

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: Thursday, December 3rd, 2015

1. Use Plank's law to plot blackbody radiation spectra between wavelengths of 0.1 and 100 μm for $T = 300\text{K}$ and 6000K using Excel. *Hint; use about 350 rows for the wavelengths in column A incrementing them by a factor of 1.02 for each row. Display plot on a log-log scale.*

see attached Excel file

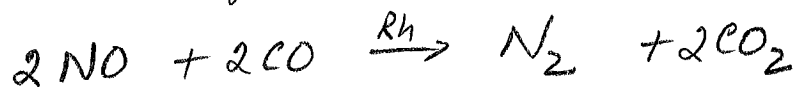
2. Describe how catalytic converters on automobiles act in a dual role in catalyzing both reduction and oxidation reactions. (Use chemical equations to illustrate your answer).

Emission control on automobiles utilize catalytic converters to reduce the amount of NO, CO, VOC's in the exhaust gases.

Two catalysts are used in series. The first is used to remove/reduce Nitric oxide (NO) and typically involves rhodium catalyst mounted on a high surface area support



is chemically reduced to N₂. The reducing agent can be CO, H₂ or VOC's present in exhaust gases. For example,



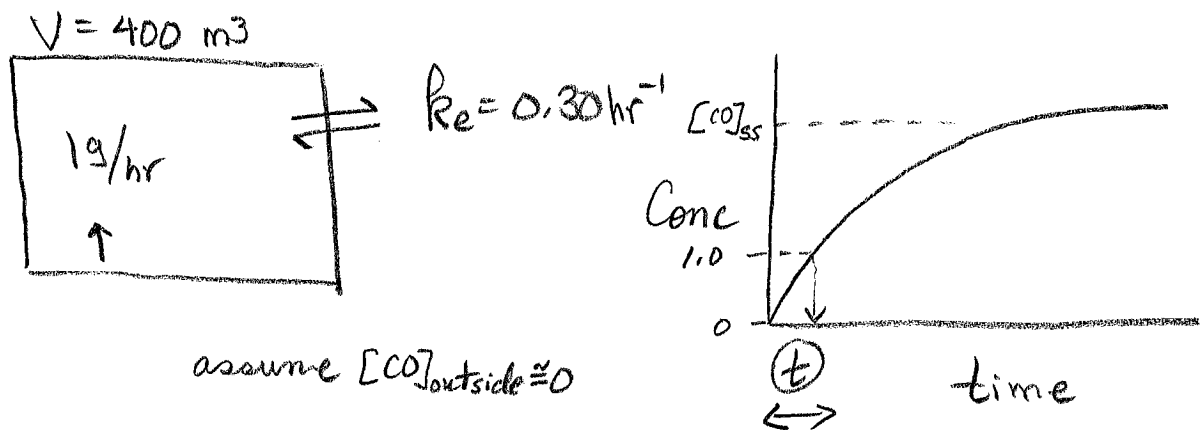
The second catalyst is used to oxidize remaining CO, VOC's, H₂ or NH₃ and typically involves platinum or palladium.



see further pg 93-94 (textbook)

3. A one compartment home of 400 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/hr . How long will it take before the indoor concentration exceeds the toxic action threshold level of 1.00 ppm_v ? When the outside concentration of a pollutant is negligible, it can be shown that;

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



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

where $[\text{CO}]_t = 1.00 \text{ ppm}$, $k_e = 0.30 \text{ hr}^{-1}$
and $[\text{CO}]_{ss}$ can be solved using
steady-state condition that
rate in = rate out

at steady state,

$$\begin{aligned} \text{rate in} &= \text{rate out} \\ \uparrow \\ \frac{1 \text{ g/hr}}{\text{in } 400 \text{ m}^3} &= k_c [\text{CO}]_{ss} \end{aligned}$$

Since we are given a threshold conc in ppmv we should convert $\frac{1 \text{ g/hr}}{400 \text{ m}^3}$ into ppm/hr

$$\frac{1 \text{ g}}{400 \text{ m}^3} \times \frac{1 \text{ mol}}{28 \text{ g}} \times \frac{(8.314 \text{ J/mol K})(298 \text{ K})}{(101,300 \text{ Pa})} = 2.18 \times 10^{-6} \text{ or } 2.18 \text{ ppmv}$$

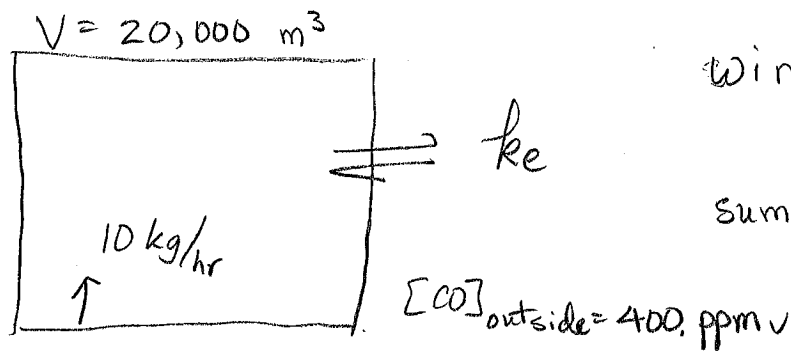
$$\therefore \text{rate in} = 2.18 \text{ ppmv/hr} = 0.30 \text{ hr}^{-1} [\text{CO}]_{ss}$$

$$\therefore [\text{CO}]_{ss} = \frac{2.18 \text{ ppmv/hr}}{0.30 \text{ hr}^{-1}} = 7.3 \text{ ppmv}$$

Therefore, time to reach $[\text{CO}] = 1.00 \text{ ppmv}$ is given by,

$$\frac{\ln\left(1 - \frac{1.00}{7.3}\right)}{-0.30 \text{ hr}^{-1}} = \frac{-0.15}{-0.30 \text{ hr}} = 0.50 \text{ hr (30 mins)}$$

4. Calculate the steady state concentrations of carbon dioxide inside an office building in summer and winter conditions with air changes per hour ranging from 5.0 to 0.1 ach. Building volume = $20,000 \text{ m}^3$, Rate of internal CO_2 emission = 10 kg hr^{-1} . Assume the outdoor CO_2 concentration is 400 ppm_v .



winter $\Rightarrow k_e = 0.1 \text{ hr}^{-1}$

summer $\Rightarrow k_e = 5.0 \text{ hr}^{-1}$

at steady state, rate in = rate out

where, rate in = $k_e [CO_2]_{\text{outside}} + R_{\text{emission}}$

and rate out = $k_e [CO_2]_{\text{inside}}$

Since our concentration of $[CO_2]_{\text{outside}}$ is given in ppm_v , we should convert emission rate from $\text{kg/hr} \rightarrow \text{ppm}_v/\text{hr}$

$$\frac{10 \text{ kg } CO_2}{20,000 \text{ m}^3} \times \frac{1 \text{ mol } CO_2}{0.044 \text{ kg}} \times \frac{(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298\text{K})}{(101,300 \text{ Pa})}$$

$$= 2.8 \times 10^{-4} \quad \text{or } 280 \text{ ppm}_v$$

$$\text{So Remission} = 280 \text{ ppmv/hr}$$

We can now calculate the indoor concentrations in both summer and winter time conditions.

Summer ($k_e = 5.0 \text{ hr}^{-1}$)

$$5.0 \text{ hr}^{-1} (400. \text{ ppmv}) + \frac{280 \text{ ppmv}}{\text{hr}} = 5.0 \text{ hr}^{-1} [\text{CO}_2]_{\text{inside}}$$

$$\begin{aligned} \therefore [\text{CO}_2]_{\text{inside}} &= \frac{(5.0 \text{ hr}^{-1})(400. \text{ ppmv}) + 280. \frac{\text{ppmv}}{\text{hr}}}{5.0 \text{ hr}^{-1}} \\ &= 460 \text{ ppmv of CO}_2 \end{aligned}$$

Winter ($k_e = 0.1 \text{ hr}^{-1}$)

$$\begin{aligned} \therefore [\text{CO}_2]_{\text{inside}} &= \frac{(0.1 \text{ hr}^{-1})(400. \text{ ppmv}) + 280 \text{ ppmv/hr}}{0.1 \text{ hr}^{-1}} \\ &= 3000 \text{ ppmv of CO}_2 \end{aligned}$$

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 CO₂.

$$1 \text{ L gasoline} \times \frac{0.75 \text{ kg}}{\text{L}} \times \frac{0.85 \text{ g C}}{\text{g gasoline}} = \frac{0.64 \text{ kg C}}{\text{L gasoline}}$$

∴ 0.64 kg of C is released as CO₂ per litre of gasoline

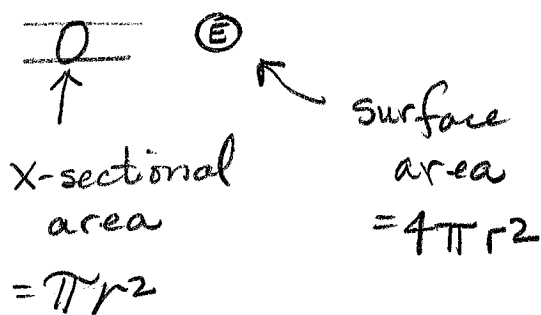
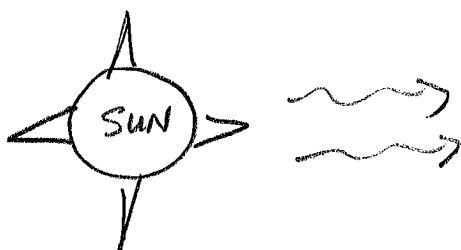
$$\text{mass of CO}_2 = 0.64 \frac{\text{kg}}{\text{L}} \times \frac{44.0 \text{ g/mol CO}_2}{12.0 \text{ g/mol C}} = 2.3 \text{ kg CO}_2$$

cost of sequester CO₂ priced at \$200 /tonne CO₂

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

6. The explosions and fires from a major nuclear war would result in so much soot and particulate aerosols, that the Earth's *albedo* is predicted to increase by 20%. Calculate the resulting average annual Earth temperature that would result.

radiative balance requires energy in = energy out



where r = radius

If we take current Albedo to be 0.31 (textbook) the 20% increase would result in this value increase to 0.37

where the total solar energy absorbed by earth is given by $E_s = \Omega (1-A) \pi r^2$ where $\Omega = 1368 \text{ W/m}^2$
 \uparrow
 average solar flux

and total energy emitted from blackbody Earth is given by $E_e = 4\pi r^2 \sigma T_e^4$ where $\sigma = 5.67 \times 10^{-8} \frac{W}{m^2 K^4}$

At steady state (i.e. radiative balance)

$$\Omega(1-A)\pi r^2 = 4\pi r^2 \sigma T_e^4$$

rearranging and solving for T_e yields,

$$T_e = \left(\frac{(1-A)\Omega}{4\sigma} \right)^{1/4}$$

at $A = 0.36$ we calculate an average Earth temperature of,

$$T_e = \left[\frac{(1-0.37) 1368 \frac{W}{m^2}}{4 (5.67 \times 10^{-8} \frac{W}{m^2 K^4})} \right]^{1/4} = 248 K$$

or $-25^\circ C$

see further pg 176-179 (textbook)

7. Information about the average chemical composition and energy content of the three major fossil fuels and global consumption rates are summarized below.¹

	Average composition	Percent combustible of total	Worldwide consumption 1980 ($\times 10^{18}$ J/yr)	Energy content
Petroleum	CH _{1.5}	98% (w/w)	135	43×10^6 J/kg
Natural Gas	CH _{3.6}	88% (v/v)	60	3.9×10^7 J/m ³ (STP)
Coal	CH _{0.8}	75% (w/w)	90	29.3×10^6 J/kg

- a) What mass of CO₂ was released to the atmosphere in 1980 from fossil-fuel burning?
 b) Rank these fossil fuels based on the mass of CO₂ released per Joule of energy produced.

a) petroleum consumption in 1980

$$135 \times 10^{18} \frac{\text{J}}{\text{yr}} \times \frac{1 \text{ kg}}{43 \times 10^6 \text{ J}} = 3.14 \times 10^{12} \frac{\text{kg}}{\text{yr}}$$

CO₂ released from petroleum in 1980

from % combustible

$$3.14 \times 10^{12} \frac{\text{kg}}{\text{yr}} \times \left(\frac{98}{100}\right) \times \left(\frac{12.0}{13.5}\right) \times \frac{44.0 \text{ g/mol CO}_2}{12.0 \text{ g/mol C}}$$

from empirical formula $\left(\frac{\text{mass C}}{\text{mass CH}_{1.5}}\right)$

$$= 1.00 \times 10^{13} \text{ kg CO}_2$$

similarly for coal

$$90 \times 10^{18} \frac{\text{J}}{\text{yr}} \times \frac{1 \text{ kg}}{29.3 \times 10^6 \text{ J}} = 3.07 \times 10^{12} \frac{\text{kg}}{\text{yr}}$$

$$3.07 \times 10^{12} \frac{\text{kg}}{\text{yr}} \times \left(\frac{75}{100}\right) \times \frac{12.0}{12.8} \times \frac{44.0 \text{ g/mol CO}_2}{12.0 \text{ g/mol C}}$$

$$= 7.92 \times 10^{12} \text{ kg CO}_2$$

¹ Adapted from **Consider a Spherical Cow: A Course in Environmental Problem Solving**, John Harte, University Science Books, Mill Valley, CA, 1988.

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

for natural gas ;

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

$$\begin{aligned} \# \text{ mols CH}_3.6 \text{ consumed} &= 1.54 \times 10^{12} \frac{\text{m}^3}{\text{yr}} \times \left(\frac{88}{100} \right) \times \left\{ \frac{101,300 \text{ Pa}}{\left(\frac{8.314 \text{ J}}{\text{mol K}} \right) (273 \text{ K})} \right\} \\ &= 6.04 \times 10^{13} \frac{\text{mols}}{\text{yr}} \end{aligned}$$

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

∴ total mass of CO₂ released in 1980 from these three sources

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

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

b) petroleum

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

$$= 7.4 \times 10^{-8} \text{ kg CO}_2/\text{J}$$

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

coal

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

$$= 8.8 \times 10^{-8} \text{ kg CO}_2/\text{J}$$

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

natural gas

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

$$= 4.4 \times 10^{-8} \text{ kg CO}_2/\text{J}$$

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

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

8. What is meant by the term 'Global Warming Potential' and why is it high for nitrous oxide and relatively low for nitric oxide and nitrogen dioxide?

The global warming potential (GWP) is a measure of radiative forcing of a substance integrated over a specified time horizon relative to that for 1 kg of CO_2 .

$$\text{GWP} = \frac{\int_{t_0}^{t_1} \alpha_x [X(t)] dt}{\int_{t_0}^{t_1} \alpha_{\text{CO}_2} [\text{CO}_2(t)] dt}$$

where α_x depends on;

- 1) absorptivity of substance in the IR region
- 2) wavelength of absorption relative to IR windows

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

N_2O , NO and NO_2 all have absorptions in the IR region however they have vastly different atmospheric residence times.

$$\tau_{N_2O} \approx 120-150 \text{ yrs} \approx 10^6 \text{ hrs}$$

$$\tau_{NO} \approx 12-48 \text{ hrs}$$

$$\tau_{NO_2} \approx 12-48 \text{ hrs}$$

Since the residence time for N_2O is $\sim 10^5 \times$ greater than either NO or NO_2 its global warming potential is significantly larger.

$$GWP(N_2O) \gg GWP(NO) \approx GWP(NO_2)$$