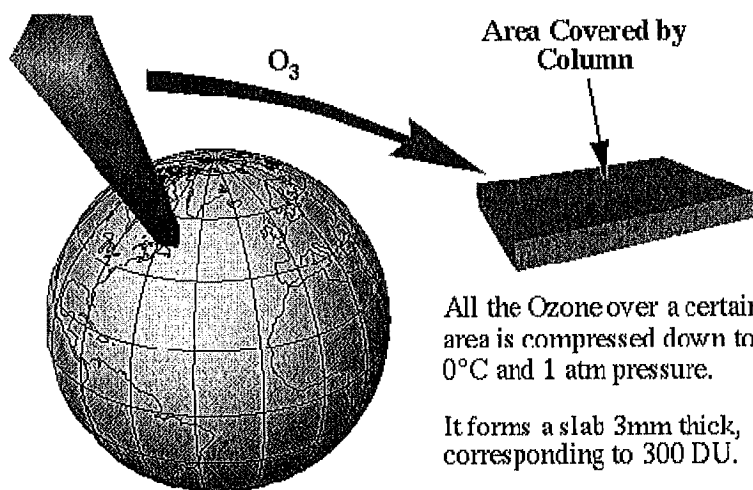
$$R = 8.314\text{ J mol}^{-1}\text{ K}^{-1}$$



$$n_{O_3} = \frac{PV}{RT} = \frac{(101,300\text{ Pa})(2.0 \times 10^{-3}\text{ m}^3)}{(8.314 \frac{\text{J}}{\text{mol K}})(273\text{ K})} = 0.08926\text{ mols}$$

$$\# \text{ molecules} = n_{O_3} \cdot N_A = 5.4 \times 10^{22}\text{ molecules}$$

Typical values for the ozone column observed in Earth's atmosphere are 280 – 300 DUs. Therefore, 200 Dobson units of ozone represents a significant thinning of the ozone layer consistent with ozone hole conditions.

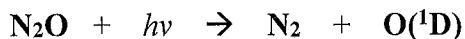


All the Ozone over a certain area is compressed down to  $0^\circ\text{C}$  and 1 atm pressure.

It forms a slab 3mm thick, corresponding to 300 DU.



8. Using the enthalpy of formation data given in Appendix B2 of your textbook, calculate the maximum wavelength of electromagnetic radiation which would have sufficient energy to effect the dissociation of nitrous oxide. In what regions of the atmosphere would such radiation be available?



### Answers

We approach this problem by first calculating the enthalpy change for the reaction using the enthalpies of formation for the products and reactants. This energy represents the minimum required energy to break the N-O bond in  $\text{NO}_2$  and hence the minimum photon energy necessary to carry out the reaction. The energy inherent in an individual photon is given by,  $E_{\text{photon}} = h c/\lambda$  or in one mole of photons as  $N_A h c/\lambda$ , where  $h$  is Planck's constant,  $c$  is the speed of light and  $N_A$  is Avogadro's number.

$$[\lambda = 391 \text{ nm}]$$

$$\begin{aligned} \Delta H_{\text{rxn}}^{\circ} &= \Delta H_f^{\circ}(\text{NO}) + \Delta H_f^{\circ}(\text{O}) - \Delta H_f^{\circ}(\text{NO}_2) \\ &= (90.3 + 249.2 - 33.2) \text{ kJ mol}^{-1} \\ &= 306.3 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \lambda &= \frac{N_A \cdot h \cdot c}{\Delta H_{\text{rxn}}^{\circ}} = \frac{(6.02 \times 10^{23} \text{ mol}^{-1})(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.0 \times 10^8 \text{ m s}^{-1})}{306,300 \text{ J mol}^{-1}} \\ &= 3.91 \times 10^{-7} \text{ m} \\ &\text{or } 391 \text{ nm} \end{aligned}$$

This wavelength of light is in the UV-a region of the electromagnetic spectrum and is prevalent throughout the stratosphere and troposphere.