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Working partial pressure of CO_2 gas in aqueous solution[†]

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Abstract

Carbonate species in aqueous solution play an important role in the determination of chemical properties of water in relation with alkalinity, buffer capacity, biological productivity, and so on. These compounds also have reactive characteristics such as interphasal reactions between solid, liquid, and gas phases. In the absence of solid materials, the total amount and relative abundance of each carbonate species are directly influenced by the partial pressure of CO_2 gas in the atmosphere, which in turn significantly affects the properties of aquatic system. In the water/wastewater treatment process along with the wastes treatment and recycling process which occurring in aquatic environment, it is essential to figure out its characteristics for their optimization and one of its most influential features upon these processes is determined by carbonate species. To understand the fundamental aspect of the relationship between the partial pressure of CO_2 gas and chemical features of water, especially pH, the *working* partial pressure of pure CO_2 gas that produced by contacting the dry ice with water has been estimated based on equilibrium calculation. The equilibrium constants for the dissociation of carbonic acid were determined using van't Hoff equation and the distribution diagram of carbonate species according to the pH has been constructed to substantiate the results of equilibrium calculation. The estimated *working* partial pressure of pure CO_2 gas was found to be a function of the concentration of carbonates in solution, which suggesting that prior evaluation of the *working* partial pressure of gas is essential for a better understanding of aquatic interactions.

Keywords : Aquatic System, Carbonate Species, CO_2, Working Partial Pressure, Equilibrium Calculation

요 약

수용액에서 탄산계 이온종들은 알칼리도, 완충 용량, 생물학적 생산지수 등과 같은 물의 여러 화학적 성질들을 결정하는데 있어 중요한 역할을 하고 있다. 이러한 화학종들은 또한 수계에서 고체, 액체, 그리고 기체 상태 등으로 변화하며 반응을 하는 특성을 지니고 있다. 고체상이 없는 상황에서 탄산계 이온종들의 총량과 각 이온종들의 상대량은 대기에서의 이산화탄소의 분압에 의해 결정되며 이는 또한 수계의 제반 성질에 직접적인 영향을 미치게 된다. 수환경에서 진행되는 정수, 혹은 폐수 처리 공정, 폐기물 처리 공정, 그리고 폐기물의 재활용과 관련된 공정들에 있어 공정의 최적화를 위해서는 수환경의 특성을 파악하는 것이 매우 중요하며 이러한 수환경의 특성에 가장 크게 영향을 미치는 요소들 가운데 하나가 탄산계 이온종들이다. 대기에서의 이산화탄소의 분압과 물의 화학적 성질, 특히 pH 와의 근본적인 연관성을 이해하기 위해 물과 접촉한 상태의 드라이아이스로부터 발생하는 순수한 이산화탄소의 *활성* 분압을 수계에서의 평형론에 근거하여 계산하였다. 탄산의 해리와 관련된 평형상수들을 van't Hoff 식에 의해 결정하였으며 평형계산의 결과를 입증하기 위해 pH 에 따른 탄산계 이온종들의 분배 곡선을 작성하였다. 계산된 이산화탄소 기체의 *활성* 분압은 수용액에서의 탄산계 이온종들의 농도의 함수인 것으로 나타났으며 수용액에서 일어나는 반응들의 체계적 이해를 위해서는 수용액과 접해있는 이산화탄소 등과 같은 기체의 *활성* 분압에 대한 선행 계산이 필요한 것으로 파악되었다.

주제어 : 수계, 탄산계 이온종, 이산화탄소 가스, *활성* 분압, 평형 계산

1. Introduction

In natural water system, there are various chemical species involved in different kinds of interactions such

as acid-base reaction, complex formation, precipitation-dissolution, and redox reaction. Through such reactions, the physicochemical features of these chemical species are changed and the characteristics of the overall system including these chemical species are also affected by a series of reactions. Among these chemical species, it is evident that carbonate species are the most

important in the determination of water properties. As it is well known, carbonate species act as major pH-buffering species; thus, making it possible for most aquatic organisms to survive.[1] In addition, the amount and kinds of carbonate species in water are directly related with its alkalinity or acidity, which is the critical factor in determining the biological productivity of water since most inorganic carbons for aquatic organisms are supplied by these compounds.[2]

The specific characteristics of carbonate species also lie in their heterogeneous reactivity. That is, these chemical species can be produced or vanished, and can be altered in their relative amounts resulting from the interphasal reactions. Many precipitates or solid materials in contact with water have the form of carbonates and when they dissolve, various carbonate compounds are produced. Also, these carbonate compounds in aqueous solution can be expected from the dissolution of gaseous CO_2 in the atmosphere.[3,4] The specific forms of carbonate species play an important role in water/wastewater treatment process as well as natural water system along with wastes treatment and its recycling. For instance, dissolved carbon dioxide gas can consume lime in the softening process[5] and the alkalinity of wastewater is closely related with its buffer capacity,[6] which determines the amount of chemicals necessary in the treatment process. In the absence of carbonaceous solids, aqueous carbonate compounds are mostly originated from the dissolution of gaseous CO_2. The dissolved carbon dioxide gas forms carbonic acid and successively dissociates into bicarbonate and carbonate ions depending on aqueous conditions, which reversely characterize the properties of water.

In general, the amount of carbonates produced from solid matters in water can be simply estimated based on the equilibrium equations for dissolution reaction if the solid matters exist stably in solution and their specific forms are known. For most natural aquatic systems and water/wastewater treatment processes, the identification of solid carbonates is not difficult to be conducted by employing conventional analytical techniques like X-ray diffraction analysis. On the other hand, the amount of aqueous carbonate species invoked by the dissolution of gaseous carbon dioxide cannot be readily reckoned due to the difficulty in the estimation of the partial pressure of gaseous carbon

dioxide. There are many sources for CO_2 gas that contributes to aqueous carbonates and except that in the atmospheric air, its partial pressure is hard to evaluate. However, it is usually regarded that the generated CO_2 within the aqueous medium via CO_2-evolving reactions such as respiration of organisms and biological degradation of organic matters is entirely composed of carbon dioxide with no significant amount of other components.

As a matter of fact, in the course of calculating the dissolved amount of gaseous carbon dioxide, it should be considered that it is not possibly estimated just based on the partial pressure of CO_2 gas if the system is not in an equilibrium state. That is, the dissolved amount of gaseous carbon dioxide is a function of contacting time between water and gaseous CO_2 under dynamic situation and there is no way to evaluate the amount of aqueous carbonates mathematically except by analyzing the dissolved carbonate species directly. Since most aquatic chemical/biochemical reactions relating to the evolution of CO_2 are rationally presumed to be in progress kinetically, the computational evaluation of the quantity of dissolved carbonates is very difficult and sometimes not possible.

Another aspect that should be taken into account in the transfer of CO_2 from gaseous phase to liquid phase is the actual partial pressure, which practically works as a driving force for the dissolution of carbon dioxide gas. Thinking of the relationship between dissolved gaseous CO_2 and the properties of water, what virtually affects the characteristics of water is not just the volume fraction of CO_2 gas in a gas mixture but its practical partial pressure which has a potential to contribute to aqueous carbonates. This pressure, which is hereby termed as *active* or *working* partial pressure must be evaluated first for a more precise description of the aquatic system in relation with the influence of gaseous phase on its property. In this study, the estimation of the *working* partial pressure of pure CO_2 gas which was generated by gasifying the dry ice in an aqueous solution has been attempted by employing thermodynamic equations to understand the fundamental aspects of the dissolution reaction of gaseous carbon dioxide into water, which is directly related to the changes in its characteristics. Based on the result of the present study, the effect of CO_2 gas generated from

various reactions on the properties of water will be understood in more detail and further systematic investigations are expected to be conducted which will account for the practical phenomena relative to the relationship between dissolution reaction of gases and water properties.

2. Experimental methods

Around 1.5 L of ultrapure water (>18 MΩ, 25°C) was prepared and reagent grade Na_2CO_3 (>99.99% Pure, Fisher Co.) was dissolved to make its concentration as 1×10^{-5} M. After measuring the initial pH solution using a pH meter (Orion, Model 420A), a couple of lumps of dry ice were put into the solution and the change in solution pH with time has been monitored. The solution temperature, which changed due to the gasification of dry ice, was also measured. In the course of monitoring the changes of pH and temperature, close attention has been paid to the possibility that there should remain sufficient amount of dry ice in the solution even after the pH and temperature reached their equilibrium values. The same experiment was also carried out for pure distilled water instead of using Na_2CO_3 solution for a comparative estimation of the dissolved CO_2 gas. All experiments were conducted repeatedly several times and the trend of the variations in the pH and temperature of solution with time showed a good reproducibility.

3. Results and discussion

Fig. 1 shows the time profiles of the pH of 1×10^{-5} M Na_2CO_3 solution and distilled water right after the dry ice was introduced into the solution. For Na_2CO_3 solution, its pH, which was originally *ca.* 9.0, decreased with time and came to be constant at 4.97 in 220 seconds. However, it almost reached a constant value earlier in 120 seconds, where the pH was 5.01. The reason for this decrease in pH is due to the formation of carbonic acid from the dissolution of CO_2 gas that was generated from dry ice and its subsequent dissociation. Actually, the dissociation reaction of carbonic acid in aqueous environment occurs extremely rapidly like most acid-base reactions. Therefore, although it was not very significant, the time lag observed between the

introduction of dry ice and attainment of equilibrium pH was attributable to the dissolution step of gaseous CO_2 into the solution. The temperature of the solution, which was initially 25°C, was also observed to decrease swiftly to around 16°C within a couple of minutes and remain constant afterwards. A similar trend was observed in the time courses of pH and temperature for pure distilled water except that its initial and equilibrium pH's were 7.0 and 4.88 respectively. Using these pH and temperature values, the equilibrium calculation has been made to determine species concentrations at equilibrium and based on its result the *working* partial pressure of pure CO_2 gas generated in aqueous solution was evaluated.
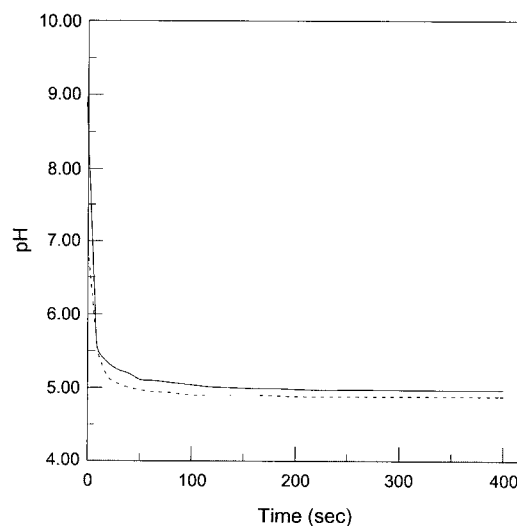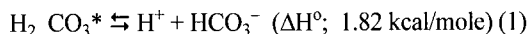

Fig. 1. Variations of the pH of 1×10^{-5} M Na_2CO_3 solution (___) and three times distilled water (....) with time in the existence of dry ice in solution.

The chemical species concerned in Na_2CO_3 solution are H^+, OH^-, Na^+, $H_2CO_3^*$, HCO_3^-, and CO_3^{2-}. Among these, the concentration of proton at equilibrium can be taken as $1 \times 10^{-4.97}$ M beforehand since the equilibrium pH of 1×10^{-5} M Na_2CO_3 solution was measured to be 4.97 in the existence of dry ice in solution. To determine the concentrations of the other species, equations describing this solution at equilibrium should be considered and those equations are equilibrium relationships, mass balance, and electroneutrality. First, the related equilibrium relationships can be suggested as follows:

$$H_2CO_3^* \leftrightarrows H^+ + HCO_3^- \quad (\Delta H^\circ;\ 1.82\ \text{kcal/mole}) \quad (1)$$

$$HCO_3^- \leftrightarrows H^+ + CO_3^{2-} \quad (\Delta H^\circ;\ 3.55\ \text{kcal/mole}) \quad (2)$$

$$H_2O \leftrightarrows H^+ + OH^- \quad (3)$$

The pK's of reactions (1) and (2) at 298 K are 6.35 and 10.33, respectively. However, the equilibrium temperature of Na_2CO_3 solution in the existence of dry ice was 289 K so that it is necessary to get the corresponding pK values to this temperature. Assuming that the ΔH°'s for these reactions remain constant in the temperature range of 289~298 K and employing the van't Hoff equation,[7,8] it was obtained that the new pK's for reactions (1) and (2) were 6.39 and 10.41, respectively. This decrease in the degree of the dissociations of $H_2CO_3^*$ and HCO_3^- as the temperature is lowered can be explained by the endothermic nature of these dissociation reactions. Reaction (3) is the auto-ionization reaction of water and its equilibrium constant, Kw, which also being a function of temperature, is known to be $1 \times 10^{-14.31}$ at 289 K[9]. Consequently, the equilibrium constants for the reactions (1), (2), and (3) at 289 K can be expressed as the following:

$$[H^+][HCO_3^-] / [H_2CO_3^*] = 1 \times 10^{-6.39} \quad (4)$$

$$[H^+][CO_3^{2-}] / [HCO_3^-] = 1 \times 10^{-10.41} \quad (5)$$

$$K_w = [H^+][OH^-] = 1 \times 10^{-14.30} \quad (6)$$

The mass balances for Na_2CO_3 solution at equilibrium are:

$$C_{T,Na} = 2 \times 10^{-5}\ M \quad (7)$$

$$C_{T,CO3} = [H_2CO_3^*] + [HCO_3^-] = [CO_3^{2-}] \quad (8)$$

and the related electroneutrality equation is:

$$[Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (9)$$

Since the mass balance and electroneutrality equations are established solely based on the species concentrations, therefore, no modifications are necessary which reflect the changes of temperature. Employing the equations from (4) to (9), the equilibrium concentrations of the species existing in 1×10^{-5} M Na_2CO_3 solution, which Na^+, H^+, OH^-, $H_2CO_3^*$, HCO_3^-, and CO_3^{2-}, were calculated to be

2×10^{-5}, $1 \times 10^{-4.97}$, $1 \times 10^{-9.34}$, 8.10×10^{-4}, 3.07×10^{-5}, and 1.11×10^{-10}, respectively, when pure carbon dioxide gas was equilibrated with the solution. The result indicated that the carbonate system was mostly composed of $H_2CO_3^*$ and the concentration of CO_3^{2-} was almost negligible. Fig. 2 represents the distribution diagram of carbonate species according to the pH, which was constructed by MINTEQ program (Version 2.0) using the modified equilibrium constants at 289 K. This shows a good agreement with the result of equilibrium calculation for the concentrations of carbonate species at the corresponding pH.
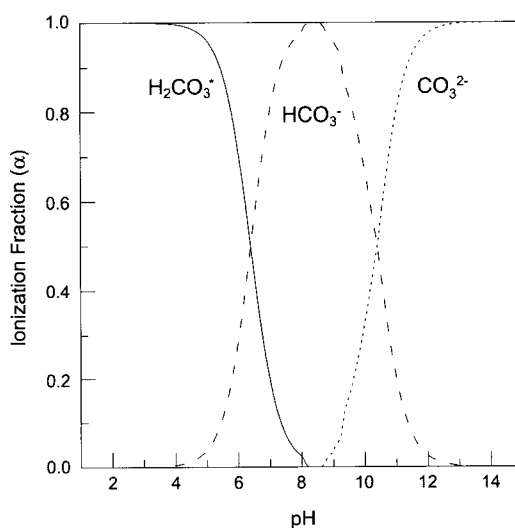

Fig. 2. Distribution diagram of carbonate species at 289 K.

In this calculation, it should have been premised that the dissolution reaction of the CO_2 gas was in an equilibrium state as well. However, since CO_2 gas was continuously generated vigorously as long as enough dry ice existed in the solution, it was reasonably assumed that pure CO_2 gas with a specific *working* partial pressure was always in contact with the solution and, thus, a pseudo-equilibrium state was established in its dissolution reaction into water. It is also to be noted that the ionic strength effect on the activities of ionic species was neglected here. As the ionic strength of solution increases, the active concentrations of ions contained in it is generally reduced, which consequently affects the equilibrium relationships. While most of the ions present in Na_2CO_3 solution are

monovalent with the concentrations lower than 10^{-4} M and the most abundant species, which is $H_2CO_3^*$, carries no charge. CO_3^{2-} is the only divalent ion in the present system, however, its concentration was estimated to be very low compared with those of other ions. Thus, its on the activities of the ions in the solution including itself can be reasonably regarded as negligible. Considering all this, the ionic strength effect on the present equilibrium calculation result was rationally thought to be negligible and could be ignored. Another aspect that must be taken into account in the present equilibrium system is the volatilization of carbonic acid that was formed by the dissolution of carbon dioxide gas. That is, since the carbonic acid has a limited solubility in water at specific temperature, it is quite possible that some of the carbonic acid formed in the solution transfers to the gaseous phase, which results in the breakdown of the equilibrium state. However, as abovementioned, the continuously generated CO_2 gas could maintain reasonably well an equilibrium state in its dissolution into water so that even in case the equilibrium were disturbed by the volatilization of carbonic acid, a new equilibrium state was considered to reestablish immediately. The con-tinuance of the pH of the solution once after it reached a constant value might substantiate this.

The total concentration of carbonate species dissolved in the Na_2CO_3 solution at equilibrium can be calculated as 8.41×10^{-4} M from equation (8). Among this, the amount of carbonates originated exclusively from the dissolved CO_2 is estimated as 8.31×10^{-4} M by subtracting the amount of carbonates initially existing in the solution, which was 1×10^{-5} M, from their total concentration. The dissolution reaction of gaseous CO_2 at equilibrium (equation (10)) follows the Henry's Law and, thus, its equilibrium constant expressed as equation (11) is the Henry's constant for CO_2 gas. The value of $[CO_2(aq)]$ in this equation can be taken as 8.31×10^{-4} M for the present system so that if the equilibrium constant were known, the *working* partial pressure of the carbon dioxide gas in equilibrium with water can be evaluated.

$$CO_2(gas) \leftrightarrows CO_2(aq) \qquad (10)$$

$$K = [CO_2(aq)] / P_{CO2} \qquad (11)$$

The effect of temperature should also be considered

here and as the Henry's constant for CO_2 gas and $\triangle H^\circ$ for reaction (10) at 298 K are known by employing the van't Hoff equation on the same assumption as before, the equilibrium constant for the dissolution reaction of CO_2 at 289 K was calculated as 0.0404. As a result, the *working* partial pressure of pure CO_2 gas contacting with water has been estimated to be 0.021 atm.

Following similar procedure, when pure distilled water is equilibrated with carbon dioxide gas, the equilibrium concentrations of the chemical species existing in solution also can be obtained except that no sodium ion is involved in this case. The concerned species are H^+, OH^-, $H_2CO_3^*$, HCO_3^-, and CO_3^{2-}, and their concentrations have been found as $1 \times 10^{-4.88}$, $1 \times 10^{-9.43}$, 4.28×10^{-4}, 1.32×10^{-5}, and 0.39×10^{-10} M, respectively. Based on this, the *working* partial pressure of CO_2 gas that was in equilibrium with distilled water was calculated to be 0.011 atm.

Comparison of the estimated *working* partial pressures of gaseous CO_2 for the two cases reveals that counter intuitively carbon dioxide gas tends to dissolve into the water more strongly in which some carbonates already exist than the water with no carbonates in it. This is probably explained by the fact that more carbonic acid was necessary in the neutralization of the solution with higher initial pH, which was Na_2CO_3 solution, and the required carbonic acid was supplied by the dissolved CO_2 gas. Although the initial pH of Na_2CO_3 solution was considerably higher than that of distilled water their equilibrium pH's were found to be almost the same, which implied that more CO_2 gas had been dissolved into the Na_2CO_3 solution. However, it may be controversial to take this as a general phenomenon because the result would have been different depending on how the carbonate solution was initially prepared. For instance, if instead of sodium carbonate, the same concentration of carbonic acid were used in the preparation of carbonate solution, its initial pH and, thus, the degree and direction in its change of pH according to the dissolution of carbon dioxide gas would have been different from those observed here.

What is noticeable in the result of the present study is that the *working* partial pressure of CO_2 gas regarding its dissolution into water was a function of the concentration of carbonates which already existed in

water and presumably in the relative amounts of specific carbonate species. Accordingly, to anticipate the effect of carbon dioxide gas on the properties of water with an increased accuracy the concentrations of each carbonate species in water should be known in advance and if possible the relevant chemical/biochemical reactions are to be figured out as well which occur in the aquatic environment and affect the amount of dissolved carbonates through their generation or consumption. These carbonates determine several important water characteristics and consequently influence the *working* partial pressure of carbon dioxide gas that is in contact with water.

In a more general sense, the above-mentioned finding may suggest that the *working* partial pressure of a gaseous substance cannot be directly estimated with its volume fraction, at least in its dissolution into liquid phase material. The partial pressure of a specific gas component in the mixture of gases is the total pressure of the gas mixture multiplied by its volume fraction. The CO_2 gas which was generated from dry ice in aqueous medium in this study was regarded to be exclusively composed of carbon dioxide so that its volume fraction can be taken as one regarding this gaseous compound for both Na_2CO_3 solution and distilled water. Further, although the total pressure of the generated CO_2 gas is not known presently, it is reasonably acceptable that it will be almost equal for the two solutions, therefore, the partial pressures of the gaseous carbon dioxide can be considered the same for both aquatic systems. However, the estimated *working* partial pressures of this gas were found to be different from each other for the two cases, which means that the extent of the influence on the properties of the two solutions that was provoked by the dissolution of CO_2 gas in the same condition is different.

4. Conclusions

All in all, close attention should be paid on the evaluation of the *working* partial pressure of the relevant gases for a better understanding of the chemical and biological reactions taking place in natural aqueous environment in which gaseous substances are involved and for an improved design and operation of the water/wastewater treatment processes such as activated-sludge process, chlorine disinfection, air-stripping of ammonia, etc., which utilizes the gases as treatment aids.

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