CHEM 302
Assignment #2

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, October 12th, 2017

1. Use the barometric pressure equation below to calculate the pressure and number density in the upper stratosphere at 35 km altitude. Why is the relative abundance of atomic oxygen greater in the upper stratosphere relative to the lower stratosphere? What impact does this have on the residence time of O_3 in the upper stratosphere?

$$P_h = P^o e^{-\left(\frac{M_{air}gh}{RT}\right)}$$

where $\bar{M}_{air} = 0.02896 \ kg \ mol^{-1}$
$g = 9.81 \ m \ s^{-2}$
$h = 35{,}000 \ m$
$R = 8.314 \ J \ mol^{-1} K^{-1}$
$T = 240 \ K \ (Fig \ 2.1)$ $\left.\right\}$ in S.I. units

$\therefore \dfrac{\bar{M}_{air} \cdot g \cdot h}{RT} = \dfrac{(0.02896)(9.81)(35{,}000)}{(8.314)(240)} \left[\dfrac{\frac{kg}{mol}\frac{m}{s^2} \ m}{\frac{J}{mol \ K} \cdot K}\right]$

$= 4.98$
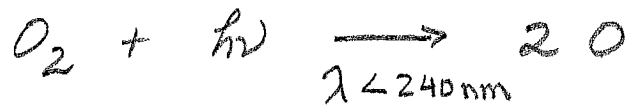
$\therefore P_h = (1.00 \ atm) \ e^{-4.98}$

$= 6.85 \times 10^{-3} \ atm \quad or \quad 694 \ Pa$

$n_h^* = n_o^* \ e^{-4.98} = \left(\dfrac{PV}{RT} \cdot N_A\right) e^{-4.98}$ using $T = 240 K$

$= 3.057 \times 10^{19} \ \dfrac{molecules}{cm^3}$

In the upper stratosphere, the relative abundance of atomic oxygen increases under the influence of increased solar flux of short wavelength (high energy) UVb and UVc light.

$$O_2 + h\nu \xrightarrow[\lambda < 240 nm]{} 2O$$

With higher concentrations of atomic O, the rate of O_3 production with increase. Since O_3 is present at some steady state amount in stratosphere, its rate of destruction will increase as well.

With higher rates of prod'n & destruction, the residence time of O_3 will decrease.

2. In 1974, Rowland and Molina suggested that the only environmental *sink* for CFC compounds was transport to the stratosphere*. The refrigerant known as Freon 12 (dichlorodifluoromethane) has an atmospheric *residence time* of ~ 200 yrs. Using the bond dissociation energies given in your text, calculate the maximum wavelength of light capable of photolyzing this compound. What additional information is required in order to predict rate of a photochemical reaction?

a)

$$F - \overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - Cl$$
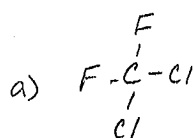
Bond enthalpies from Appendix B.3 (text)

$$C - F \quad 484 \; kJ/mol$$
$$C - Cl \quad 338 \; kJ/mol \quad \longleftarrow weakest \; bond$$

$$E_{photon} = h\nu = \frac{hc}{\lambda} \qquad \therefore \; \lambda \leq \frac{hc}{E_{photon}}$$

$$E_{photon} = 338 \times 10^3 \; J/mol \times \frac{1 \; mol}{6.02 \times 10^{23}} = 5.61_2 \times 10^{-19} \; J$$

$$\therefore \; \lambda \leq \frac{(6.626 \times 10^{-34} \; J \cdot s)(3.00 \times 10^8 \; m \; s^{-1})}{(5.61_2 \times 10^{-19} \; J)} = 3.54_2 \times 10^{-7} \; m$$

$$\lambda \leq 354 \; nm$$

b) Although photons of this wavelength are available in the troposphere, Freon-12 has no chromophore that absorbs light in this region. Therefore, this rxn' is limited to the stratosphere where even shorter λ light is available.

c) rate of photochemical reaction
depends on conc. of absorbing species
and the photochemical rate constant, f.

$$Rate = f [A]$$

$$f = \int_{\lambda_1}^{\lambda_2} \overline{\Phi}_\lambda \; \sigma_\lambda \; J_\lambda \; d\lambda$$

The photochemical rate constant itself
depends on the photochemical quantum
yield $(\overline{\Phi})$, the absorption x-section
(σ) and the photon flux (J).

3. HCFC-22 is one of the compounds recommended as a replacement for CFCs. Its current tropospheric concentration is about 0.10 ppb$_v$. It is known to react with tropospheric hydroxyl radical with a rate constant of 4.0 x 10^{-15} cm^3 molec^{-1} s^{-1}.
a) Using a constant value for the hydroxyl radical concentration of 6.6 x 10^5 molec cm^{-3}, determine the rate of tropospheric oxidation via hydroxyl radical and estimate the tropospheric residence time of HCFC-22.
b) Draw the structure of HCFC-22 and suggest a reaction sequence consistent with its oxidation in the troposphere.

a) $HCF_2Cl + \cdot OH \xrightarrow{k} \cdot$ pdts.
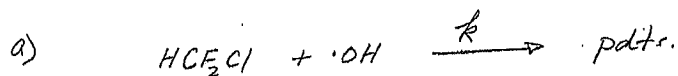
Rate $= k\,[HCF_2Cl]\,[OH]$

where $k = 4.0 \times 10^{-15}$ cm^3 molec^{-1} s^{-1}

$[OH] = 6.6 \times 10^5$ molec cm^{-3}

$[HCF_2Cl] = \dfrac{0.10 \times 10^{-9}\,mol}{1\,mol/air} \times \dfrac{6.02 \times 10^{23}\,molec}{1\,mol} \times \dfrac{1\,mol/air}{22.4\,L} \times \dfrac{1\,L}{10^3\,cm^3}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \uparrow$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ at STP

$= 2.69 \times 10^9\, \dfrac{molec}{cm^3}$

$\therefore$ Rate $= \left(4.0 \times 10^{-15}\,cm^3\,molec^{-1}s^{-1}\right)\left(6.6 \times 10^5\,molec\,cm^{-3}\right)\left(2.69 \times 10^9\,\dfrac{molec}{cm^3}\right)$

$= 7.1\, \dfrac{molecules}{cm^3 \cdot s}$

$\tau^{trop} = \dfrac{[stock]}{Rate} = \dfrac{1}{k[OH]} = \dfrac{1}{\left(4.0 \times 10^{-15}\,cm^3\,molec^{-1}s^{-1}\right)\left(6.6 \times 10^5\,\dfrac{molec}{cm^3}\right)}$

$= 3.8 \times 10^8\,s$

$\Rightarrow 12\,yrs$

(see further table 3.2 text)

b)

$$\overset{\displaystyle Cl}{\underset{\displaystyle F}{H-C-F}} \quad + \quad \cdot OH \quad \longrightarrow \quad \overset{\displaystyle Cl}{\underset{\displaystyle F}{\cdot C-F}} \quad + \quad H_2O$$

$$\overset{\displaystyle Cl}{\underset{\displaystyle F}{\cdot C-F}} \quad + \quad O_2 \quad \longrightarrow \quad \overset{\displaystyle Cl}{\underset{\displaystyle F}{\cdot O-O-C-F}}$$

$$\overset{\displaystyle Cl}{\underset{\displaystyle F}{\cdot O-O-C-F}} \quad + \quad NO \quad \longrightarrow \quad \overset{\displaystyle Cl}{\underset{\displaystyle F}{\cdot O-C-F}} \quad + \quad NO_2$$

$$\overset{\displaystyle (Cl)}{\underset{\displaystyle F}{\cdot O \curvearrowright C-F}} \quad \longrightarrow \quad O=C\overset{\displaystyle F}{\underset{\displaystyle F}{}} \quad + \quad Cl\cdot$$

$\downarrow H_2O \qquad\qquad\qquad \downarrow R-H$

$\downarrow -HF \qquad\qquad\qquad \downarrow -R\cdot$

$H_2CO_{3\,(aq)} \qquad\qquad\qquad HCl_{\,(aq)}$
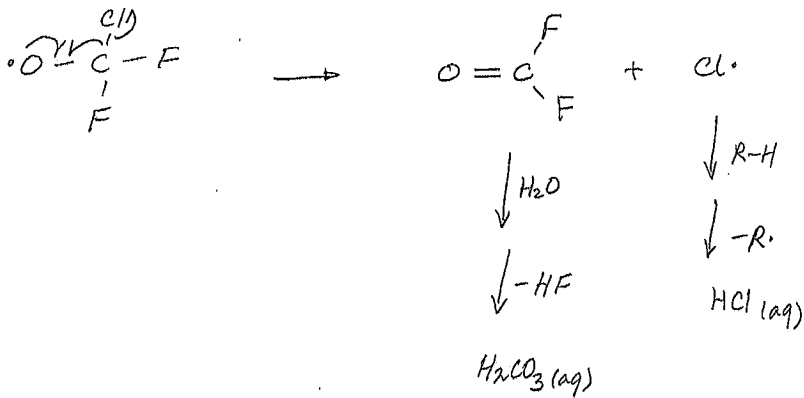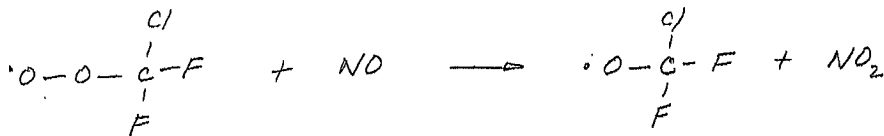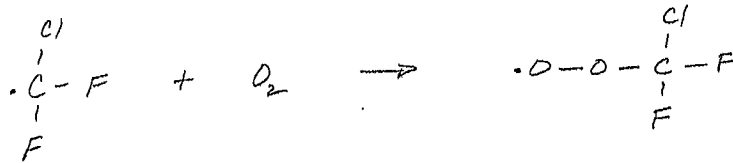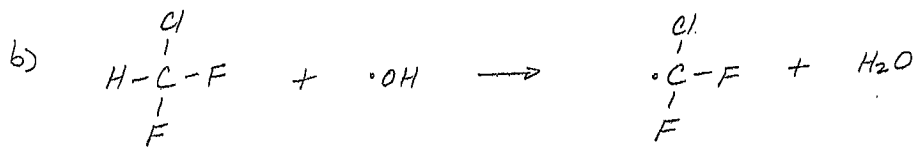
4. The following atmospheric reaction behaves as if it were first order with respect to **NO₂** with a *pseudo*-first order rate constant of 2.2×10^{-5} s^{-1} at 25°C.

$$NO_2 \;+\; O_2 \;\rightarrow\; NO \;+\; O_3$$
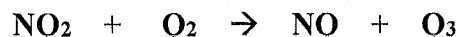
a) Determine the second order rate constant (molec^{-1} cm^3 s^{-1}) at 25°C and P$_T$= 1.00 atm.

b) Assuming no new inputs of **NO₂** and no other loss processes, what percentage of **NO₂** remains after 60 mins?

a)

$$\text{Rate} = k_{obs}[NO_2]$$

where $k_{obs} = k_2[O_2] = 2.2 \times 10^{-5}$ s^{-1} at 298K

$$\therefore k_2 = \frac{k_{obs}}{[O_2]}$$

and

$$[O_2] = \frac{0.2095 \times 10^{-2} \text{ mol}}{1 \text{ mol air}} \times \frac{6.02 \times 10^{23}}{\text{mol}} \times \frac{1 \text{ mol air}}{24.5 L}$$

$$\times \frac{1 L}{10^3 cm^3} \qquad \text{↑ at 298K, } P_T = 1.0 \text{ atm}$$

$$= 5.15 \times 10^{18} \frac{\text{molec}}{cm^3}$$

So

$$k_2 = \frac{2.2 \times 10^{-5} s^{-1}}{5.15 \times 10^{18} \frac{\text{molec}}{cm^3}} = 4.3 \times 10^{-24} cm^3 \text{ molec}^{-1} s^{-1}$$

b)   Conc $\longleftrightarrow$ time

∴ use integrated rate equation

$$\frac{[NO_2]_t}{[NO_2]_0} = e^{-k_{obs} \cdot t}$$

where $k_{obs} = 2.2 \times 10^{-5} s^{-1}$

and $t = 60$ mins

$= 3.6 \times 10^4$ s

∴ $\frac{[NO_2]_t}{[NO_2]_0} = e^{-0.0792} = 0.92$

So after 60 mins, 92% of NO_2 remains.

5. Explain what is meant by a 'holding cycles' and explain how these reactions can be related to polar stratospheric ozone depletion events. Illustrate your answer with examples from your textbook.
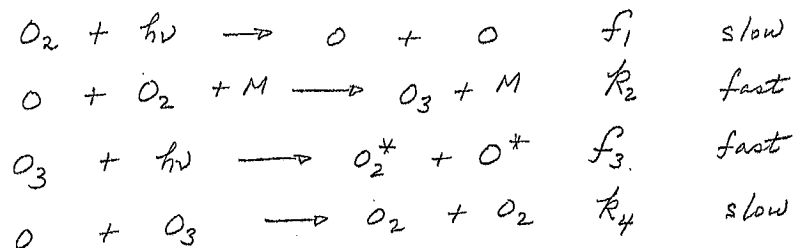
Holding cycles are reactions that convert reactive radical species into less reactive species that can be released later to take part in ozone depletion. The less reactive species are often referred to as reservoir species which can be transported greater distances due to their longer residence time. Polar statospheric ozone depletion events are often driven by the photolysis of reservoir species which release ozone depletion catalysts (eg. $Cl\cdot$, NO_2 etc) during the polar spring.

reservoir species
↓

$$NO_2 + NO_3 \xrightarrow{M} N_2O_5$$
$$NO_2 + \cdot OH \xrightarrow{M} HNO_3$$
$$Cl + RH \longrightarrow HCl + R\cdot$$
$$ClO\cdot + HOO\cdot \longrightarrow HOCl + O_2$$
$$ClO\cdot + NO_2 \xrightarrow{M} ClONO_2$$

$$HNO_3 + h\nu \longrightarrow HO\cdot + NO_2$$
$$HOCl + h\nu \longrightarrow HO\cdot + Cl$$

ozone depletion catalysts
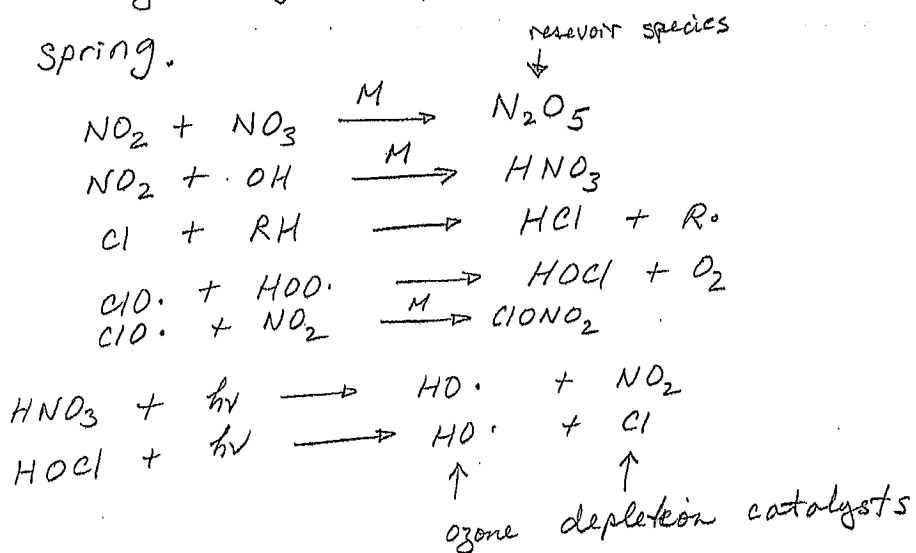
6. Applying the *steady state approximation* to **O** and **O₃** in the Chapman reactions, it can be shown that; $k_2[O_2][O][M] \cong f_3[O_3]$ and $f_1[O_2] \cong k_4[O][O_3]$

Given the information below about the temperature dependence of the rate constants, predict the ozone concentration at 60 km altitude. The rate constants k_2 and k_4 vary with temperature as follows;

$$k_2 = 6.0 \times 10^{-34}\left(\frac{T}{300}\right)^{-2.3} \text{ cm}^6 \text{ molec}^{-2} \text{ s}^{-1} \qquad k_4 = 8.0 \times 10^{-12} e^{\left\{\frac{-2060}{T}\right\}} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

The photochemical rate constants f_1 and f_3 do not vary appreciably with temperature and are given by 1×10^{-11} s⁻¹ and 1×10^{-3} s⁻¹, respectively.

$$O_2 + h\nu \longrightarrow O + O \qquad f_1 \quad \text{slow}$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad k_2 \quad \text{fast}$$

$$O_3 + h\nu \longrightarrow O_2^* + O^* \qquad f_3 \quad \text{fast}$$

$$O + O_3 \longrightarrow O_2 + O_2 \qquad k_4 \quad \text{slow}$$

$$k_2 [O_2][O][M] = f_3 [O_3]$$

$$\therefore [O_3] = \frac{k_2 [O_2][O][M]}{f_3}$$

and $\quad f_1 [O_2] = k_4 [O][O_3]$

$$\therefore [O] = \frac{f_1 [O_2]}{k_4 [O_3]}$$

Therefore, $[O_3] = \dfrac{k_2 [O_2] \cdot \dfrac{f_1 [O_2]}{k_4 [O_3]} \cdot [M]}{f_3} = \dfrac{k_2 f_1 [O_2]^2 [M]}{k_4 f_3 [O_3]}$

$$\therefore [O_3]^2 = \frac{k_2 f_1 [O_2]^2 [M]}{k_4 f_3} \implies [O_3] = \left(\frac{k_2 f_1}{k_4 f_3}\right)^{1/2} [O_2][M]^{1/2}$$

Therefore,

$$[O_3] = \left[\frac{(8.34 \times 10^{-34})(1 \times 10^{-11})}{(2.90 \times 10^{-15})(1 \times 10^{-3})}\right]^{1/2} (4.67 \times 10^{15})(2.23 \times 10^{16})^{1/2}$$

$$= 3.7 \times 10^{10}$$

dimensional analysis;
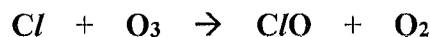
$$\left[\frac{cm^6 \; molec^{-2} \; s^{-1} \cdot s^{-1}}{cm^3 \; molec^{-1} \; s^{-1} \cdot s^{-1}}\right]^{1/2} \cdot \left[\frac{molec}{cm^3}\right] \cdot \left[\frac{molec}{cm^3}\right]^{1/2}$$

$$\Rightarrow \left[cm^3 \; molec^{-1}\right]^{1/2} \cdot \left[\frac{molec}{cm^3}\right] \cdot \left[\frac{molec}{cm^3}\right]^{1/2}$$

$$\Rightarrow \left[\frac{molec}{cm^3}\right]$$

$$\boxed{[O_3] = 3.7 \times 10^{10} \; \frac{molec}{cm^3}}$$

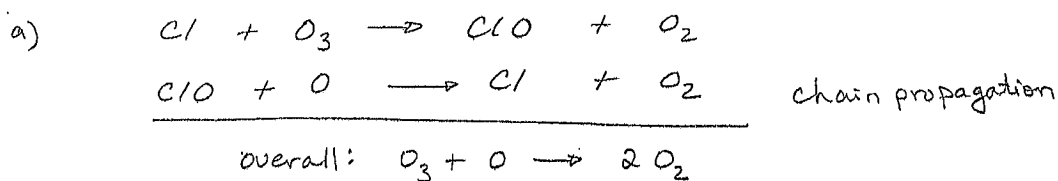**7.** An important reaction in the destruction of ozone is

$$Cl + O_3 \rightarrow ClO + O_2$$

The rate constant for this reaction as a function of temperature is given as
$k(T) = 2.9 \times 10^{-11}\ e^{-260/T}$, in units of molecules^{-1} cm^3 s^{-1}.
a) What is the rate of ozone destruction by this reaction at an altitude of 30 km near the
Earth's equator, where the average atomic chlorine concentration is about 4×10^3
molecules cm^{-3}?
b) How does this compare to the atmosphere above the Antarctic, where the temperature
is about -80°C, the ozone concentration is 2×10^{11} molecules cm^{-3} and the atomic
chlorine concentration is about 4×10^5 molecules cm^{-3}.

a)
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2 \qquad \text{chain propagation}$$
$$\overline{\text{overall:} \quad O_3 + O \longrightarrow 2\,O_2}$$

b) rate O_3 loss $= k\,[Cl][O_3]$ at 30 km, $T \cong 240\,K$

where $k = 2.9 \times 10^{-11}\ e^{-260/240}$ Fig. 2.1

$= 9.8 \times 10^{-12}$ cm^3 molec^{-1} s^{-1} $[O_3] = 10^{12.2}$
$= 1.6 \times 10^{12}\ \dfrac{\text{molec}}{\text{cm}^3}$

and $[Cl] = 4 \times 10^3$ molec/cm^3 Fig. 3.1

and $[O_3] = 1.6 \times 10^{12}$ molec/cm^3

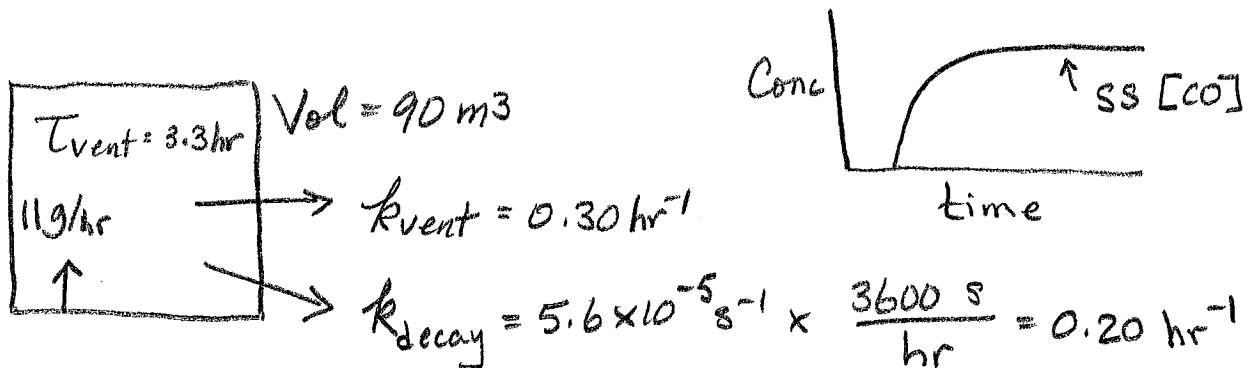∴ Rate $= 6.2 \times 10^4$ molec cm^{-3} s^{-1}

c) $k = 2.9 \times 10^{-11}\ e^{-260/193} = 7.4 \times 10^{-12}$ cm^3 molec^{-1} s^{-1}

∴ Rate $= 5.9 \times 10^5$ molec cm^{-3} s^{-1}

About 10 times faster O_3 destruction above Antarctic

8. An individual who hasn't taken CHEM 302 is running their old lawnmower in their garage (don't ask). The lawnmower is spewing carbon monoxide at a rate of 11 g/hr and the garage (which has a volume of 90 m³) is being ventilated such that the residence time of the air in the garage is 3.3 hr. Let us assume that the **CO** is lost from the garage by two processes: first, by simple flushing as it mixes with the clean ventilated air and second by some unspecified decay process with a rate constant of 5.6×10^{-5} s⁻¹. Under these conditions estimate the *residence time* (in hrs) and *steady state concentration* (ppm$_v$) of **CO** in the garage.

$\tau_{vent} = 3.3\,hr$, $Vol = 90\,m^3$

$11\,g/hr \rightarrow k_{vent} = 0.30\,hr^{-1}$

$\rightarrow k_{decay} = 5.6 \times 10^{-5}\,s^{-1} \times \dfrac{3600\,s}{hr} = 0.20\,hr^{-1}$

Conc vs time — $ss\ [CO]$

$$\tau_{overall}^{CO} = \frac{1}{\Sigma k} = \frac{1}{k_{vent} + k_{decay}} = \frac{1}{(0.30 + 0.20)\,hr^{-1}}$$

$$= 2.0\,hr$$

$$\tau_{overall}^{CO} = \frac{stock}{flux} \quad \text{and @ steady state, flux} = 11\,g/hr$$

$$\therefore stock = (\tau_{overall}^{CO})(flux) = (2.0\,hr)(11\,g/hr) = 22\,g$$

$$\therefore [CO]_{ss} = \frac{22\,g}{90\,m^3} \times \frac{1\,mol}{28\,g} \times \frac{22.41\,L}{1\,mol\,air} \times \frac{1\,m^3}{10^3\,L} \times 10^6$$

$$= 112.5\,ppm_v$$

$$\Rightarrow 110\,ppm_v\ CO$$