

## CHEM 302 Assignment #4

*Answers the following questions and submit solutions to even numbered questions ONLY in a neat and well organized manner, including dimensional analysis, where appropriate. Reference data and information sources.*

Due: Tuesday, December 5<sup>th</sup>, 2017

1. Calculate the thickness of the Earth's atmosphere that contains 99% of the air molecules. If a model of the Earth were the size of a basketball (diameter = 24 cm), how thick would the atmosphere be?

$$n_z = n_0 e^{-\left\{z: \frac{gM}{RT}\right\}}$$

calculate  $z$  at  $\frac{n_z}{n_0} = 0.01$

$$0.01 = e^{-z \frac{(9.8 \frac{m}{s^2})(28.96 \times 10^{-3} \frac{kg}{mol})}{(8.314 \frac{J}{mol \cdot K})(273 K)}}$$

$$\ln(0.01) = -z (1.25 \times 10^{-4} m^{-1})$$

$$\therefore z = \frac{-4.61}{-1.25 \times 10^{-4} m^{-1}}$$

$$= 3.68 \times 10^4 m$$

$$\text{or } \boxed{36.8 \text{ km}}$$

scaling

$$\text{radius of Earth} = 6378 \text{ km}$$

$$\therefore \text{diameter} = 12,756 \text{ km} \quad \longrightarrow \quad 24 \text{ cm}$$

$$\therefore \text{scaling factor} = \frac{24 \times 10^{-2} m}{12,756 \times 10^3 m} = 1.9 \times 10^{-8}$$

$$\text{So } 36.8 \text{ km} \times 1.9 \times 10^{-8}$$

$$= 6.9 \times 10^{-7} \text{ km} \quad \text{or } 6.9 \times 10^{-2} \text{ cm}$$

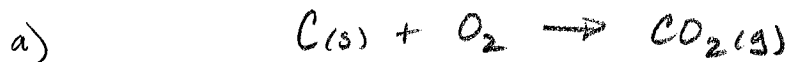
$$\boxed{0.7 \text{ mm}}$$

2. A coal-burning power station burns 8,500 tonnes of coal per day.

a) Calculate the sulfur content of coal if the flue gas contains 1700 ppm<sub>v</sub> of SO<sub>2</sub>.

b) What mass of lime is needed per day to react with this sulfur dioxide?

c) What mass of CaSO<sub>4</sub> is produced per year during this process?



$$8,500 \times 10^6 \text{ g coal} \times \frac{1 \text{ mol}}{12.01 \text{ g}} = 7.08 \times 10^8 \text{ mol } C = 7.08 \times 10^8 \text{ mol } O_2 \text{ consumed}$$

$$\therefore \# \text{ mol } N_2 = 7.08 \times 10^8 \text{ mol } O_2 \times \frac{78.01}{20.95} = 2.64 \times 10^9 \text{ mol } N_2 \text{ produced}$$

Stack flue gases contain

$$\begin{array}{r} 7.08 \times 10^8 \text{ mol } CO_2 \\ + 2.64 \times 10^9 \text{ mol } N_2 \\ \hline n_T = 3.35 \times 10^9 \text{ mol flue gas} \end{array}$$

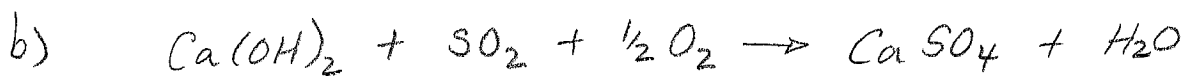
$$n_{SO_2} = \frac{1700}{10^6} \cdot n_T = 5.69 \times 10^6 \text{ mol } SO_2$$

$$= 5.69 \times 10^6 \text{ mol } S \text{ present in coal}$$

$$\therefore \text{mass \% of sulfur in coal} = \frac{n_S \cdot MW_S}{\text{mass coal}} \times 100\%$$

$$= \frac{5.69 \times 10^6 \text{ mol} (32 \text{ g/mol})}{8500 \times 10^6 \text{ g}} \times 100\%$$

$$= 2.14\% \text{ S (by mass)}$$



$$\text{mass of lime} = n_{\text{Ca(OH)}_2} \cdot \text{MW}_{\text{Ca(OH)}_2}$$

$$= n_{\text{SO}_2} \times \frac{1 \text{ mol Ca(OH)}_2}{1 \text{ mol SO}_2}$$

$$= (5.69 \times 10^6 \text{ mol}) (74.0 \text{ g/mol})$$

$$= 4.21 \times 10^8 \text{ g Ca(OH)}_2$$

$$= 4.21 \times 10^2 \text{ tonnes Ca(OH)}_2 \text{ per day.}$$

c)  $\text{mass calcium sulfate} = n_{\text{CaSO}_4} \cdot \text{MW}_{\text{CaSO}_4}$

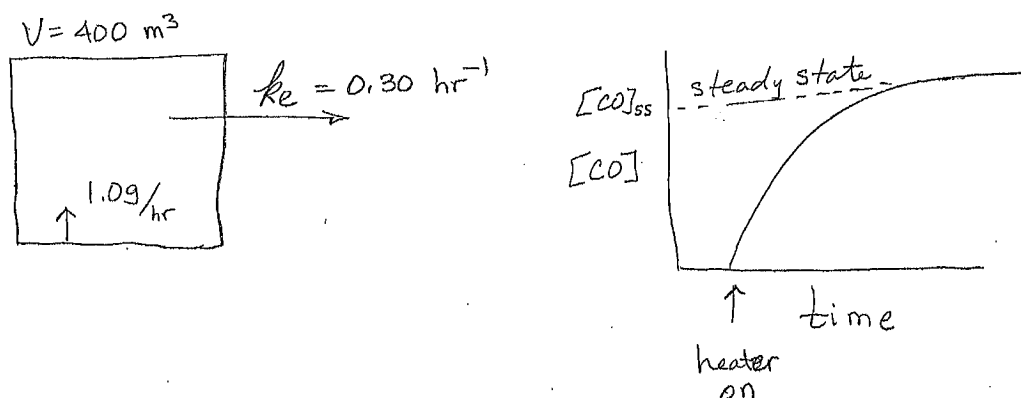
$$= (5.69 \times 10^6 \text{ mol}) (136 \text{ g/mol})$$

$$= 7.74 \times 10^8 \text{ g CaSO}_4$$

$$= 7.74 \times 10^2 \text{ tonnes CaSO}_4 \text{ per day.}$$

3. A one compartment home of  $400 \text{ m}^3$  has a ventilation rate of 0.30 air changes per hour with its doors and windows closed. Carbon monoxide is produced from a kerosene heater at a rate 1 g per hour. How long will it take before the indoor concentration exceeds the toxic action threshold level of  $1.00 \text{ ppm}_v$ ? When the outside concentration of a pollutant is negligible, it can be shown that;

$$\ln\left(1 - \frac{[X]_t}{[X]_{ss}}\right) = -k_e t$$



At steady state,  
rate in = rate out

$$\frac{1.0 \text{ g}}{\text{hr}} = k_e [\text{CO}]_{ss}$$

$$\therefore [\text{CO}]_{ss} = \frac{1.0 \text{ g}}{\text{hr}} \div 0.30 \text{ hr}^{-1} = 3.3 \text{ g in } 400 \text{ m}^3$$

$$\therefore [\text{CO}]_{ss} = \frac{3.3 \text{ g}}{400 \text{ m}^3} = 8.3 \frac{\text{mg}}{\text{m}^3}$$

converting to  $\text{ppm}_v$

$$8.3 \text{ mg CO} \times \frac{1 \text{ mol}}{28.0 \text{ g}} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 2.96 \times 10^{-4} \text{ mols CO}$$

$$1 \text{ m}^3 \times \frac{1 \text{ mol}}{22.4 \text{ L}} \times \frac{10^3 \text{ L}}{1 \text{ m}^3} = 44.6 \text{ mols air at STP}$$

$$[\text{CO}]_{ss} = \frac{2.96 \times 10^{-4} \text{ mols CO}}{44.6 \text{ mols air}} \times 10^6 = 6.63 \text{ ppmv}$$

Therefore, time required to reach 1.00 ppmv  
is given by

$$\ln \left( 1 - \frac{[\text{CO}]_t}{[\text{CO}]_{ss}} \right) = -k_e t$$

$$\ln \left( 1 - \frac{1.00}{6.63} \right) = -0.30 \text{ hr}^{-1} (t)$$

$$\begin{aligned} \text{and } t &= \frac{\ln \left( 1 - \frac{1.00}{6.63} \right)}{-0.30 \text{ hr}^{-1}} \\ &= \frac{-0.163}{-0.30 \text{ hr}^{-1}} = 0.55 \text{ hr} \end{aligned}$$

$$\text{or } \boxed{33 \text{ mins}}$$

4. The planet Venus has a surface temperature of about 460°C and a surface pressure of 92 atmospheres. The mixing ratios for CO<sub>2</sub> and N<sub>2</sub> are 96.5% and about 3.5%, respectively.

(i) Calculate the density of surface 'air' on Venus.

(ii) The mixing ratio of SO<sub>2</sub> on Venus is 150 ppm<sub>v</sub>. Determine the number density and the partial pressure for this gas on the surface.

$$\rho_{\text{air}}^{\text{Venus}} = \frac{\text{mass}}{\text{Volume}} \quad \begin{array}{l} \text{mass of 1 mol of Venus air} \\ \text{vol. of 1 mol of Venus air} \\ \text{at } T = 733\text{K}, P = 92\text{atm} \end{array}$$

$$\begin{aligned} \text{1 mol air mass} &= \chi_{\text{N}_2} = \frac{3.5}{100} & \therefore \text{mass} \left( \frac{3.5}{100} \right) \left( 28.02 \frac{\text{g}}{\text{mol}} \right) \\ & \chi_{\text{CO}_2} = \frac{96.5}{100} & + \left( \frac{96.5}{100} \right) \left( 44.0 \frac{\text{g}}{\text{mol}} \right) \\ & & \overline{MW}_{\text{air}} = 43.44 \frac{\text{g}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \text{1 mol air volume} &= \frac{V}{n} = \frac{RT}{P} = \frac{(0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})(733\text{K})}{(92.\text{atm})} \\ &= 0.654 \text{ L/mol} \end{aligned}$$

$$\begin{aligned} \therefore \rho_{\text{air}}^{\text{Venus}} &= \frac{43.44 \text{ g/mol}}{0.654 \text{ L/mol}} = 66.4 \frac{\text{g}}{\text{L}} \\ &\text{or } 66.4 \text{ kg/m}^3 \end{aligned}$$

For comparison  $\rho_{\text{air}}(\text{Earth at STP}) = 1.29 \text{ kg/m}^3$

$$X_{\text{SO}_2} = 150 \text{ ppmv.}$$

$$n_{\text{SO}_2}^* = X_{\text{SO}_2} n_T^*$$

$$n_T^* = \frac{P \cdot V}{R \cdot T} \times N_A$$

$$= \frac{(92 \text{ atm})(1.00 \times 10^{-3} \text{ L})}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(733 \text{ K})} \times 6.023 \times 10^{23} \frac{1}{\text{mol}}$$

$$= 9.21 \times 10^{20} \frac{\text{molec}}{\text{cm}^3}$$

$$n_{\text{SO}_2}^* = \left(\frac{150}{10^6}\right) \left(9.21 \times 10^{20} \frac{\text{molec}}{\text{cm}^3}\right) = \boxed{1.38 \times 10^{17} \frac{\text{molec}}{\text{cm}^3}}$$

$$P_{\text{SO}_2} = X_{\text{SO}_2} P_T$$

$$= \left(\frac{150}{10^6}\right) 92 \text{ atm} = \boxed{1.38 \times 10^{-2} \text{ atm}}$$

5. Given that the gasoline is about 85% by mass carbon and has a density of about 0.75 kg/L, estimate the adjusted 'life cycle' cost that would need to be added to a liter of gasoline that would offset the cost associated with carbon capture and sequestration (CCS) at \$200/tonne of CO<sub>2</sub>.

$$1 \text{ L gasoline} \times \frac{0.75 \text{ kg}}{\text{L}} \times \frac{0.85 \text{ g C}}{\text{g gas}}$$

$$= \frac{0.64 \text{ kg C}}{1 \text{ L gas}}$$

∴ 0.64 kg C is released as CO<sub>2</sub>

$$\text{and mass CO}_2 = 0.64 \text{ kg} \times \frac{44.0}{12.0}$$

$$= 2.3 \text{ kg CO}_2$$

Cost to sequester @ \$200 / tonne CO<sub>2</sub>

$$\frac{200 \text{ \$}}{1000 \text{ kg CO}_2} \times \frac{2.3 \text{ kg CO}_2}{1 \text{ L}} = \frac{0.46 \text{ \$}}{\text{L}}$$

At \$200/tonne, the life cycle cost adjustment is 46 cents per litre.



6. It has recently been suggested that nitrogen trifluoride (a solvent used in the manufacture of new LCD monitors) has the potential to be a significant 'greenhouse' gas<sup>1</sup>. What is meant by the term 'Global Warming Potential' and what information would you need in order to estimate the global warming potential of NF<sub>3</sub>? What additional information is relevant to determine if this gas actually makes a significant contribution to global warming?

The GWP is a measure of the radiative forcing of a compound integrated over a given time horizon relative to that of one kilogram of CO<sub>2</sub>.

$$GWP = \frac{\int_{t_0}^{t_1} a_x [X(t)] dt}{\int_{t_0}^{t_1} a_{CO_2} [CO_2(t)] dt}$$

where  $a_x$  depends on the molecules intrinsic ability to absorb IR radiation (absorptivity) and the wavelengths of absorption relative to IR windows.

$[X(t)]$  term depends on the atmospheric residence time

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<sup>1</sup> For more information of this issue see M.J. Prather and J. Hsu, *NF<sub>3</sub>, the greenhouse gas missing from Kyoto*, *Geophysical Res. Letters*, 35, L12810, 2008 and Velders et al., *The large contribution of projected HFC emissions to future climate forcing*, *Proceedings of the National Academy of Science*, 106, 10949, 2009.

Therefore, in order to estimate the GWP for  $\text{NF}_3$  one would need to measure the IR absorption spectra for a known amount of  $\text{NF}_3$  (yields  $\lambda$  of absorption as well as absorptivity) and the atmospheric residence time (perhaps by measuring gas phase rate constants;  $\tau = \frac{1}{\Sigma k}$ ).

To determine the actual contribution to radiative forcing in Earth's atmosphere one needs to consider the actual atmospheric concentration.

7. Information about the average chemical composition and energy content of the three major fossil fuels and global consumption rates are summarized below.<sup>2</sup>

	Average composition	Percent combustible of total	Worldwide consumption in 1980 (x 10 <sup>18</sup> J/yr)	Energy content
Petroleum	CH <sub>1.5</sub>	98% (w/w)	135	43 x 10 <sup>6</sup> J/kg
Natural Gas	CH <sub>3.6</sub>	88% (v/v)	60	3.9 x 10 <sup>7</sup> J/m <sup>3</sup> (STP)
Coal	CH <sub>0.8</sub>	75% (w/w)	90	29.3 x 10 <sup>6</sup> J/kg

- a) What mass of CO<sub>2</sub> was released to the atmosphere in 1980 from fossil-fuel burning?  
 b) Rank these fossil fuels based on the mass of CO<sub>2</sub> released per Joule of energy produced.

$$\begin{aligned} \text{a) petroleum consumption in 1980} &= 135 \times 10^{18} \frac{\text{J}}{\text{yr}} \times \frac{1 \text{ kg}}{43 \times 10^6 \text{ J}} \\ &= 3.14 \times 10^{12} \text{ kg/yr} \end{aligned}$$

$$\begin{aligned} \text{CO}_2 \text{ released from petroleum in 1980} &= 3.14 \times 10^{12} \frac{\text{kg}}{\text{yr}} \times \left(\frac{98}{100}\right) \times \frac{12.0}{13.5} \times \frac{44.01}{12.0} \\ &= 1.00 \times 10^{13} \text{ kg CO}_2 \end{aligned}$$

$$\begin{aligned} \text{similarly for coal} &= 7.92 \times 10^{12} \text{ kg CO}_2 \end{aligned}$$

<sup>2</sup> Adapted from **Consider a Spherical Cow: A Course in Environmental Problem Solving**, John Harte, University Science Books, Mill Valley, CA, 1988.

b) petroleum

$$\frac{1.00 \times 10^{13} \text{ kg CO}_2/\text{yr}}{135 \times 10^{18} \text{ J/yr}}$$
$$= 7.4 \times 10^{-8} \text{ kg CO}_2/\text{J}$$

or  $0.074 \text{ g CO}_2/\text{kJ}$

coal

$$\frac{7.92 \times 10^{12} \text{ kg CO}_2/\text{yr}}{90 \times 10^{18} \text{ J/yr}}$$
$$= 8.8 \times 10^{-8} \text{ kg CO}_2/\text{J}$$

or  $0.088 \text{ g CO}_2/\text{kJ}$

natural gas

$$\frac{2.66 \times 10^{12} \text{ kg CO}_2/\text{yr}}{60 \times 10^{18} \text{ J/yr}}$$
$$= 4.4 \times 10^{-8} \text{ kg CO}_2/\text{J}$$

or  $0.044 \text{ g CO}_2/\text{kJ}$

	mass CO <sub>2</sub> emitted g/kJ	relative mass CO <sub>2</sub> / Joule
natural gas	0.044	1.0
petroleum	0.074	1.7
coal	0.088	2.0

for natural gas ;

$$\text{annual consumption} = 60 \times 10^{18} \frac{\text{J}}{\text{yr}} \times \frac{1 \text{ m}^3}{3.9 \times 10^7 \text{ J}} = 1.54 \times 10^{12} \frac{\text{m}^3}{\text{yr}}$$

$$\begin{aligned} \# \text{mols CH}_4 \text{ consumed} &= 1.54 \times 10^{12} \frac{\text{m}^3}{\text{yr}} \times \left( \frac{88}{100} \right) \times \left\{ \frac{101,300 \text{ Pa}}{\left( \frac{8.314 \text{ J}}{\text{mol K}} \right) (273 \text{ K})} \right\} \\ &= 6.04 \times 10^{13} \frac{\text{mols}}{\text{yr}} \end{aligned}$$

$$\begin{aligned} \text{mass CO}_2 \text{ released} &= 6.04 \times 10^{13} \frac{\text{mols}}{\text{yr}} \times 44.01 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \\ &= 2.66 \times 10^{12} \text{ kg CO}_2 \end{aligned}$$

∴ total mass of CO<sub>2</sub> released in 1980 from these three sources

$$\begin{array}{cccc} (10.0 + 7.92 + 2.66) \times 10^{12} \text{ kg} \\ \uparrow \quad \quad \uparrow \quad \quad \uparrow \\ \text{petroleum} \quad \text{coal} \quad \quad \text{natural gas} \end{array}$$

$$\boxed{20.6 \times 10^{12} \text{ kg CO}_2}$$

8. How much would the Earth's atmospheric temperature change for 1.5% increase from their current value in each of the following:

- i) 'greenhouse effect',  $\Delta E$
- ii) solar irradiance constant
- iii) Earth's *albedo*

$$\sigma T^4 = \frac{(1-A)\mathcal{S}_0}{4} + \Delta E$$

use  $\mathcal{S}_0 = 1372 \frac{\text{W}}{\text{m}^2}$  for solar flux

$T = 288 \text{ K}$  for average Earth temp.

$A = 0.30$  for albedo

$\sigma = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}$  for Stephan-Boltzmann

Calculate  $\Delta E = \sigma T^4 - \frac{(1-A)\mathcal{S}_0}{4}$

$$= \left(5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}\right) (288 \text{ K})^4 - \frac{(1-0.30)(1372 \frac{\text{W}}{\text{m}^2})}{4}$$
$$= 390.08 \frac{\text{W}}{\text{m}^2} - 240.10 \frac{\text{W}}{\text{m}^2}$$
$$= 149.98 \frac{\text{W}}{\text{m}^2}$$

i)  $\Delta E$  increases by 1.5%

$$\Delta E' = 152.23 \frac{\text{W}}{\text{m}^2}$$

$$\therefore T = \left[ \frac{(1-A)\bar{\rho}_s}{4} + \Delta E' \right]^{\frac{1}{4}} \sigma$$

$$= 288.41 \text{ K}$$

$$\therefore \Delta T = 0.41 \text{ K}$$

ii)  $\bar{\rho}_s$  increases by 1.5%

$$\bar{\rho}_s' = 1392.58 \frac{\text{W}}{\text{m}^2}$$

$$\therefore T = \left[ \frac{(1-A)\bar{\rho}_s}{4} + \Delta E \right]^{\frac{1}{4}} \sigma$$

$$= 288.66 \text{ K}$$

$$\therefore \Delta T = 0.66 \text{ K}$$

iii)  $A$  increases by 1.5%

$$A' = 0.3045$$

$$\therefore T = 287.71$$

$$\Delta T = -0.29 \text{ K}$$