Class 8) What is the equilibrium pH of pure water kept open to the atmosphere? Also find the C_T and alkalinity of the system.

Given: Henry' constant for carbon dioxide gas $[CO_{2(g)}]$, $K_H = 10^{1.5}$ atm M^{-1}. The average concentration of $CO_{2(g)}$ in air is taken to be 310 ppm ($10^{-3.5}$ atm) at 25° C.
Look for latest $CO_{2(g)}$ as being continuously monitored at Mauna Loa observatory in Hawaii, USA. https://www.esrl.noaa.gov/gmd/obop/mlo/

Sol: Due to partitioning of $CO_{2(g)}$ in water, some amount of the gas would dissolve in water until an equilibrium is reached.

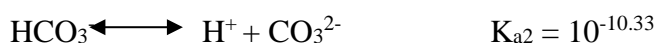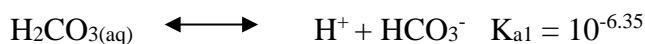Species: H^+, OH^-, (H_2O), CO_3^{2-}, HCO_3^-, $H_2CO_{3(aq)}$.

Components: - H^+, (H_2O), CO_3^{2-}

This equilibrium is governed by a constant ratio between the partial pressure of $CO_{2(g)}$ in air to the concentration of carbon dioxide dissolved in water, $CO_{2(aq)}$, also called $H_2CO_{3(aq)}$. This can be written as the Henry's Law,

$$K_H = \frac{p_{CO_2}}{[H_2CO_{3(aq)}]} \qquad (1)$$

$$[H_2CO_{3(aq)}] = 10^{-3.5}/10^{1.5} = 10^{-5} M$$

Acid-base reactions and equilibrium constants: -

$H_2CO_{3(aq)} \longleftrightarrow H^+ + HCO_3^-$ $K_{a1} = 10^{-6.35}$

$HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$ $K_{a2} = 10^{-10.33}$

$K_{a1} = 10^{-6.35} = [H^+] * [HCO_3^-]/[H_2CO_{3(aq)}]$

Or $[HCO_3^-] = 10^{-11.35} / [H^+]$

$K_{a2} = 10^{-10.33} = [H^+] *[CO_3^{2-}]/ [HCO_3^-]$

Or $[CO_3^{2-}] = 10^{-21.68} / [H^+]^2$

Charge Balance:-

$[H^+] = [OH^-] + [HCO_3^-] + 2* [CO_3^{2-}]$

Since dissolution of $CO_{2(aq)}$ in water is generating carbonic acid, $H_2CO_{3(aq)}$, to pure water, we can assume pH < 7 sufficiently so as to neglect $[OH^-]$ and $[CO_3^{2-}]$ from the charge balance equation relative to the other two species.

Or $[H^+] \sim 10^{-11.35} / [H^+]$

Or $[H^+] = $ sqrt $(10^{-11.35}) = 2.113*10^{-6}$ M or **pH = 5.675**

Or $[H^+] = 2.114*10^{-6}$ M or pH = 5.675

Now check back our assumption, $[OH^-] = 4.73*10^{-9} = 10^{-8.325}$ M $<< 2.114*10^{-6}$ M, and

$[CO_3^{-2}] = 10^{-21.68} / [H^+]^2 = 10^{-10.48}$ M $<< 2.114*10^{-6}$ M (verified)

$[HCO_3^-] = 10^{-11.35} / [H^+] = 10^{-5.75}$ M

$C_T = [H_2CO_{3(aq)}] + [HCO_3^-] + [CO_3^{2-}] = 10^{-5}$ M $+ 10^{-5.75}$ M $+ 10^{-10.48}$ M (negligible here) $=$ **$10^{-4.92}$ M**

$Alk_{mix} = - [H^+] + [OH^-] + [HCO_3^-] + 2*[CO_3^{2-}]$

$\quad = -2.114*10^{-6} +4.73*10^{-9} + 10^{-5.75} +2* 10^{-10.48}$

.$\quad$ **$= 1.04*10^{-6}$ M**

Note that C_T for open system is a function of pH. If to the above system you begin titrating by adding a strong base the pH would gradually increase, but at any pH value the $[H_2CO_{3(aq)}]$ would be constant, governed by Henry's Law given by eq. 1. However, C_T would continue to increase with pH as the water would keep on facilitating formation of bicarbonate ions and later carbonate ions.

[Plot $logC_T$ as a function of pH]

Table 5-2. Henry's Constants of Some Environmentally Important Gases

Compound	$H^{(a)}$	
	H_{cc} or H_{mm} $(L_L/L_G)^{(b)}$	H_{pm} $(atm/(mol/L_L))$
Nitrogen	63.8	1560
Hydrogen	51.5	1260
Carbon monoxide	42.9	1050
Oxygen	32.3	790
Methane	31.7	776
Cyclohexane	7.17	175
Ozone	4.37	107
Radon	1.85	45.3
Carbon dioxide	1.18	28.8
Carbon tetrachloride	1.11	27.2
Tetrachloroethylene (PCE)	0.82	20
Trichloroethylene (TCE)	0.45	11
Hydrogen sulfide	0.40	9.8
Ethylbenzene	0.32	7.8
Toluene	0.27	6.6
Chloroform	0.16	4.0
2,2',5,5' Tetrachlorobiphenyl(s)	0.038	0.93
Sulfur dioxide	0.033	0.81
Bromoform	0.029	0.70
Benzene	0.0090	0.22
Ethyl acetate	0.0053	0.13
Hydrogen cyanide	0.0016	0.040
Acetone	0.0015	0.037
Ammonia	6.95e−4	0.017
Acetic acid	5.31e−5	0.0013

[a] Values are for 25°C.[10]

[b] Values in this column are valid for any units of concentration, provided that the same units are used for both the liquid and gas phases.

Source: manuscript in preparation by Benjamin and Lawler, 2004