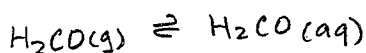
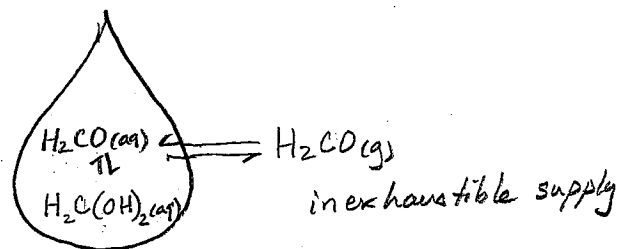


Chemistry of Aqueous Gases: Acid Rain

1. Given that formaldehyde dissolves in water ($K_H = 1.7 \text{ M atm}^{-1}$) and reacts to form a hydrate ($K_{eq} = 2 \times 10^3$), calculate the total concentration of formaldehyde in rainwater if its atmospheric concentration $6 \times 10^9 \text{ molec cm}^{-3}$ (0.22 ppbv).

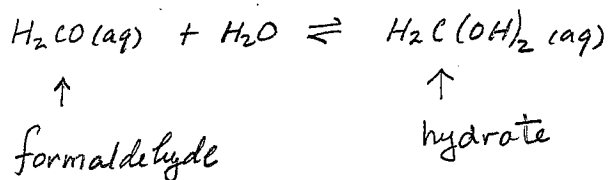
[Answer: Total (CH_2O) = $0.75 \mu\text{M}$]



$$K_{eq} = \frac{[\text{H}_2\text{CO(aq)}]}{P_{\text{H}_2\text{CO(g)}}}$$

↑
 K_H (Henry's Law Const.)

$$\therefore [\text{H}_2\text{CO(aq)}] = K_H \cdot P_{\text{H}_2\text{CO}}$$



$$K_{eq} = \frac{[\text{H}_2\text{C(OH)}_2\text{(aq)}]}{[\text{H}_2\text{CO(aq)}]} \quad \therefore [\text{H}_2\text{C(OH)}_2\text{(aq)}] = K [\text{H}_2\text{CO(aq)}]$$

The total amt of formaldehyde dissolved; $T_{\text{H}_2\text{CO}}$

$$\begin{aligned} T_{\text{H}_2\text{CO}} &= [\text{H}_2\text{CO(aq)}] + [\text{H}_2\text{C(OH)}_2\text{(aq)}] \\ &= [\text{H}_2\text{CO(aq)}] + K [\text{H}_2\text{CO(aq)}] \\ &= [\text{H}_2\text{CO(aq)}] (1 + K) = K_H \cdot P_{\text{H}_2\text{CO}} (1 + K) \end{aligned}$$

where $K_H = 1.7 \text{ M atm}$

$$K = 2 \times 10^3$$

$$P_{\text{H}_2\text{CO}} = \frac{0.22}{10^9} \cdot P_T = 2.2 \times 10^{-10} \text{ atm}$$

$$\therefore T_{\text{H}_2\text{CO}} = 7.5 \times 10^{-7} \text{ M}$$

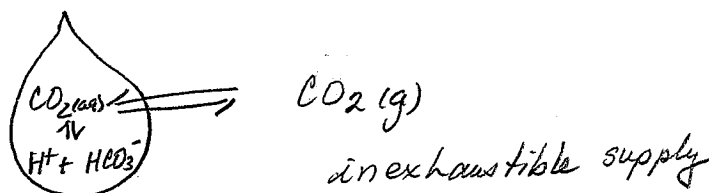
2. Calculate the pH of natural rainwater in equilibrium with CO_2 at an atmospheric concentration of 380 ppm_v.

$$K_H = 0.039 \text{ M atm}^{-1}$$

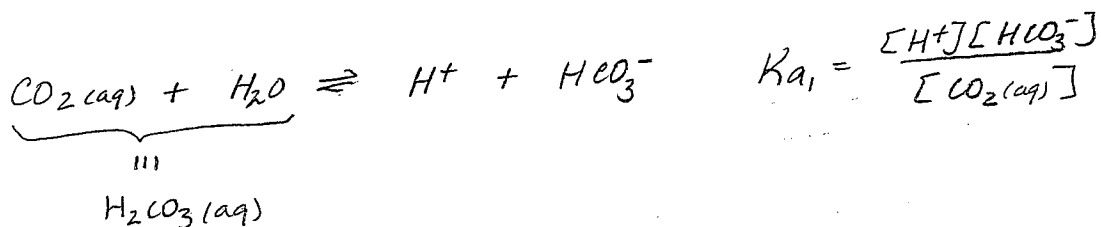
$$K_{a1} = 4.5 \times 10^{-7}$$

$$K_{a2} = 4.7 \times 10^{-11}$$

[Answer: pH = 5.60]



$$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq}) \quad K_H = \frac{[\text{CO}_2(\text{aq})]}{P_{\text{CO}_2}} = 0.039 \text{ M atm}^{-1}$$



Since $\text{CO}_2(\text{aq})$ is from an inexhaustible supply in atmosphere $[\text{CO}_2(\text{aq})]$ in rain drop remains constant at $K_H \cdot P_{\text{CO}_2}$

So at 380 ppm_v of CO_2 and a total atm. pressure of 1.00 atm, we have $\frac{380}{106} = 3.80 \times 10^{-4} \text{ atm}$

$$\therefore [\text{CO}_2(\text{aq})] = (0.039 \text{ M atm}^{-1})(3.80 \times 10^{-4} \text{ atm}) = 1.48 \times 10^{-5} \text{ M}$$

This dissociates in water to yield H^+ and HCO_3^- .

Since the second dissociation constant $K_{a2} \ll K_{a1}$ the amt of H^+ from the second dissociation is negligible and we can write $[\text{H}^+] \approx [\text{HCO}_3^-]$

$$K_{a_1} = \frac{[H^+]^2}{[CO_2(aq)]} \leftarrow 1.48 \times 10^{-5} M$$

↑
K_H · P_{CO₂}

4.5 × 10⁻⁷

$$\therefore [H^+]^2 = 6.67 \times 10^{-12}$$

$$\text{and } [H^+] = 2.58 \times 10^{-6} M$$

$$\text{and } pH = 5.6$$

In general, the pH of rain drop in equilibrium with an inexhaustible supply of an acidic gas with one dominant acid dissociation constant is given by

$$[H^+] = [K_{a_1} K_H \cdot P_{CO_2}]^{1/2}$$

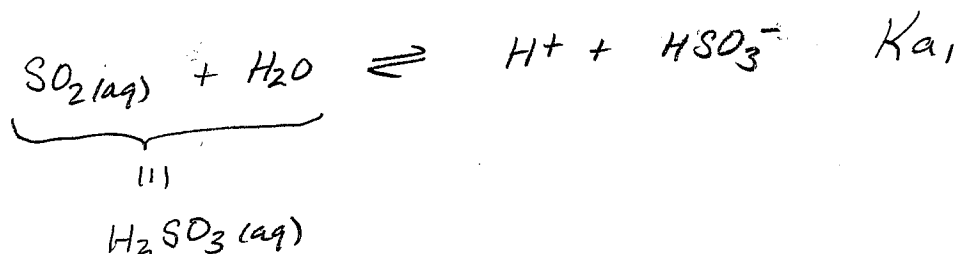
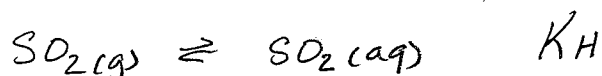
3. Calculate the pH of natural rainwater in equilibrium with SO_2 at an atmospheric concentration of 5.0 ppbv.

$$K_H = 5.4 \text{ M atm}^{-1}$$

$$K_{a1} = 1.7 \times 10^{-2}$$

$$K_{a2} = 6.4 \times 10^{-8}$$

[Answer: pH = 4.57]



$$[\text{H}^+] = [K_{a1} K_H \cdot P_{\text{SO}_2(\text{g})}]^{1/2}$$

$$= 4.57$$

Note 1: SO_2 partitions into water from gas phase more favourably than $\text{CO}_2(\text{g})$ ($K_H^{\text{SO}_2} > K_H^{\text{CO}_2}$) and is more acidic than $\text{CO}_2(\text{aq})$ ($K_{a1}^{\text{SO}_2} > K_{a1}^{\text{CO}_2}$) \therefore smaller conc. of $\text{SO}_2(\text{g})$ has greater impact on lowering the pH!