

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.

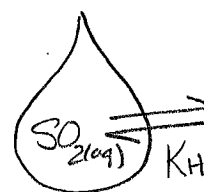
Due: Thursday, November 16th, 2017

1. The annual mean concentration of sulfur dioxide in an industrialized region of Bulgaria was $31.8 \mu\text{g}/\text{m}^3$. Calculate the pH of rainwater in equilibrium with this SO_2 .

$$K_H(\text{SO}_2) = 1.2 \times 10^{-5} \text{ M Pa}^{-1}$$

$$K_{a1}(\text{H}_2\text{SO}_3) = 1.7 \times 10^{-2}$$

$$K_{a2}(\text{HSO}_3^-) = 6.4 \times 10^{-8}$$



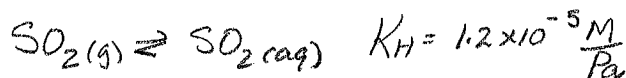
$\text{SO}_2(\text{g})$

↑

$31.8 \mu\text{g}/\text{m}^3$

"inexhaustible supply"

convert to Pa



↑

↑

↑

$$K_{a1} = \frac{x^2}{[\text{SO}_2(\text{aq})]}$$

$$K_H \cdot P_{\text{SO}_2}$$

$$\therefore x^2 = K_{a1} [\text{SO}_2(\text{aq})]$$

$$= K_{a1} K_H P_{\text{SO}_2}$$

$$\text{and } [\text{H}^+] = \sqrt{K_{a1} K_H P_{\text{SO}_2}}$$

$$31.8 \frac{\mu\text{g}}{\text{m}^3} \times \frac{1 \text{ mol}}{64.0 \text{ g}} \times \frac{1 \text{ g}}{10^6 \mu\text{g}} \times 8.314 \frac{\text{J}}{\text{mol K}} \cdot 298 \text{ K} = 1.23 \times 10^{-3} \text{ Pa}$$

$$(P = \frac{n}{V} RT) \quad \left[\frac{\text{mol}}{\text{m}^3} \cdot \frac{\text{kg m}^2 \text{ s}^{-2}}{\text{mol K}} \cdot \text{K} \right] \Rightarrow \left[\text{kg m}^{-1} \text{ s}^{-2} \right] \Rightarrow [\text{Pa}]$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log \left[(1.7 \times 10^{-2}) (1.2 \times 10^{-5}) (1.23 \times 10^{-3}) \right]^{1/2}$$

$$= 4.80$$

2. In an effort to compare the water solubility of two atmospheric sulfur containing gases, you manage to track down the following Henry's law constants from two independent sources (both reported at 25°C). K_H for methane thiol (methyl mercaptan) is reported as $830 \text{ Pa m}^3 \text{ mol}^{-1}$ whereas the K_H given for dimethyl sulfide was reported as 0.41 M atm^{-1} . Which gas is more water soluble? (Note that the reaction used to define K_H in these two sources is reversed).

$$K_H^{\text{CH}_3\text{SH}} = 830 \text{ Pa m}^3 \text{ mol}^{-1}$$

\uparrow pressure \uparrow conc⁻¹

$$K_H = \frac{P_{\text{CH}_3\text{SH}}}{[\text{CH}_3\text{SH}]}$$

$$K_H^{\text{DMS}} = 0.41 \text{ M atm}^{-1}$$

\uparrow conc \uparrow pressure⁻¹

$$K_H = \frac{P_{\text{DMS}}}{[\text{DMS}]}$$

There are two issues here; ① units are different
 ② definitions of K_H different

Let's convert the first one from Pa and mol m^{-3} to atm and M.

$$830 \text{ Pa} \frac{\text{m}^3}{\text{mol}} \times \frac{1 \text{ atm}}{101,300 \text{ Pa}} \times \frac{10^3 \text{ L}}{1 \text{ m}^3} = 8.19 \text{ atm} \frac{\text{L}}{\text{mol}}$$

Now, let's invert this value to compare it to DMS

$$\frac{0.12 \text{ M atm}^{-1}}{\uparrow K_H^{\text{CH}_3\text{SH}}} \quad \text{vs} \quad \frac{0.41 \text{ M atm}^{-1}}{\uparrow K_H^{\text{DMS}}}$$

Therefore, in equilibrium between gas phase and water, DMS will have greater aqueous conc.

3. Derive each of the following.

a) The equilibrium vapour pressure of water in the atmosphere is given by;

$$P_{\text{H}_2\text{O}} = [\text{H}_2\text{O}(\text{g})] RT, \text{ where } [\text{H}_2\text{O}(\text{g})] \text{ is the molar concentration of water vapour.}$$

b) The fractional abundance (α_x) for a species 'x' in an aqueous phase aerosol (partitioning between the gas and aqueous phases) is given by;

$$\alpha_x = \frac{P_x K_H V_L}{P_x K_H V_L + (P_x / RT)}$$

where K_H is the Henry's law constant for x and v_L is the volume of the liquid aerosol per volume of air.

a) $PV = nRT$ for any gas

$$\therefore P_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{V} RT = [\text{H}_2\text{O}(\text{g})] RT$$

b)
$$\alpha_x = \frac{n_{x(\text{aq})}}{n_{x(\text{aq})} + n_{x(\text{g})}}$$

where $n_{x(\text{aq})} = [X(\text{aq})] \cdot V_{\text{aerosol}}$

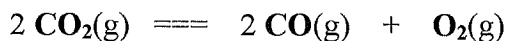
$$= K_H \cdot P_{x(\text{g})} \cdot V_L \cdot V_{\text{air}}$$

where $V_L = \frac{V_{\text{aerosol}}}{V_{\text{air}}}$

and $n_{x(\text{g})} = (P_{x(\text{g})} / RT) V_{\text{air}}$

$$\begin{aligned} \therefore \alpha_x &= \frac{K_H \cdot P_x \cdot V_L \cdot V_{\text{air}}}{(K_H \cdot P_x \cdot V_L \cdot V_{\text{air}}) + (P_x / RT) V_{\text{air}}} \\ &= \frac{K_H \cdot P_x \cdot V_L}{K_H \cdot P_x \cdot V_L + (P_x / RT)} \end{aligned}$$

4. At the high temperatures of exhaust gases that are emitted from automobiles, the reaction below has an equilibrium constant of 1×10^{-13} atm.



a) If the percentages by volume of the exhaust gases are 0.30, 13 and 4.0 for CO , CO_2 , and O_2 (respectively), what is the reaction quotient for the above reaction and which products will be produced as the reaction proceeds towards equilibrium?

a) $K = \frac{P_{\text{CO}}^2 \cdot P_{\text{O}_2}}{P_{\text{CO}_2}^2} = 1 \times 10^{-13} \text{ atm}$, where partial pressures are given in atm.

since $P_x = X \cdot P_T$, $P_{\text{CO}} = \left(\frac{0.3}{100}\right) P_T$

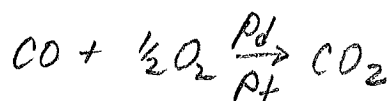
$$P_{\text{O}_2} = \left(\frac{4}{100}\right) P_T$$

$$P_{\text{CO}_2} = \left(\frac{13}{100}\right) P_T$$

\therefore reaction quotient, $Q = \frac{(0.003 P_T)^2 (0.04 P_T)}{(0.13 P_T)^2} = 2.1 \times 10^{-5} P_T$

$Q \gg K$ \therefore reaction shifts LEFT toward reactants

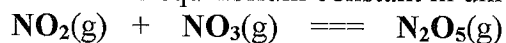
b) See page 94 (text)



chemically reduces NO and oxidizes CO on high surface area catalyst

oxidized on Palladium or Platinum catalyst

5. The elementary reaction below is a possible source of cloud water nitrate. If the rate coefficients for the forward and reverse reactions are $1.5 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}$ and $5.0 \times 10^{-2} \text{ s}^{-1}$, respectively, what is the value of the equilibrium constant in units of M?



$$\begin{aligned} \text{rate forward} &= k_2 [\text{NO}_2(\text{g})][\text{NO}_3(\text{g})] \\ &= 1.5 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1} [\text{NO}_2(\text{g})][\text{NO}_3(\text{g})] \end{aligned}$$

$$\begin{aligned} \text{rate reverse} &= k_1 [\text{N}_2\text{O}_5(\text{g})] \\ &= 5.0 \times 10^{-2} \text{ s}^{-1} [\text{N}_2\text{O}_5(\text{g})] \end{aligned}$$

at steady state (ie. equilibrium),

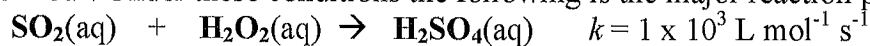
$$\text{rate forward} = \text{rate reverse}$$

$$\therefore 1.5 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1} [\text{NO}_2(\text{g})][\text{NO}_3(\text{g})] = 5.0 \times 10^{-2} \text{ s}^{-1} [\text{N}_2\text{O}_5(\text{g})]$$

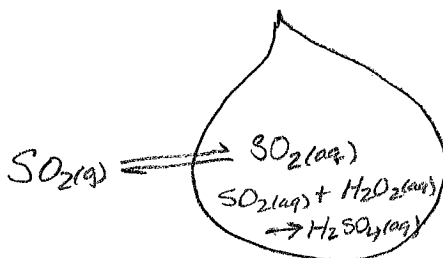
$$\frac{[\text{N}_2\text{O}_5(\text{g})]}{[\text{NO}_2(\text{g})][\text{NO}_3(\text{g})]} = \frac{1.5 \times 10^{-12} \text{ M}^{-1} \text{ s}^{-1}}{5.0 \times 10^{-2} \text{ s}^{-1}}$$

$$\therefore K = 3.0 \times 10^{-11} \text{ M}^{-1}$$

6. Under very humid conditions, SO_2 oxidation has been observed to occur at rates up to 30% per hour. Under these conditions the following is the major reaction pathway.



Assuming that $\text{SO}_2(\text{g})$ and $\text{SO}_2(\text{aq})$ are at all times equilibrated, what does this suggest about the concentration of $\text{H}_2\text{O}_2(\text{aq})$ under these conditions?



If oxidation rate is 30% per hour, this means

$$k' = 0.3 \text{ hr}^{-1} \text{ (pseudo first order)}$$

$$\text{rate oxidation} = k [\text{SO}_2(\text{aq})] [\text{H}_2\text{O}_2(\text{aq})]$$

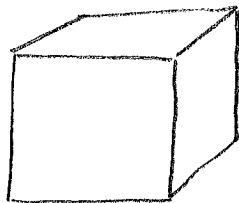
$$= k' [\text{SO}_2(\text{aq})]$$

$$\text{where } k' = k [\text{H}_2\text{O}_2(\text{aq})]$$

$$\therefore [\text{H}_2\text{O}_2(\text{aq})] = \frac{k'}{k} = \frac{0.3 \text{ hr}^{-1} \times \frac{1 \text{ hr}}{3600 \text{ s}}}{1 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}}$$

$$= 8.3 \times 10^{-8} \text{ M}$$

7. Consider two clouds in which $5 \times 10^{-4} \text{ kg m}^{-3}$ of water condenses. The CCN concentration in each cloud is 100 and 1000 cm^{-3} , respectively. Assuming that the liquid water is equally distributed among the CCN, what is the droplet size (diameter in μm) in each cloud? What might the different concentrations of CCN indicate about the locations of the clouds?



$$\text{CCN} = 100 \text{ cm}^{-3} = 1 \times 10^8 \text{ m}^{-3}$$

$$\text{mass H}_2\text{O}(l) = 5 \times 10^{-4} \text{ kg m}^{-3}$$

\therefore mass of each droplet

$$= \frac{5 \times 10^{-4} \text{ kg m}^{-3}}{1 \times 10^8 \text{ m}^{-3}}$$

$$= 5 \times 10^{-12} \text{ kg}$$

and since $\rho = 1.0 \frac{\text{kg}}{\text{L}}$

$$\therefore V = 5 \times 10^{-12} \text{ L} \times \frac{10^3 \text{ cm}^3}{\text{L}} = 5 \times 10^{-9} \text{ cm}^3$$

since $V_{\text{sphere}} = \frac{4}{3} \pi r^3$

$$r = \sqrt[3]{\frac{V}{\frac{4}{3} \pi}}$$

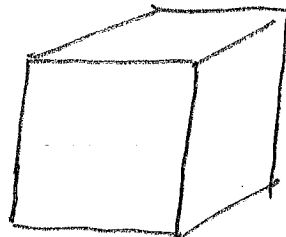
$$= 1 \times 10^{-3} \text{ cm}$$

converting to microns

$$(1 \times 10^{-3} \text{ cm}) \times \frac{1 \text{ m}}{100 \text{ cm}} \times \frac{10^6 \mu\text{m}}{1 \text{ m}}$$

$$r = 10 \mu\text{m}$$

\therefore diameter = $20 \mu\text{m}$



$$\text{CCN} = 1000 \text{ cm}^{-3} = 1 \times 10^9 \text{ m}^{-3}$$

$$\text{mass H}_2\text{O}(l) = 5 \times 10^{-4} \text{ kg m}^{-3}$$

mass per droplet

$$= \frac{5 \times 10^{-4} \text{ kg m}^{-3}}{1 \times 10^9 \text{ m}^{-3}}$$

$$= 5 \times 10^{-13} \text{ kg}$$

and $V = 5 \times 10^{-13} \text{ L}$

or $5 \times 10^{-10} \text{ cm}^3$

$$\therefore r = \sqrt[3]{\frac{5 \times 10^{-10} \text{ cm}^3}{\frac{4}{3} \pi}}$$

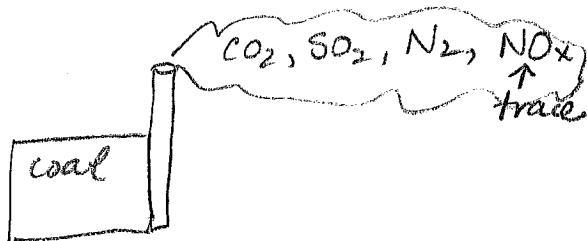
$$= 5 \times 10^{-4} \text{ cm}$$

$$= 5 \mu\text{m}$$

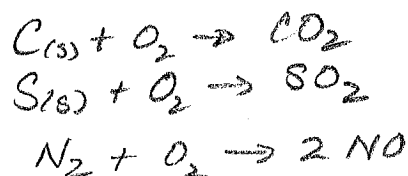
\therefore diameter = $10 \mu\text{m}$

(ie. 10x more droplets with each droplet half the diameter)

8. A coal burning power station burns 10,000 tonnes of coal per day. The coal is 2.35% sulfur by mass (assume the remaining mass is carbon). The stack gases contain CO_2 , SO_2 from the coal plus 150 ppm_v of NO_x and unreacted N_2 . Using an average molar mass of 38 g mol^{-1} for NO_x , calculate the total amount (tonnes) of acidic gases CO_2 , SO_2 and NO_x from the plant per day as well as the mole ratio of SO_2/NO_x in the flue gas.



10,000 tonnes per day
2.35% S by mass



mass sulfur dioxide per day = mass sulfur burned
 $\times \frac{\text{MW}_{\text{SO}_2}}{\text{MW}_\text{S}}$

$$= \left(\frac{2.35}{100} \right) 10,000 \text{ t} \times \frac{64.1 \text{ g/mol}}{32.1 \text{ g/mol}} = 469 \text{ t}$$

mass carbon dioxide per day = mass carbon burned $\times \frac{\text{MW}_{\text{CO}_2}}{\text{MW}_\text{C}}$

$$= \left(\frac{97.65}{100} \right) 10,000 \text{ t} \times \frac{44.0 \text{ g/mol}}{12.0 \text{ g/mol}} = 3.58 \times 10^4 \text{ t}$$

to calculate the amount of N_2 in flue gas, we need to determine the number of moles of O_2 consumed

$$\begin{aligned} n_{\text{O}_2 \text{ consumed}} &\approx n_{\text{CO}_2 \text{ produced}} + n_{\text{SO}_2 \text{ produced}} \\ &= 8.14 \times 10^8 \text{ mol} + 7.32 \times 10^6 \text{ mol} \\ &= 8.2 \times 10^8 \text{ mol O}_2 \text{ consumed/day} \end{aligned}$$

$$\therefore n_{\text{N}_2 \text{ in flue gas/day}} = \left(\frac{78.05}{20.95} \right) \times 8.2 \times 10^8 \frac{\text{mol}}{\text{day}} = 3.1 \times 10^9 \frac{\text{mol}}{\text{day}}$$

Therefore, the total emissions of all gases in stack are:

CO ₂	8.1 × 10 ⁸	mol/day
SO ₂	7.3 × 10 ⁶	mol/day
N ₂	3.1 × 10 ⁹	mol/day

$$3.9 \times 10^9 \text{ mol/day}$$

Since the NO_x emissions are 150 ppmv

$$\begin{aligned} n_{\text{NO}_x} &= \left(\frac{150}{10^6} \right) 3.9 \times 10^9 \frac{\text{mol}}{\text{day}} \\ &= 5.8 \times 10^5 \text{ mol/day} \end{aligned}$$

using average molar mass = 38 g/mol,

$$\begin{aligned} \text{total emission NO}_x &= 5.8 \times 10^5 \frac{\text{mol}}{\text{day}} \times 38 \text{ g/mol} \\ &= 2.2 \times 10^7 \text{ g/day} = 22 \text{ t/day} \end{aligned}$$

mole ratio of SO₂/NO_x in flue gas

$$= \frac{7.3 \times 10^6}{5.8 \times 10^5} = 12$$

9. A fly ash aerosol with a density of 1.8 g mL^{-1} consists of particles averaging $10 \text{ }\mu\text{m}$ in diameter and a concentration of $800 \text{ }\mu\text{g/m}^3$. Use this information to calculate the average settling velocity (cm s^{-1}) and deposition rate ($\text{g m}^{-2} \text{ s}^{-1}$) of particles in still air.

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

$$\rho_p = 1.8 \frac{\text{g}}{\text{mL}} \times \frac{1 \text{ mL}}{1 \text{ cm}^3} \times \frac{10^6 \text{ cm}^3}{1 \text{ m}^3} = 1.8 \times 10^6 \text{ g m}^{-3}$$

$$\rho_{air} = 1.2 \times 10^3 \text{ g m}^{-3} \quad (\text{pg. 142}) \quad \text{at } 25^\circ\text{C}$$

$$C = 1.016 \quad (\text{Table 6.4, pg. 143})$$

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

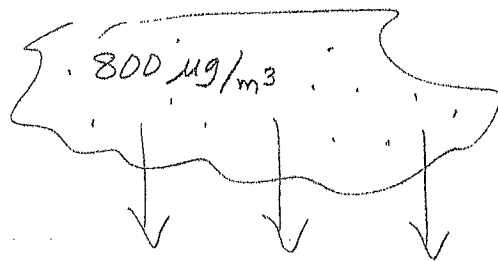
$$d_p = 10 \text{ }\mu\text{m} = 10 \times 10^{-6} \text{ m}$$

$$\eta_{air} = 1.9 \times 10^{-2} \text{ g m}^{-1} \text{ s}^{-1} \quad \text{at } 25^\circ\text{C} \quad (\text{pg. 142})$$

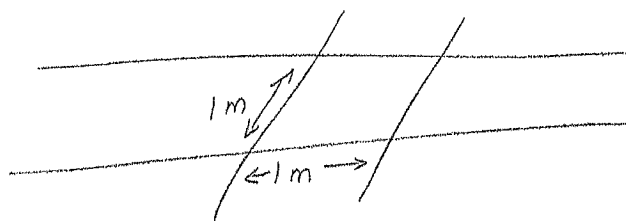
$$\therefore V_t = \frac{[(1.8 \times 10^6 - 1.2 \times 10^3) \frac{\text{g}}{\text{m}^3}] (1.016) (9.8 \frac{\text{m}}{\text{s}^2}) (10 \times 10^{-6} \text{ m})^2}{18 (1.9 \times 10^{-2} \text{ g m}^{-1} \text{ s}^{-1})}$$

$$= \frac{1.8 \times 10^{-3} \text{ g s}^{-2}}{0.342 \text{ g m}^{-1} \text{ s}^{-1}} = 5.3 \times 10^{-3} \text{ m s}^{-1}$$

$$V_t = 0.53 \text{ cm s}^{-1}$$



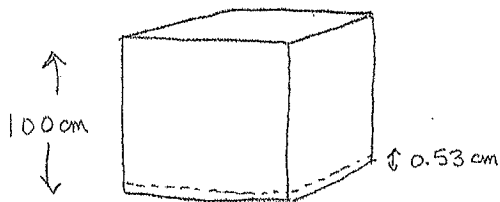
0.53 cm s^{-1}



1 m^3 of air contains 800 μg particles
settling at velocity of 0.53 cm per second

\therefore mass of particles that settle out
per square meter per second

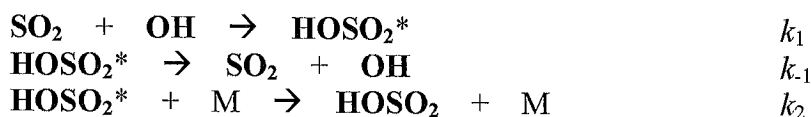
= mass of particles in a 0.53 cm
slab of air



$$\frac{800 \mu\text{g}}{\text{m}^3} \times \frac{5.3 \times 10^{-3} \text{m}^3}{\text{m}^2 \text{s}^{-1}}$$

$$= 4.2 \mu\text{g m}^{-2} \text{s}^{-1}$$

10. The homogeneous gas phase reaction of SO_2 with OH is represented by the following mechanism, where HOSO_2^* represents an electronically excited state.



- a) Write an expression for the rate of formation of HOSO_2
 b) Modify the answer to part (a) by applying the steady state approximation to HOSO_2^*
 c) Does your answer to (b) change if you consider the first two steps above as a pre-equilibrium step (Note: $K_{\text{eq}} = k_1/k_{-1}$)

a) $\text{rate of formation of HOSO}_2 = k_2 [\text{HOSO}_2^*] [\text{M}]$

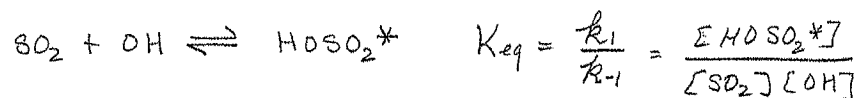
b) $\text{rate prodn HOSO}_2^* = \text{rate loss of HOSO}_2^*$

$$\begin{aligned} k_1 [\text{SO}_2] [\text{OH}] &= k_{-1} [\text{HOSO}_2^*] + k_2 [\text{HOSO}_2^*] [\text{M}] \\ &= (k_{-1} + k_2 [\text{M}]) [\text{HOSO}_2^*] \end{aligned}$$

$$\therefore [\text{HOSO}_2^*] = \frac{k_1 [\text{SO}_2] [\text{OH}]}{k_{-1} + k_2 [\text{M}]}$$

So $\text{rate of formation of HOSO}_2 = \frac{k_1 k_2 [\text{SO}_2] [\text{OH}] [\text{M}]}{k_{-1} + k_2 [\text{M}]}$

- c) If $k_{-1} [\text{HOSO}_2^*] \gg k_2 [\text{HOSO}_2^*]$, then a pre-equilibrium exists and we can write



So $[\text{HOSO}_2^*] = \frac{k_1}{k_{-1}} [\text{SO}_2] [\text{OH}]$

$$\text{So rate of formation of } \text{HOSO}_2 = \frac{k_1 k_2 [\text{SO}_2][\text{OH}][\text{M}]}{k_{-1}}$$

So, when step ② is faster than step ③
we have a pre-equilibrium and the rate
expression for formation of HOSO_2 simplifies

Note from b)
$$\text{Rate} = \frac{k_1 k_2 [\text{SO}_2][\text{OH}][\text{M}]}{k_{-1} + k_2 [\text{M}]}$$

when step ② is faster than step ③

we can write $k_{-1} [\text{HOSO}_2^*] \gg k_2 [\text{M}][\text{HOSO}_2^*]$

and therefore $k_{-1} \gg k_2 [\text{M}]$

and the expression simplifies to

$$\text{Rate} = \frac{k_1 k_2 [\text{SO}_2][\text{OH}][\text{M}]}{k_{-1}}$$