CHEM 302
Assignment #3

Provide solutions to the following questions in a neat and well organized manner, including dimensional analysis, where appropriate.
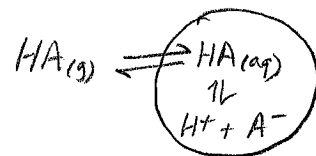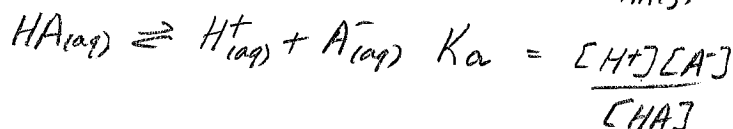*Reference data sources for any constants and state assumptions, if any.*
Attempt all questions. Submit even number questions only for grading.
Due Tuesday, Nov 10th, 2015

1. The pH of suspended water droplets is sensitive to the amount of covalent oxide gases present in the atmosphere.
a) Derive a general expression for the pH of rainwater in equilibrium with a monoprotic gas and explain if this will apply to common atmospheric gases like **CO$_2$** and **SO$_2$**?
b) Using Excel, plot a graph of pH (y-axis) versus partial pressure of **CO$_2$** (0-1000 ppm$_v$) and **SO$_2$** (0-1000 ppb$_v$).
c) Why is the pH of rain much more sensitive to P$_{SO2}$ than P$_{CO2}$?

a)

$$HA_{(g)} \rightleftharpoons HA_{(aq)} \qquad K_H = \frac{[HA_{(aq)}]}{P_{HA_{(g)}}}$$

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$HA_{(g)} \rightleftharpoons HA_{(aq)} \atop \qquad\qquad\quad H^+ + A^-$$

Since $HA_{(g)}$ is in exhaustible supply in atmosphere

we can write $[HA_{(aq)}] = P_{HA_{(g)}} K_H$

Also $[H^+] = [A^-]$ as they arise from same source

So $\dfrac{[H^+]^2}{[HA]} = K_a$

Isolating $[H^+]^2 = K_a[HA]$ and substituting in using Henry's law constant yields

$$[H^+]^2 = K_a P_{HA_{(g)}} K_H$$

Therefore, $[H^+] = \sqrt{K_a P_{HA} K_H}$

and $pH = -\log (K_a P_{HA} K_H)^{1/2}$

b) see attached

c) pH of rain is much more sensitive to
   SO_2 than CO_2 for two reasons

1) SO_2 is a stronger acid than CO_2

compare $K_{a_1}(H_2SO_3) = 1.7 \times 10^{-2}$ (textbook Appendix)

and $K_{a_1}(H_2CO_3) = 4.5 \times 10^{-7}$

2) SO_2 is more water soluble than CO_2

compare $K_H(SO_2) = 1.2 \times 10^{-5}$ M Pa^{-1}

and $K_H(CO_2) = 3.3 \times 10^{-7}$ M Pa^{-1}

(textbook pg 252)

2. Peroxyacetyl nitrate (PAN) decomposes thermally with a temperature dependent unimolecular rate constant of $k = 1.95 \times 10^{16} \, e^{-\{13540/T\}} \, s^{-1}$.

    a) Suggest the products of the decomposition reaction.
    b) Calculate the activation energy of this reaction using the Arrhenius relation.
    c) Calculate the half-life of PAN in the atmosphere at 25 and -10 °C?

a)

$$CH_3-\overset{O}{\overset{\|}{C}}-O-O-\overset{\oplus}{N}-O^{\ominus} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-O\cdot \; + \; NO_2$$
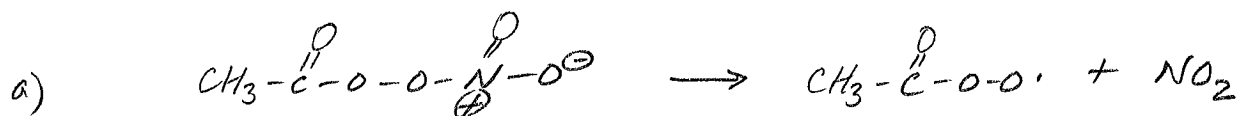
b)

$$k = A\,e^{-E_a/RT}$$

$$\therefore \ln k = \ln A - \frac{E_a}{RT}$$

at T_1 we can write $\ln k_1 = \ln A - \frac{E_a}{RT_1}$

at T_2 we can write $\ln k_2 = \ln A - \frac{E_a}{RT_2}$

Subtracting yields,

$$\ln k_1 - \ln k_2 = -\frac{E_a}{RT_1} - \left(-\frac{E_a}{RT_2}\right)$$

$$\ln\left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and $$E_a = \frac{-\ln\left(\frac{k_1}{k_2}\right)\cdot R}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

So, we can use any two rate constants at any two temperatures to calculate Ea.

at $T = 25°C = 298K$

$$k_{298} = 1.95 \times 10^{16} \, e^{-(13540/298)} \, s^{-1}$$

$$= 3.61 \times 10^{-4} \, s^{-1}$$

at $T = -10°C = 263K$

$$k_{263} = 1.95 \times 10^{16} \, e^{-(13540/263)} \, s^{-1}$$

$$= 8.54 \times 10^{-7} \, s^{-1}$$

$$\therefore E_a = -\frac{\ln\left(\frac{3.61 \times 10^{-4}}{8.54 \times 10^{-7}}\right)(8.314 \, J/mol\,K)}{\left(\frac{1}{298} - \frac{1}{263}\right)}$$

$$= \frac{50.27 \, J/mol\,K}{4.46 \times 10^{-4} \, K^{-1}}$$

$$= 112.6 \, kJ/mol$$

c) $t_{1/2}^{298} = \frac{0.693}{3.61 \times 10^{-4} s^{-1}} = 1.92 \times 10^{3} s = 32 \, mins$

$t_{1/2}^{263} = \frac{0.693}{8.54 \times 10^{-7} s^{-1}} = 8.11 \times 10^{5} s$

$$= 9.4 \, days$$

3. The ionic composition (in units of ng m^{-3}) of an atmospheric aerosol in a tropical rain forest is **SO$_4^{2-}$**, 207; **NO$_3^-$**, 18; **NH$_4^+$**, 385; **K$^+$**, 180; **Na$^+$**, 247. The pH is 5.22. Use these data to calculate the total positive and negative charge 'concentration' (in units µmol m^{-3}) in the aerosol and suggest reasons, which might account for a discrepancy in the charge balance. (Note a mole of charge is referred to as an equivalent, therefore µmol charge m^{-3} is equal to µequiv m^{-3})

4. The least volatile oxidation products of hydrocarbons are usually the corresponding carboxylic acid. The following transformations have been observed and the corresponding vapour pressures are given in the table below.

Compound	1-decene →	nonanoic acid	Cyclohexene →	1,6-hexandioic acid
Vapour Pressure (torr)	1.7	6×10^{-4}	89	6×10^{-8}

a) What concentration (ppm_v) of each of the hydrocarbon (separately) would be needed to cause the formation of haze, if 1% is converted to the corresponding carboxylic acid? Are these concentrations likely to occur?

b) Look up the structure of α-pinene (emitted from coniferous trees). Do you think it could be responsible for the summer haze in remote BC valleys.

a) Haze will be produced when liquid droplets (aerosols) are formed. This will occur first for the semi-volatile oxidation products, which are seen to be much _much_ less volatile than the alkenes that produced them.

$$X_{(g)} \rightleftharpoons X_{(\ell)} \qquad K = \frac{1}{P_{X_{(g)}}}$$

When vapour pressure of the gas is exceeded condensation will occur, so all we need to do is convert the vapour pressure in torr to a mixing ratio in ppm_v.

$$X_{nonanoic\ acid} = \frac{6. \times 10^{-4}\ torr \times \frac{1\ atm}{760\ torr}}{1\ atm} \times 10^6 = 0.79\ ppm_v$$
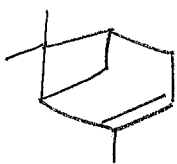
∴ $X_{1-decene} = 100 \times X_{nonanoic\ acid} = 79\ ppm_v$

Similarly for cyclohexene

$$X_{1,6\text{-hexandioic acid}} = \frac{6. \times 10^{-8} \text{ torr} \times \dfrac{1 \text{ atm}}{760 \text{ torr}}}{1 \text{ atm}} \times 10^{6}$$

$$= 7.9 \times 10^{-5} \text{ ppm}_v$$

$$\therefore X_{cyclohexene} = 7.9 \times 10^{-3} \text{ ppm}_v \quad \text{or} \quad 7.9 \text{ ppb}_v$$

Note the dicarboxylic acid formed from the oxidation of cyclohexene is much less volatile than nonanoic acid and consequently, haze will form at considerably lower atmospheric concentrations.

b)

α-pinene will oxidize to form a dicarboxylic acid. Tropospheric concentrations of α-pinene around 10 ppb$_v$ are typical of air masses near coniferous forests.

Therefore, it is very likely that this biogenic VOC contributes to haze formation in BC interior.

5. A coal burning power station burns 10,000 tonnes of coal per day. The coal is 1.25% sulfur by mass (assume the remaining mass is carbon).

    a) Calculate the mass of CO_2 and SO_2 produced per day, assuming complete combustion.

    b) Estimate the mixing ratios of N_2, CO_2 and SO_2 in the stack gases, assuming all the oxygen has been consumed in the combustion process.

    c) Calculate the mass of lime ($Ca(OH)_2$) needed per day to react with 95% of the SO_2 produced.

$$Ca(OH)_2 \; + \; SO_2 \; + \; \tfrac{1}{2}O_2 \; \rightarrow \; CaSO_4$$

a)
$$C + O_2 \longrightarrow CO_2$$
$$S + O_2 \longrightarrow SO_2$$
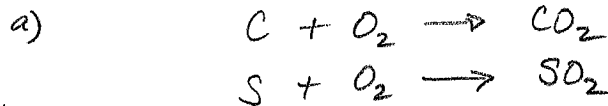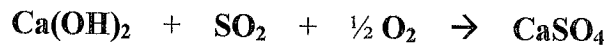
$$\text{mass of } C = 10,000 \times \frac{98.75}{100} = 9875 \text{ tonnes}$$

$$\text{mass of } S = 10,000 \times \frac{1.25}{100} = 125 \text{ tonnes}$$

$$\text{mass } CO_2 = \#mols\ CO_2 \times MW_{CO_2}$$

$$= 9875 \text{ tonnes} \times \frac{10^3 kg}{1\ tonne} \times \frac{10^3 g}{kg} \times \frac{1\ mol\ C}{12.0 g} \times \frac{44.0 g}{1\ mol\ CO_2} = 36,200 \text{ tonnes of } CO_2 \text{ per day}$$

$$\text{mass } SO_2 = \#mols\ SO_2 \times MW_{SO_2}$$

$$= 125 \text{ tonnes} \times \frac{10^3 kg}{1\ tonne} \times \frac{10^3 g}{1 kg} \times \frac{1\ mol\ S}{32.0 g} \times \frac{64.0 g}{1\ mol\ SO_2} = 250 \text{ tonnes of } SO_2 \text{ per day}$$

b) $$\text{mixing ratio} = \frac{\#mols\ individual\ gas}{total\ \#mols\ of\ all\ gases}$$

assuming complete combustion the major gases in the stack will be N_2, CO_2 and SO_2 since all of the O_2 has been consumed.

Let's calculate the number of moles of gases consumed and produced each day, and use this to determine the mixing ratios.

Per Day:

#moles O_2 consumed by rxn $\bar{w}$ C = #mols C $\times \dfrac{1\,mol\,O_2}{1\,mol\,C}$

$\therefore$ 9875 tonnes $\times \dfrac{10^3 kg}{1\,tonne} \times \dfrac{10^3 g}{1\,kg} \times \dfrac{1\,mol\,C}{12.0g} \times \dfrac{1\,mol\,O_2}{1\,mol\,C} = 8.23 \times 10^8\,mol\,O_2$

#moles O_2 consumed by rxn $\bar{w}$ S =

125 tonnes $\times \dfrac{10^3 kg}{1\,tonne} \times \dfrac{10^3 g}{1\,kg} \times \dfrac{1\,mol\,S}{32.0g} \times \dfrac{1\,mol\,O_2}{1\,mol\,S} = 3.91 \times 10^6\,mols\,O_2$

Therefore, total #mols O_2 consumed per day

$= 8.27 \times 10^8\,mols\,O_2$

Since this is being supplied from the air, which is only 21% O_2, we can calculate the total #mols N_2 that is being supplied per day as,

$8.27 \times 10^8\,mols\,O_2 \times \dfrac{0.78\,mol\,N_2}{0.21\,mol\,O_2} = 3.1 \times 10^9\,mol\,N_2$

So total #mols gas produced per day

$= $ #mols N_2 + mols CO_2 + #mols SO_2

$= 3.1 \times 10^9 + 8.2 \times 10^8 + 3.9 \times 10^6 = 3.9 \times 10^9\,mol$

$\therefore X_{N_2} = \dfrac{3.1 \times 10^9}{3.9 \times 10^9} = 0.79 \Rightarrow 79\%$ $X_{SO_2} = \dfrac{3.9 \times 10^6}{3.9 \times 10^9} = 0.0010$

$X_{CO_2} = \dfrac{8.2 \times 10^8}{3.9 \times 10^9} = 0.21 \Rightarrow 21\%$ $\Rightarrow 0.1\%$ or 1000 ppm$_v$

c) mass of $Ca(OH)_2$ required per day to react w̄ SO_2

$$250 \text{ tonnes } SO_2 \times \frac{10^6 \text{ g}}{\text{tonne}} \times \frac{1 \text{ mol } SO_2}{64.0 \text{ g}} \times \frac{1 \text{ mol } (Ca(OH)_2)}{1 \text{ mol } SO_2}$$

$$\times \frac{74 \text{ g}}{1 \text{ mol } Ca(OH)_2} \times 0.95 = 274 \times 10^6 \text{ g of}$$
$$Ca(OH)_{2 \, (s)}$$

274 tonnes of lime

6. Soot particles have a density close to 2.2 g cm^{-3}.

a) Use Stokes Law to estimate the rate of settling of particles having the diameters below using the viscosity of air to be 182 µpoise (1 poise = 1 g cm^{-1} s^{-1});

    i) 15 µm

    ii) 0.3 µm

b) How long will it take particles of these sizes to settle out of the atmosphere from a height of 5 km assuming the air is still?

c) Under highly polluted conditions, concentrations of particulates up to 4000 µg/m^3 have been recorded. Assuming the density given above and the average particle diameter of 1 µm, estimate the number of particles inhaled per hour by a person breathing this polluted air.

a) Stokes law calculates the settling velocity as follows

$$V_t = \frac{(\rho_p - \rho_{air}) \, C \, g \, d_p^2}{18 \, \eta}$$

where ρ is the density in g/m^3

    C is a correction term from Table 6.4

    g is acceleration due to gravity

    d_p is diameter of particle in m

    η is viscosity of air in g m^{-1} s^{-1}

where $\rho_p = 2.2$ g cm^{-3} $\times \dfrac{10^6 \text{ cm}^3}{1 \text{ m}^3} = 2.2 \times 10^6$ g m^{-3}

    $\rho_{air} = 1.2 \times 10^3$ g m^{-3}

    $g = 9.8$ m s^{-2}

    $\eta = 182 \times 10^{-6}$ g cm^{-1} s^{-1} $\times \dfrac{10^2 \text{ cm}}{1 \text{ m}} = 0.0182$ g m^{-1} s^{-1}

Therefore for

i) 15 μm particle

$$V_t = \frac{(2.2 \times 10^6 - 1.2 \times 10^3)(1.01)(9.8)(15 \times 10^{-6})^2}{18(0.0182)}$$

$$= 0.015 \text{ m/s} \Rightarrow 0.054 \text{ km/hr}$$

$$\left[\frac{g/m^3 \quad m/s^2 \quad m^2}{g/ms} \right] \Rightarrow \left[\frac{g/s^2}{g/ms} \right]$$

$$\Rightarrow \left[m/s \right]$$

ii) 0.3 μm particle

$$V_t = \frac{(2.2 \times 10^6 - 1.2 \times 10^3)(2.1)(9.8)(0.3 \times 10^{-6})^2}{18(0.0182)}$$

$$= 1.2 \times 10^{-5} \text{ m/s} \Rightarrow 4.3 \times 10^{-5} \text{ km/hr}$$

b) time for 5 km travel

i) $t = d/V_t = (5000 \text{ m})/(0.015 \text{ m/s}) = 3.3 \times 10^5 \text{ s}$

$$\Rightarrow 93 \text{ hr or } 3.9 \text{ days}$$

ii) $t = (5000 \text{ m})/(1.2 \times 10^{-5} \text{ m/s}) = 4.2 \times 10^8 \text{ s}$

$$\Rightarrow 4800 \text{ days}$$

c) $4000 \mu g/m^3$

We need the # particles per m^3 and the volume of air breathed in one hour.

mass of each particle $= 1.2 \times 10^{-12} g$

$$\frac{4000 \mu g}{m^3} \Bigg/ \underbrace{\frac{4}{3} \pi r^3}_{\substack{\uparrow \\ \text{volume of} \\ \text{particle} \\ r = 0.5 \mu m}} \times \underbrace{\rho_p}_{\substack{\uparrow \\ \text{density of} \\ \text{particle} \\ = 2.2 \, g/cm^3}}$$

$$= \frac{4000 \mu g}{m^3} \cdot \frac{1 \text{ particle}}{1.2 \times 10^{-12} g} \cdot \frac{1 g}{10^6 \mu g} = 3.3 \times 10^9 \frac{\text{particles}}{m^3}$$
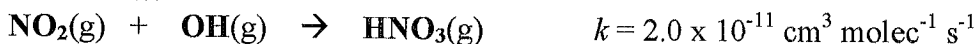
At a typical breathing rate of 15 breaths/min and typical volume of air exchanged per breathe = 2 L

Volume inhaled per hour $= 15 \frac{\text{breath}}{\text{min}} \times \frac{60 \text{ min}}{\text{hr}} \times \frac{2 L}{\text{breath}} = 1800 L$

$\Rightarrow 1.8 \, m^3$

$\therefore$ #particles inhaled $\cong 6 \times 10^9$
       per hour

7. Nitrogen dioxide is oxidized to nitric acid in the presence of a third body according the reaction below.

$$NO_2(g) \; + \; OH(g) \; \rightarrow \; HNO_3(g) \qquad k = 2.0 \times 10^{-11} \; cm^3 \; molec^{-1} \; s^{-1}$$

If in a laboratory experiment, [OH] is maintained at a constant concentration of 2.4×10^6 molec cm^{-3} and 10.0 L of air initially containing 3.5 ppm$_v$ of NO_2 is maintained in contact with 0.010 L of liquid water, calculate the pH of the water after 4.5 hr.

Conc $\leftrightarrow$ Time : use integrated rate law

for psuedo first order process

$$\ln\left(\frac{[NO_2]_t}{[NO_2]_0}\right) = -kt \qquad \text{where } [NO_2]_0 = 3.5 \; ppm_v$$

$$k = 2.0 \times 10^{-11} \frac{cm^3}{molec \; s} \cdot 2.4 \times 10^6 \frac{molec}{cm^3}$$

$$= 4.8 \times 10^{-5} \; s^{-1}$$

So when $t = 4.5 \, hr \times \dfrac{60 \, min}{1 \, hr} \times \dfrac{60 \, s}{1 \, min}$

$$= 1.62 \times 10^4 \; s$$

$$\ln\left(\frac{[NO_2]_t}{3.5 \, ppm_v}\right) = -\left(4.8 \times 10^{-5} s^{-1}\right)\left(1.62 \times 10^4 s\right) = -0.778$$

$$[NO_2]_t = \left(3.5 \; ppm_v\right) e^{-0.778} = 1.6 \; ppm_v$$

$$\therefore [HNO_3]_t = 3.5 - 1.6 = 1.9 \; ppm_v$$

$$HNO_{3(g)} \rightleftharpoons HNO_{3(aq)} \qquad K_H \cong 2 \times 10^5 \; M \; atm^{-1}$$

nitric acid is very water soluble (as seen by high Henry's Law constant) and virtually all $HNO_{3(g)}$ dissolves in water where it subsequently dissociates as a strong acid.

$$HNO_{3(g)} \longrightarrow HNO_{3(aq)} \longrightarrow H^+ + NO_3^-$$
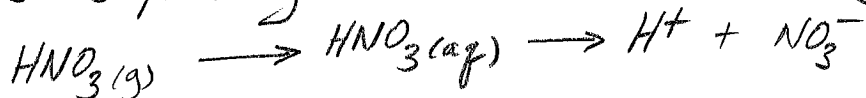
So let's convert the 1.9 ppmv in the 10.0 L container to an equivalent # mols HNO_3 which then gets dissolved in 0.010 L of water to calculate the $[H^+]$ and consequently the pH.
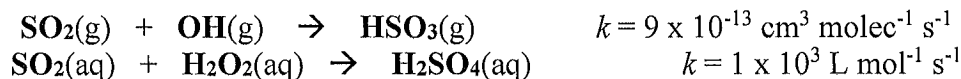
$$\frac{1.9 \times 10^{-6} \text{ mol } HNO_3}{1 \text{ mol air}} \times \frac{1 \text{ mol air}}{22.41 \text{ L}} \times 10.0 \text{ L} = 8.48 \times 10^{-7} \text{ mol } HNO_3$$

$$\frac{8.48 \times 10^{-7} \text{ mol } HNO_3}{0.010 \text{ L water}} = 8.48 \times 10^{-5} \frac{\text{mol } HNO_3}{L}$$

Since HNO_3 is a strong acid, it completely dissociates and $[H^+] = 8.48 \times 10^{-5} \frac{\text{mol}}{L}$

$$\therefore pH = -\log [H^+]$$

$$= 4.07$$

**8.** Suppose the only reactions important in oxidizing SO_2 are the two given below with the second order rate constants reported at 300 K.

$$SO_2(g) + OH(g) \rightarrow HSO_3(g) \qquad k = 9 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$
$$SO_2(aq) + H_2O_2(aq) \rightarrow H_2SO_4(aq) \qquad k = 1 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$$

a) Given the information below at 300K and assuming a constant $[OH] = 5 \times 10^6$ molec cm^{-1}, calculate the amount of liquid water in the atmosphere (expressed g L^{-1}) for the rate of the aqueous phase reaction to equal the rate of the gas phase reaction.

K_H (SO_2)	P_{SO2}	K_H (H_2O_2)	P_{H2O2}
1.2 mol L^{-1} atm^{-1}	1.0 ppm$_v$	1 x 10^5 mol L^{-1} atm^{-1}	1.0 ppb$_v$

b) How does the half-life of SO_2 in the atmosphere vary as the water content increases?
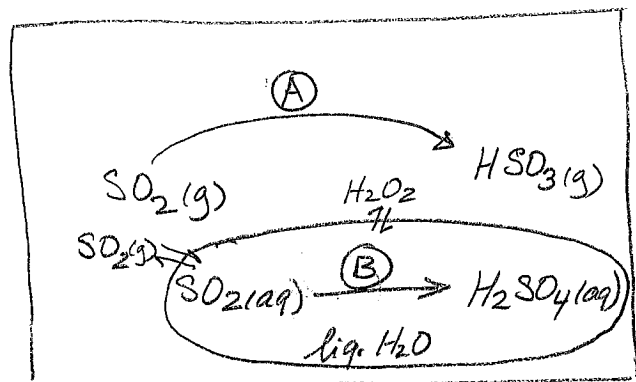
Write an expression for rate in gas phase

$$\text{rate gas phase} = \left(9 \times 10^{-13} \frac{cm^3}{molec\ s}\right)\left(5 \times 10^6 \frac{molec}{cm^3}\right) 1.0\ ppm_v$$

$$= 4.5 \times 10^{-6}\ ppm_v/s$$

convert to mol/L to compare with aqueous rate

$$\frac{n}{V} = \frac{P}{RT} = \frac{4.5 \times 10^{-12}\ atm}{\left(0.0821 \frac{L \cdot atm}{mol/K}\right)(300K)} = 1.8 \times 10^{-13} \frac{mol}{L}/s$$

$$= 1.8 \times 10^{-13}\ M\ s^{-1}$$

This is the rate per liter of air

rate in aqueous solution

$$= k \, [SO_{2\,(aq)}] \, [H_2O_{2\,(aq)}]$$

$K_H(H_2O_2) \cdot P_{H_2O_2}$
$= (1 \times 10^5 \, M \, atm^{-1})(1 \times 10^{-9} \, atm)$
$= 1. \times 10^{-4} \, M$

$1 \times 10^3 \, M^{-1} s^{-1}$

$K_H(SO_2) \cdot P_{SO_2} = (1.2 \, M \, atm^{-1})(1.0 \times 10^{-6} \, atm)$
$= 1.2 \times 10^{-6} \, M$

$\therefore$ rate $= (1 \times 10^3 \, M^{-1} s^{-1})(1.2 \times 10^{-6} M)(1.0 \times 10^{-4} \, M)$
in aqueous phase

$$= 1 \times 10^{-7} \, M \, s^{-1}$$

This is the rate per liter of water

In order to compare these rates in a unit of the atmosphere containing both gases and liquid water, we need to convert the rates to the same units.

Converting aqueous phase rate to $mol/L \,(air)$ per s yields,

$$1. \times 10^{-7} \frac{mol}{L \,(of \, water) \, s} \times y \frac{g \,(of \, water)}{L \,(air)} \times \frac{1 \, L \,(water)}{10^3 \, g \,(water)}$$

density of water

$$= 1 \times 10^{-10} \, y \, \frac{mol}{L \,(air) \, s^{-1}}$$

where y is mass of liquid water per liter of air in units of g/L

∴ rate gas phase = rate aqueous phase

$$1.8 \times 10^{-13} \frac{mol}{L(air)\ s} = 1 \times 10^{-10} \frac{mol}{L(air)\ s} \cdot y$$

$$\text{and } y = \frac{1.8 \times 10^{-13}}{1 \times 10^{-10}} = 1.8 \times 10^{-3}\ g/L$$

or 1.8 mg $H_2O(l)$ per liter air