

pH Control in Water Treatment Plant by the Addition of Carbon Dioxide

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Abstract

pH Control is often carried in the pretreatment section of water treatment plant into two locations, in the primary and secondary steps. In the primary step, sulfuric acid (H_2SO_4) is added into the softened water just before filtration to maintain a pH level of about 6.5 to allow any un-precipitated materials to be filtered. A further addition of sulfuric acid is applied to the filtered water through secondary acidification step. The main purpose of this secondary acidification is to reduce the bicarbonate content and avoid calcium carbonate precipitation. The pH is reduced into the range of 5.9 to 6.4 to meet the RO membrane specifications. In the post treatment section, sodium carbonate is dosed for final pH correction to 7.5-8.0 range as to ensure the desired quality of product water.

Carbon dioxide, CO_2 , is gaining acceptance for pH control in water treatment plant. It reduces high pH levels quickly. It is not stored as an acid solution so it is considered safer than sulfuric acid. It is non-corrosive to pipes and equipment. It requires less equipment and monitoring costs. It requires no handling costs. It can be utilized via a completely automated system.

In this paper, the utilization of carbon dioxide for pH control in water treatment plant will be reviewed. Comparison between sulfuric acid and carbon dioxide will be discussed. The variation of carbon dioxide concentrations with pH value are also presented. It was found that carbon dioxide gives better control of pH than sulfuric acid.

Introduction

Carbon dioxide, the final oxidation product of carbon, is not very reactive at ordinary temperatures. However, in water solution it forms carbonic acid, HCO_3 which forms salts and esters through the typical reactions of a weak acid. The first ionization constant is 3.5×10^{-7} at 291 K, the second is 4.4×10^{-11} at 298 K. The pH of saturated carbon dioxide solutions varies from 3.7 at 101 kPa (1 atm) to 3.2 at 2.370 kPa (23.4 atm). A solid hydrate, $CO_2 \cdot 8H_2O$, separates from aqueous solutions of carbon dioxide that are chilled at elevated pressures.

Carbon dioxide shows a self-buffering as it reaches neutral pH levels. This self-buffering feature allows precise end-point control without the danger of overshooting into undesirable low pH levels. Carbon dioxide also exhibits greater storage capacity which makes it possible to store up to twice as much neutralizing agent in the same amount of storage space with no increase in weight. Raw water in Water Treatment Plants with a temperature in the range of 50-60 °C is pumped from deep wells into the plants. The first step in treatment of the raw water is cooling. The temperature of water is brought down to 30-35 °C. Cooling towers also serve to assist in iron removal by oxidation. Carbon dioxide (CO_2) is also removed by partial declassification. The effluent from the cooling towers is divided into two streams. The mainstream goes to the pretreatment facilities and then fed to the reverse osmosis (RO) units. The second stream, the slipstream, is sent directly to filters and then to a mixing chamber for blending with the RO permeate.

The chemical pretreatment of the mainstream includes lime-soda softening, flocculation, coagulation and acidification. Acidification is carried into two locations within the plant. In the primary acidification step, sulfuric acid (H_2SO_4) is added into the softened water just before

filtration to maintain a pH level of about 6.5-7.0 to allow any un-precipitated materials to be dissolved. A further addition of sulfuric acid is applied to the filtered water through secondary acidification step. The main purpose of this secondary acidification is to reduce the carbonate content and avoid calcium carbonate precipitation. The pH is reduced into the range 5.9 to 6.4 to meet the RO membrane requirements. So in secondary acidification step, the softened water from the precipitators is pH adjusted by means of addition of sulfuric acid just before the upflow filtration.

The filtered mainstream water flows into a low-capacity buffer storage tank, which not only ensures a steady supply to the RO plant, but also acts as a reserve for washing of sand filters. The softened and filtered water is stored in a filtered water tank so called buffer tank. Before entering the RO system, an antiscalant (sodium hexametaphosphate, $\text{Na}_6\text{P}_6\text{O}_{18}$) is added into the water in the amount of 3-4 ppm to prevent calcium deposition. Sulfuric acid is also added to bring the pH level to 6.0. Membrane requirements should not be exceeded to avoid membrane deterioration. These include a pH of 5.9 to 6.4 and maximum silica and aluminum contents of 18 mg/l and 0.05 mg/l, respectively. Fouling index should be below 3 and temperature is maintained in the range 35 to 40 °C.

After RO unit, the product water (permeate) is cascaded (to remove carbon dioxide) into a blending chamber where it is mixed with the slipstream water. The slipstream flow rate is varied in such a way, as to ensure the desired quality and quantity of blended water. At the same time, the blended water is dosed with sodium carbonate for final (soda ash) pH correction to 7.5-8.0 range, and chlorine for disinfection. From the blending chamber, the water is then pumped to a storage tank and then to the Riyadh city distribution system.

Factors Affecting pH

pH is a measure of the activity of hydrogen ions present in water. It is the negative logarithm of hydrogen ion concentrations. It can be written as

$$\text{pH} = -\log [\text{H}^+]$$

Water molecules dissociate into hydrogen and hydroxyl ions. The multiplication of these ions is constant known as dissociation constant, K.

$$K = [\text{H}^+] [\text{OH}^-] = 10^{-14}$$

At neutral condition, equal concentrations of hydrogen and hydroxyl ions are present. So the pH is equal to 7. When pH value is below 7, more hydrogen ions exist and water trends to be acidic.

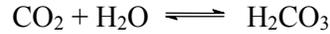
pH reflects the acidity or the basic nature of water. It is affected by the chemical constituents of water, e.g. carbon dioxide (CO_2), bicarbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}), hydroxyl ions (OH^-) and the equilibrium among these constituents. Temperature effects this equilibrium. The pH values decrease by about 0.45 as the temperature increases by 25 °C[1].

The addition of chlorine decreases the pH. Chlorine effectiveness is reduced due to reduction in the hypochlorous acid with the increase in the pH[2] as presented by the following reaction:



Chlorine becomes more effective at a pH value lower than 7[3]. At a pH level above 4, chlorine combines with water molecules to form hydrochloric acid plus hypochlorous acid which, in turn, yields the hypochlorite ion. The degree of ionization is dependent on pH, with HOCl occurring below 6 and almost complete ionization above 9.

Carbon dioxide dissolve in water forming carbonic acid according to the following reaction



Carbonic acid is then ionized into HCO_3^- species



The ionization constant for this reaction is 4.31×10^{-7} at 25 °C. The pH value is reduced to about 6.0 by dissolving carbon dioxide. Evolution of carbon dioxide from water leads an increase in the pH value according to the reverse of the net reaction of the preceding two reactions:



The decrease in the carbon dioxide concentration in water is due to the conversion of bicarbonate into carbonate. Carbon dioxide at concentrations of about 100 ppm or more increases water corrosivity significantly specially of traces amount of oxygen are existed [4].

The intensive growth of carbon dioxide that generated bacteria causes a reduction in the pH. Iron bacteria grow at a pH of 6.5. They turn water into red due to the formation of ferric hydroxide [5].

Alkalinity is considered an important parameter effecting the pH. Alkalinity depends on the concentration of bicarbonate, carbonate and hydroxide ions. Its value varies according to the temperature, pH and total dissolved solid (TDS) [6]. Alkalinity (Alk) often represented by the following equation;

$$\text{Alk} = [\text{OH}^-] + [\text{HCO}_3^-] - [\text{H}^+]$$

Where $[\text{OH}^-]$, $[\text{HCO}_3^-]$ and $[\text{H}^+]$ are concentrations of hydroxide, bicarbonate and hydrogen ions. Hydrogen ion concentration can be calculated from the alkalinity value by the following equation [7]:

$$[\text{H}^+] = \left[-\text{Alk} + \left\{ \text{Alk}^2 + 4(10^{-7.81} [\text{CO}_2]_{\text{gas}} + 10^{-14}) \right\}^{0.5} \right] / 2$$

At 25 °C, the alkalinity can be estimated by the following equations [8]:

$$\text{Bicarbonate Alk. as mg CaCO}_3 / \text{L} = \text{BA} = \{ \text{Talk} - 5 \times 10^{(\text{pH}-10)} \} / \{ 1 + 0.94 \times 10^{(\text{pH}-10)} \}$$

$$\text{Carbonate Alk. as mg CaCO}_3 / \text{L} = \text{CA} = 0.94 \times \text{BA} \times 10^{(\text{pH}-10)}$$

$$\text{Hydroxide Alk. as mg CaCO}_3 / \text{L} = \text{HA} = 5.0 \times 10^{(\text{pH}-10)}$$

$$\text{Free Carbon Dioxide mg CO}_2 / \text{L} = \text{FC} = 2.0 \times \text{BA} \times 10^{(\text{pH}-10)}$$

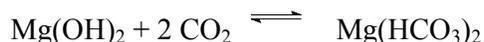
$$\text{Total Carbon Dioxide mg CO}_2 / \text{L} = \text{FC} + 0.44 (2\text{BA} + \text{CA})$$

Where Talk is the total alkalinity, BA is the bicarbonate alkalinity, CA is the carbonate alkalinity, HA is the hydroxide alkalinity and FC is the free carbon.

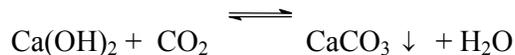
Role of pH in Lime Softening process

pH is increased during the soda and lime softening. The pH in the precipitators can be raised by the addition of an excess amount of lime. The addition of about 1.25 Meq/l of lime is sufficient to raise the pH to 11.0 [9]. It is clear that carbon dioxide and carbonate hardness (calcium and magnesium bicarbonate) are reduced by the addition of lime. The pH of the softened water is about 11. Sulfuric acid is then used to lower the pH to about 7.5 in order to prevent any deposition of the remained hardness. Calcium and magnesium are converted back into the soluble bicarbonate forms. This practice is known as recarbonation. Carbon dioxide is often used for this purpose [10]. Recarbonation is used for two purposes in a lime-softening plant: (1) for pH adjustment, and (2) for the neutralization and precipitation of the calcium hydroxide in the primary basin effluent in cases where high-magnesium waters are softened by application of excess lime followed by recarbonation [11].

The conversion of calcium and magnesium back into the soluble bicarbonate forms are presented by the following equations:



If excess lime followed by recarbonation is used, there is too much calcium hydroxide present after sedimentation, and converting it to the soluble bicarbonate would unduly increase the hardness. It is necessary to precipitate it as calcium carbonate according to the reaction [11]:

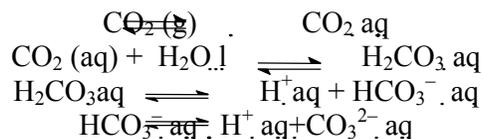


Sometimes it is possible to add enough additional carbon dioxide to convert a portion of the carbonate to the bicarbonate in the recarbonation basin between the primary and secondary basins and thus lower the pH to the desired figure, but because of the danger of redissolving some of the precipitated calcium carbonate, it is better to make a final pH adjustment by a final recarbonation just after filtration [11].

Recarbonation is usually used to adjust the pH value between 9.0 and 9.6 leaving the water slightly supersaturated [12]. A pH value of 8.3 would indicate equilibrium. When true equilibrium is reached, after-deposition will still occur, and if recarbonation is sufficient to prevent after-deposition, the water becomes corrosive when true equilibrium is reached.

Carbonate Species in Water

The reactions which take place when carbon dioxide dissolves in water can be represented by the following series of equilibria:



the notations (g), (l), (aq) refer to the state of the species, *i. e.* a gas, a liquid or in aqueous solution respectively. Unfortunately, it is difficult to distinguish between the species $\text{CO}_2(\text{aq})$ and $\text{H}_2\text{CO}_3(\text{aq})$

by analytical means. It is thus usual to lump the concentrations of $\text{CO}_2 \text{ aq}$ and $\text{H}_2\text{CO}_3 \text{ aq}$ together and to express this sum as the concentration of a hypothetical species, $\text{CO}_2^* \text{ aq}$.

The first three reactions are redefined in terms of these species:



The equilibrium relationships between the concentrations of these various species can then be written as:

$$\begin{aligned} K_0 &= \frac{[\text{CO}_2^*]}{f \cdot C_{\text{CO}_2}} \\ K_1 &= \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2^*]} \\ K_2 &= \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \end{aligned}$$

In these equations, $f \cdot C_{\text{CO}_2}$ is the fugacity of carbon dioxide in the gas phase and brackets represent total stoichiometric concentrations of the particular chemical species enclosed. $f \cdot C_{\text{CO}_2}$ is nearly equal the carbon dioxide partial pressure if assuming it behaves ideally. These equilibrium constants are functions of the temperature, pressure and composition (salinity) of the salt water. These constants can be given by following expressions [13,14,15]:

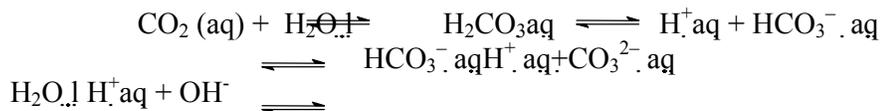
$$\ln(K_0) = 93.4517(100/T) - 60.2409 + 23.3585 \ln(T/100) + S(0.023517 - 0.023656(T/100) + 0.0047036(T/100)^2)$$

$$\ln(K_1) = -2307.1266/T + 2.83655 - 1.5529413 \ln(T) + (-4.0484/T - 0.20760841)S^{1/2} + 0.08468345S - 0.0065408S^{3/2} + \ln(1 - 0.001005S)$$

$$\ln(K_2) = -3351.6106/T - 9.226508 - 0.2005743 \ln(T) + (-23.9722/T - 0.106901773)S^{1/2} + 0.1130822S - 0.00846934S^{3/2} + \ln(1 - 0.001005S)$$

where K_0 , K_1 and K_2 are in mol/kg solution, S is the salinity in gm/kg solution and T is the temperature in degree Kelvin. At 25 °C and salinity of 35 gm/kg solution, $K_0 = 0.02839$, $K_1 = 1.392 \times 10^{-6}$ and $K_2 = 1.189 \times 10^{-9}$.

The previous two reactions can be combined for simplicity, then the carbonic acid system will be



The equilibrium constants of these reactions in water can be given by following relationship [16]:

$$pK_1 = 17,052/T + 215.21 \log(T) - 0.12675T - 545.56$$

$$pK_2 = 2902.39/T + 0.02379T - 6.498$$

$$pK_w = 4787.3/T + 7.1321 \log(T) + 0.010365T - 22.801$$

At 25 °C,

$$K_1 = 4.305 \times 10^{-7}, K_2 = 4.667 \times 10^{-11} \text{ and } K_w = 1.003 \times 10^{-14}.$$

The total dissolved inorganic carbon in a saline water sample:

$$C_T = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

can be measured directly by acidifying the sample, extracting the CO₂ gas that is produced and measuring its amount. By relating the value of C_T with the equilibrium constants equations, values of the carbonic species can be obtained at different level of C_T values. Table 1 shows the concentrations of CO₂*, HCO₃⁻ and CO₃²⁻ for value of C_T equal 0.01 moles/L. The effect of pH on the carbonate species distribution is shown in Figure 1. At high pH values, carbonate ions predominate; below 11.1 bicarbonate ions are increasingly formed from the carbonate ions. Monovalent bicarbonate ions predominate between 10.1 and 6.4. At pH values below 8.2 carbonic acid and dissolved carbon dioxide gas are increasingly formed. Below a pH of 6.4 carbonic acid and dissolved carbon dioxide gas exist in equilibrium as the predominate species.

Table 1 Concentrations of CO₂*, HCO₃⁻ and CO₃²⁻ at C_T=0.01 moles/L.

pH	CO ₂ *	HCO ₃ ⁻	CO ₃ ²⁻	H ⁺	OH ⁻
1	0.01	4.3047E-8	2.0089E-17	0.1	1E-13
2	9.9996E-3	4.3045E-7	2.0088E-15	0.01	1E-12
3	9.9957E-3	4.3028E-6	2.008E-13	0.001	1E-11
4	9.9571E-3	4.2862E-5	2.0003E-11	0.0001	1E-10
5	9.5873E-3	4.127E-4	1.926E-9	0.00001	1E-9
6	6.9906E-3	3.0092E-3	1.4043E-7	0.000001	1E-8
7	1.8844E-3	8.1118E-3	3.7856E-6	0.0000001	0.0000001
8	2.26E-4	9.7286E-3	4.5401E-5	1E-8	0.000001
9	2.2146E-5	9.533E-3	4.4488E-4	1E-9	0.00001
10	1.5836E-6	6.8171E-3	3.1814E-3	1E-10	0.0001
11	4.0994E-8	1.7647E-3	8.2353E-3	1E-11	0.001
12	4.8734E-10	2.0979E-4	9.7902E-3	1E-12	0.01
13	4.9672E-12	2.1382E-5	9.9786E-3	1E-13	0.1
14	4.9768E-14	2.1424E-6	9.9979E-3	1E-14	1

The total alkalinity of a sample of sea water is a form of mass-conservation relationship for hydrogen ion. It is rigorously defined as [17] : “. . . the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant K < 10^{-4.5}, at 25 °C and zero ionic strength) over proton donors (acids with K > 10^{-4.5}) in one kilogram of sample.” Thus

$$A_T = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{OH}^-].$$

If value of A_T with the equilibrium constants equations, concentrations of the carbonic species can be expressed as

$$[\text{HCO}_3^-] = \frac{A_T + [\text{H}^+] - k_w / [\text{H}^+]}{1 + 2k_2 / [\text{H}^+]}$$

$$[\text{CO}_3^{2-}] = \frac{A_T + [\text{H}^+] - k_w / [\text{H}^+]}{2(1 + [\text{H}^+] / 2k_2)}$$

Table 2 below shows the concentrations of CO₃²⁻ and HCO₃⁻ at a pH of 10.1.

Table 2 Concentrations of CO₃²⁻ and HCO₃⁻ at a pH of 10.1

Alk	CO ₃ ²⁻	HCO ₃ ⁻
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20	8.9036	6.28571
25	12.15181	8.578865
30	15.40003	10.87202
35	18.64824	13.16518
40	21.89646	15.45833
45	25.14467	17.75149
50	28.39288	20.04464
55	31.6411	22.3378
60	34.88931	24.63095
65	38.13753	26.9241
70	41.38574	29.21726
75	44.63395	31.51041
80	47.88217	33.80357
85	51.13038	36.09673
90	54.3786	38.38988
100	60.87502	42.97619

A complete description of the carbon dioxide system in a sample of saline water at a particular temperature and pressure is possible provided that the following information is known:

- the solubility constant for CO₂ in sea water, K_0 ,
- the equilibrium constants for each of the acid/base pairs that are assumed to exist in the solution,
- the total concentrations of all the non-CO₂ acid/base pairs,
- the values for at least two of the CO₂ related parameters: C_T , A_T , $f(\text{CO}_2)$, $[H^+]$.

Normal air contains about 0.03 percent by volume of carbon dioxide. The Henry's law constant for carbon dioxide at 25°C is about 1500 mg/l atm; therefore the equilibrium concentration of carbon dioxide with air is 0.0003 x 1500 or about 0.45 mg/l. So from the value of K_1 , it can be calculated that a water with an alkalinity of 100 mg/l, aerated until in equilibrium with the carbon dioxide in air, would have a pH of about 8.6. A water with higher alkalinity would tend to have a higher pH upon aeration, and one with lower alkalinity would tend to have a lower pH.

Comparison of Addition of Carbon Dioxide and Sulfuric Acid

The solubility equilibrium for CaCO₃ is described by the following reaction:



The addition of Ca(OH)₂ to a water increases the hydroxyl ion concentration and elevates the pH which, according to Figure 1, shifts the equilibrium of the carbonic acid system in favor of the carbonate ion, CO₃²⁻, i.e., it changes the alkalinity from the bicarbonate form to the carbonate. This increases the concentration of the CO₃²⁻ ion and, according to Le Châtelier's¹ principle, shifts the equilibrium described by the above equation to the left. Such a response results in the precipitation of CaCO₃ and a corresponding decrease in the soluble calcium concentration. Precipitation of the supersaturated solution of CaCO₃ will continue slowly. It is therefore necessary to stabilize the

¹ Le Châtelier's principle states: "A reaction, at equilibrium, will adjust itself in such a way as to relieve any force, or stress, that disturbs the equilibrium".

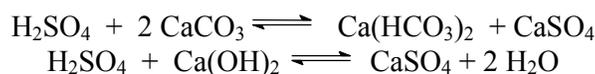
water by converting the supersaturated CaCO_3 back to the soluble form. Stabilization can be accomplished by addition of carbon dioxide or by sulfuric acid.

The solubility equilibrium for $\text{Mg}(\text{OH})_2$ is described by the following equation :

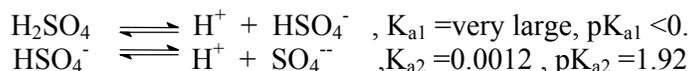


According to Le Châtelier's principle, the addition of hydroxyl ions shifts the equilibrium described by the above equation to the left, resulting in the precipitation of $\text{Mg}(\text{OH})_2$ and a corresponding decrease in the soluble magnesium concentration.

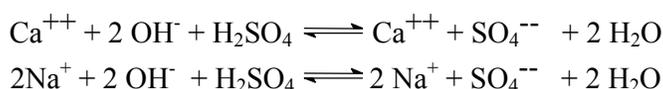
The amounts of calcium and magnesium which can be removed are limited by the number of carbonate ions that can be formed by pH adjustment, which is, in turn, limited by the amount of alkalinity initially present in the water [18]. Adjustment of the pH toward neutrality is accomplished by addition of carbon dioxide or by sulfuric acid. The addition of carbon dioxide is preferred over the addition of sulfuric acid because it is less hazardous to use. Extreme caution must be utilized in handling and adding concentrated sulfuric acid to water. The main chemical reactions which take place when adding sulfuric acid are:



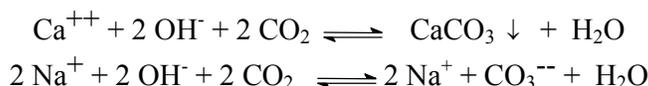
Sulfuric acid dissociates in water in two steps losing one hydrogen atom in each step according to the following reactions:



If the pH has been raised to facilitate the precipitation of magnesium, it will be necessary to neutralize the excess hydroxyl ions prior to stabilization. This necessitates a two-stage treatment process [9]. Typical reactions with sulfuric acid are :



With carbon dioxide:



The pH must be lowered to approximately 9.5 before significant stabilization occurs.

Conclusions

The addition of carbon dioxide for pH control in water treatment plant was reviewed in detailed. Comparison between the addition of sulfuric acid and carbon dioxide for pH adjustment was discussed. The variation of carbon dioxide concentrations with pH value was also presented.

Carbon dioxide is gaining acceptance for pH control in water treatment plant. The addition of carbon dioxide is preferred over the addition of sulfuric acid because it is less hazardous to use. Extreme caution must be utilized in handling and adding concentrated sulfuric acid to water. Carbon dioxide reduces high pH levels quickly. It was found that carbon dioxide gives better control of pH than sulfuric acid. It shows a self-buffering as it reaches neutral pH levels. This self-buffering feature allows precise end-point control without the danger of overshooting into undesirable low pH levels. It is not stored as an acid solution so it is considered safer than sulfuric acid. It is non-corrosive to pipes and equipment. It requires less equipment and monitoring costs. It also exhibits greater storage capacity which makes it possible to store up to twice as much neutralizing agent in the same amount of storage space with no increase in weight. It requires no handling costs. It can be utilized via a completely automated system.

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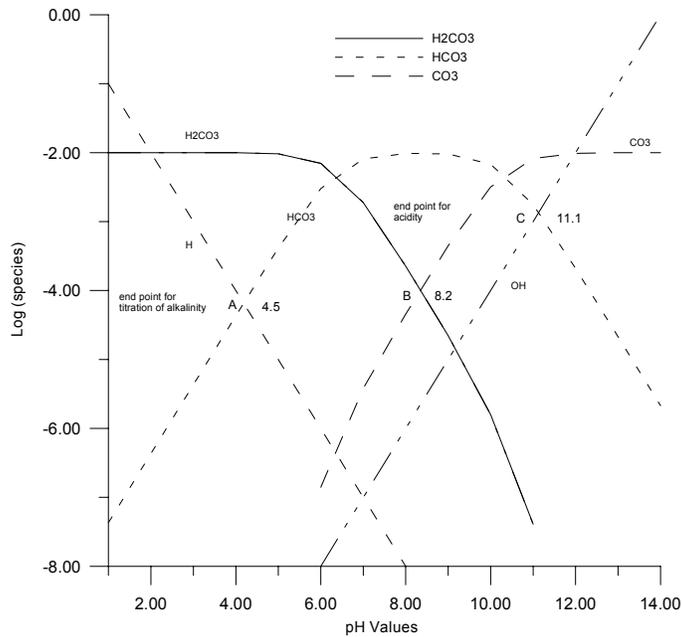


Figure 1 Distribution of Carbonic Species with pH for $C_t=0.01$ moles/L.

Procedure to estimate the carbonic species in water

$$T=t+273$$

$$-\log(k_1)=(17052/T + 215.21 \cdot \log(T) - 0.12675 \cdot T - 545.56)$$

$$-\log(k_2)=(2902.39/T + 0.02379 \cdot T - 6.498)$$

$$-\log(k_w)=(4787.3/T + 7.1321 \cdot \log(T) + 0.010365 \cdot T - 22.801)$$

$$H = 10^{-pH}$$

$$X = H/k_1 + k_2/H + 1$$

$$C_t = H \cdot HCO_3/k_1 + HCO_3 + k_2 \cdot HCO_3/H$$

$$HCO_3 = C_t/X$$

$$H_2CO_3 = (H/k_1) \cdot C_t/X$$

$$CO_3 = (k_2/H) \cdot C_t/X$$

$$\log(HCO_3) = \log(C_t) - \log(X)$$

$$\log(H_2CO_3) = \log(C_t) - \log(X) + \log(H/k_1)$$

$$\log(CO_3) = \log(C_t) - \log(X) + \log(k_2/H)$$

$$\log(OH) = -14 + pH$$