## CH3041 Tutorial 1 Answers

1. The exhaust of an automobile is found to contain 2 percent CO (20 000 ppmv) at a temperature of 80° C. Express the concentration of CO in the exhaust gas in  $\mu$ g/m<sup>3</sup> which is another commonly used gas concentration unit. Assume ideal gas behaviour for the gas.

2% = 20,000 ppm eg. 20,000 L of CO /10<sup>6</sup> L of exhaust

 $T = 273 + 80 = 353^{\circ} \text{ K} \qquad p = 1.013 \text{ x } 10^{5} \text{ Pa} \qquad R = 8.314 \text{ Pa m}^{3} \text{ mol}^{-1} \text{ K}^{-1}$ molar mass of CO  $M_{CO} = 12 + 16 = 28 \text{ g/mole}$ 

From the ideal gas law

рV

rearranging:

 $g_{\rm CO} = pV (M_{\rm CO}) / RT$ 

 $= \frac{(1.01315 \text{ x } 10^5 \text{ Pa})(20,000 \text{ x } 10^{-3} \text{ m}^3) (28 \text{ g/mol})}{(8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}) (353 \text{ K})}$ 

 $= 1.93 \text{ x} \ 10^4 \text{ g in } 20 \ 000 \text{L}$ 

 $= nRT = (g_{CO}/M_{CO}) RT$ 

thus

$$\begin{array}{ll} 20,000 \ L \ of \ CO/\ 10^6 \ L \ of \ exhaust &= 1.93 \ x \ 10^4 \ g/10^6 \ L \\ convert \ L \ to \ m^3 \ (factor \ x \ 10^{-3}) &= 1.93 \ x \ 10^4 \ g/10^3 \ m^3 \\ &= 19.3 \ g \ / \ m^3 \\ convert \ g \ to \ \mu g \ (factor \ x \ 10^6) &= \textbf{1.93 } \textbf{x} \ \textbf{10}^7 \ \ \mu g/\textbf{m}^3 \end{array}$$

## Another approach:

The conversion between  $\mu g/m^3$  and ppm may also be based on the fact that under standard conditions (25°C and 101.325 kPa), one mole of an ideal gas occupies 22.414 L. Thus, we may write an equation that converts the mass of the carbon monoxide  $g_{CO}$  in grams to its equivalent volume  $V_{CO}$  in litres:

$$V_{CO} = g_{CO} / M_{CO} x 22.414 L/mole$$

Since ppm is a volume ratio, we may write

$$ppm = \frac{V_{CO}}{V_{air}} = \frac{XL}{10^6}L$$

where  $V_{air}$  is the total volume of air being considered in cubic meters at the temperature and pressure of the reading. We then combine the above equations with temperature and pressure corrections to form:

ppm = 
$$\underline{g_{CO}} \times \underline{22.414} \times \underline{T_2} \times \underline{101.325 \text{ kPa}}$$
  
 $\underline{M_{CO}} \qquad \underline{273K} \quad \underline{P_2}$  (here  $P_2 = 101.325$ )  
V.

when  $\underline{g_{CO}}$  is converted to  $\mu g$  and as  $V_{air}$  is in millions of L these factors cancel one another. No pressure correction is needed.

20 000 ppm = 
$$(\mu g_{CO} / M_{CO}) \times 10^6 \times (22.414 \times 10^{-3}) \times (353 / 273)$$
  
 $10^6 L$   
conv to  $\mu g$  conv to  $m^3$ 

Rearrange:

$$\mu g_{CO} / m^3 = 20\ 000 \ x M_{CO} \ x \ 273 / (22.414 \ x \ 10^{-3} \ x \ 353)$$
  
= **1.93 x 10<sup>7</sup> µg / m<sup>3</sup>**

2. Using the Barometric Law  $p_z = p_o e(-z / H)$  where the scale factor *H* is 8.4 km calculate the partial pressure of oxygen in Pa at 6.2 km given that the volume percentage of oxygen in air at sea level is 20.946%. Atmospheric pressure at sea level is 1.013 x 10<sup>5</sup> Pa.

at STP 1mol of any gas occupies 22.41 L

 $\frac{VO_2}{VO_{total}} = \underbrace{nO_2}_{nO_{total}} \Rightarrow \underbrace{pO_2}_{pO_2} = \underbrace{nO_2}_{nO_{total}} pO_{total}$ 

 $pO_2 = 0.20946 \text{ x } 1.013 \text{ x } 10^5$ = 21218.3 Pa

pO2 at 6.2 km = 21218.3 Pa exp( - 6.2 km / 8.4 km) = 10142.8 Pa

3. CFCs are responsible for the depletion of stratospheric ozone in the polar regions. Explain the physicochemical basis for this phenomenon.

CFCs are chlorofluorcarbons such as CFC-12 CF<sub>2</sub>Cl<sub>2</sub>. These chemicals were produced in large quantities (kt / y) for use as refrigerants, propellants and cleaning products. Once released into the atmosphere these halocarbons are quite inert in the troposphere and migrate upwards to the stratosphere over 3 - 10 years. The lifetime of the CFCs in the stratosphere is 110 yrs for CFC 12 which means that the removal rate here is also quite slow. The decay process is:

$$CF_2CI_2 \rightarrow CF_2CI^{-} + CI^{-}$$

This generates he reactive Cl radical which catalytically removes ozone, 100 000 ozone molecules are removed per Cl radical:

Cl' +  $O_3 \rightarrow ClO' + O_2$  (chlorine monoxide) ClO' +  $O \rightarrow Cl' + O_2$  (net loss of  $O_3$ )

This then is a general mechanism for the removal of ozone in the stratosphere which occurs globally.

At the poles extreme weather conditions in the winter mean that the air circulates locally in a circumpolar pattern without extensive mixing with warmer higher latitude air. No light is present and so the ozone level will not be replenished. The very low temperatures (< -70 °C)results in the formation of water ice / HNO<sub>3</sub> solid particles in the air called polar stratospheric clouds (PSC) HNO<sub>3</sub>.3H<sub>2</sub>O,HCl.

The chlorine nitrate available in the stratosphere may be catalytically broken down on the surface of the acidic ice crystals to form  $Cl_2$  gas.

## $CIONO_{2(g)} + HCI_{(s)} \rightarrow CI_{2(g)} + HNO_{3(s)}$

In early spring the available light breaks down further CFC molecules and the usual sink for ClO<sup>•</sup>, NO<sub>x</sub>, is at this stage tied up in the PSC ice. (**ClO<sup>•</sup> + NO<sub>2</sub><sup>•</sup> \rightarrow ClONO<sub>2</sub>) What occurs is a very rapid formation of chlorine radicals with the incoming photons able to break the Cl-**

Cl bond readily.

$$1Cl_{2(g)} + h_V \rightarrow 2Cl_{(g)}$$

The normal process for the removal of ozone involving the Cl<sup>-</sup> radical then proceeds rapidly on the fixed amount of ozone inside the polar vortex. As there is no interruption to the catalytic cycle for the destruction of ozone this reaction then runs unabated and this quickly consumes the available ozone until the column density of ozone drops significantly enough for it to be measured using remote sensing spectrometers on satellites.

4. Draw a figure illustrating the different regions of the atmosphere and the accompanying temperature profile. Explain the variation in temperature with altitude.

