

Article

Determination of Concentration of Free Carbon Dioxide in Artificial Seawater by Difference Balance System/Henry's Law

Guang-Hu Liu ^{1,2}, Li-Ting Deng ³, Ming-Ming Wen ^{4,*}, Hao-Nan Cui ⁵, Jing-Yi Huang ^{1,2}, Chen-Fei Wang ¹, Hang-Yi Zhao ¹, Chu-Ping Wang ¹ and Tian-Rui Chen ¹

¹ China Institute of Disaster Prevention, Sanhe 065201, China

² Hebei Key Laboratory of Earthquake Dynamics, Sanhe 065201, China

³ School of Earth Science, Hebei GEO University, Shijiazhuang 050031, China

⁴ Guangzhou Marine Geological Survey, Guangzhou 510760, China

⁵ College of Oceanography, Hohai University, Nanjing 210024, China

* Correspondence: wmingming@mail.cgs.gov.cn

Abstract: The concentration of dissolved carbon dioxide in seawater affects the formation of seabed biogenic minerals, and controls the development and evolution of marine organisms, which is one of the most important indices in the marine environment and geology survey. The concentration of free carbon dioxide in bottom seawater has important academic value for the exploration of seabed minerals, marine environment monitoring, the study of the carbon cycle in seabed sediments and even the global carbon cycle. Titration is used to determine the index, whose range is between 4 mg/L and 400 mg/L. However, the concentration of free carbon dioxide in bottom seawater in some sea areas is lower than this range, thus titration may not be suitable. A method for the determination of free carbon dioxide in artificial seawater, whose name is D.B.S/Henry's Law, is described in this paper. D.B.S/Henry's Law indirectly determines the content of free carbon dioxide in seawater instead of directly titrating with reagents. It is simple, fast and accurate, and it is based on the law of conservation of mass/Henry's law and CO₂ dissolution mechanisms. This discovery mainly provides a new scientific perspective for the determination of trace free carbon dioxide concentration in seawater. In addition, Henry's law constants of carbon dioxide in artificial seawater at 3–20 degrees Celsius are determined with D.B.S/Henry's Law. These data will be used as an important reference for the determination of free carbon dioxide in seawater in the future. D.B.S/Henry's Law may be used as a supplement of the methods specified in national and industrial standards, which are applied to the detection of carbon dioxide Henry's constant and free carbon dioxide content in various temperature and salinity seawater. D.B.S/Henry's Law provides a new perspective for CO₂ determination and has extensive practical application value.

Keywords: seawater; free carbon dioxide; D.B.S/Henry's Law; Henry's law constant; industrial standards



Citation: Liu, G.-H.; Deng, L.-T.; Wen, M.-M.; Cui, H.-N.; Huang, J.-Y.; Wang, C.-F.; Zhao, H.-Y.; Wang, C.-P.; Chen, T.-R. Determination of Concentration of Free Carbon Dioxide in Artificial Seawater by Difference Balance System/Henry's Law. *Sustainability* **2023**, *15*, 5096. <https://doi.org/10.3390/su15065096>

Academic Editors: Changdong Li, Guang-Liang Feng, Hong-Hu Zhu and Guo-Feng Liu

Received: 6 December 2022

Revised: 22 February 2023

Accepted: 27 February 2023

Published: 13 March 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

As marine environment and mineral resources surveys and evaluations are upgraded and deepened, the concentration of dissolved carbon dioxide in water has attracted the attention of many scientists [1–7]. The concentration of free carbon dioxide in bottom seawater affects the formation of seabed biogenic minerals and controls the development and evolution of marine organisms. The index has important academic significance for the exploration of seabed minerals, the marine environment monitoring and the study of the carbon cycle in seawater and seabed sediments, even the global carbon cycle.

At present, the concentration of carbon dioxide in water is determined mainly by methods specified in national, industrial and American standards [8–12]. The determined concentration of carbon dioxide is mainly for the total concentration of carbon dioxide, carbonic acid, bicarbonate ions and carbonate ions in water. Titration is applicable for the

determination of free carbon dioxide in underground water; however, it is not applicable in seawater. The reason is not only the lower concentration of $\text{CO}_2(\text{aq})$ in seawater, but also the much higher concentration of other species in the carbonate system. It can be used to determine the index, whose range is between 4 mg/L and 400 mg/L, and is not suitable for seawater with lower concentration of dissolved carbon dioxide [9,13].

D.B.S/Henry's Law, a method for the determination of the concentration of free carbon dioxide in seawater, is proposed in this paper. This method can be used to determine an index whose range covers the parts below 4 mg/L and above 400 mg/L, making it suitable for seawater with lower concentration of dissolved carbon dioxide. Furthermore, it is beneficial to find out the key reason for the difference of Henry's constant of carbon dioxide in different solutes; however, the detection time of this method is fairly long and the theory is relatively complex. First, the Henry's law constant of carbon dioxide in artificial seawater in a closed balance system and the initial value M_0 of total carbon dioxide in the original system are determined; then, the concentration of free carbon dioxide in the liquid phase is calculated based on the concentration of carbon dioxide in the headspace gas phase in the balance system according to Henry's Law. The key to this method is to determine the Henry's law constant of carbon dioxide in seawater samples first. The Henry's law constant of gas is determined by many methods [14,15]. The static equilibrium method is more commonly used and only applicable to volatiles whose concentration can be easily determined in both gas and liquid phases [16]; multiple phase equilibrium/gas chromatography is suitable for volatile chlorinated hydrocarbons in water, but is not suitable for high-temperature seawater and carbon dioxide with low concentrations [17]; vapor pressure solubility calculation is not suitable for samples with high accuracy requirements [18]; static headspace is not suitable for samples with extremely low concentration [19]; UL-VIS spectrophotometry that determines the Henry's law constant based on the principle of spectral absorption is applicable to solutions where chemical reactions occur in the dissolved gases [20]; A.R.M/headspace is applicable to stock solution samples with extremely low gas concentrations, but is not applicable to solutions where chemical reactions occur in the dissolved gas [21].

D.B.S/Henry's Law is a new method for the determination of the concentration of free carbon dioxide in seawater, which also solves the determination of the Henry's law constant of the carbon dioxide gas. The method is used to indirectly determine the concentration of free carbon dioxide in seawater based on the carbon dioxide dissolution mechanism instead of by direct titration with reagents, and this is a simple, fast and accurate way to provide a new scientific perspective for determining the concentration of trace free carbon dioxide in seawater. D.B.S/Henry's Law may be used a supplement of the methods specified in national and industrial standards, and are applied to the detection of the Henry's law constant of carbon dioxide and the concentration of free carbon dioxide in seawater of various temperatures and salinities.

2. Experimental Design Principles

The dissolution of carbon dioxide in seawater is complex, which involves not only the physical changes of gas dissolution, but also a series of chemical reactions where carbon dioxide dissolves in water to form carbonic acids, carbonic acids are decomposed into bicarbonate radicals and hydrogen ions, and the former dissociate into carbonate radicals and hydrogen ions (Figure 1).

The dissolved carbon dioxide exists in the four forms of CO_2 , H_2CO_3 , HCO_3^- and CO_3^{2-} , and the sum of their concentrations is total carbon dioxide (TCO_2). Most of the methods in national or industrial standards are for the determination of TCO_2 . Of the four forms, CO_2 and H_2CO_3 exist in molecular form, and the sum of carbon dioxide in these forms is denoted as "free carbon dioxide". Accordingly, the sum of carbon dioxide in HCO_3^- and CO_3^{2-} is denoted as "ionic carbon dioxide"; the ratio of the two is denoted as the carbon dioxide hydration coefficient. The two-stage dissociation reaction of carbon dioxide dissolution involves the thermodynamic equilibrium of various molecules and

ions, and factors such as the composition, temperature, pressure and salinity of the solution will directly affect the equilibrium constant of the dissociation reaction [14], and the carbon dioxide hydration coefficient. Therefore, the carbon dioxide hydration coefficient varies under different temperature, pressure and salinity conditions. The solubility of the gas in water mainly depends on the strength of interstitial filling and hydration [15]. The physical dissolution of carbon dioxide in water is related to interstitial filling, while the series of chemical reactions causing the formation and dissociation of carbonic acids determine the strength of hydration, to a certain extent.

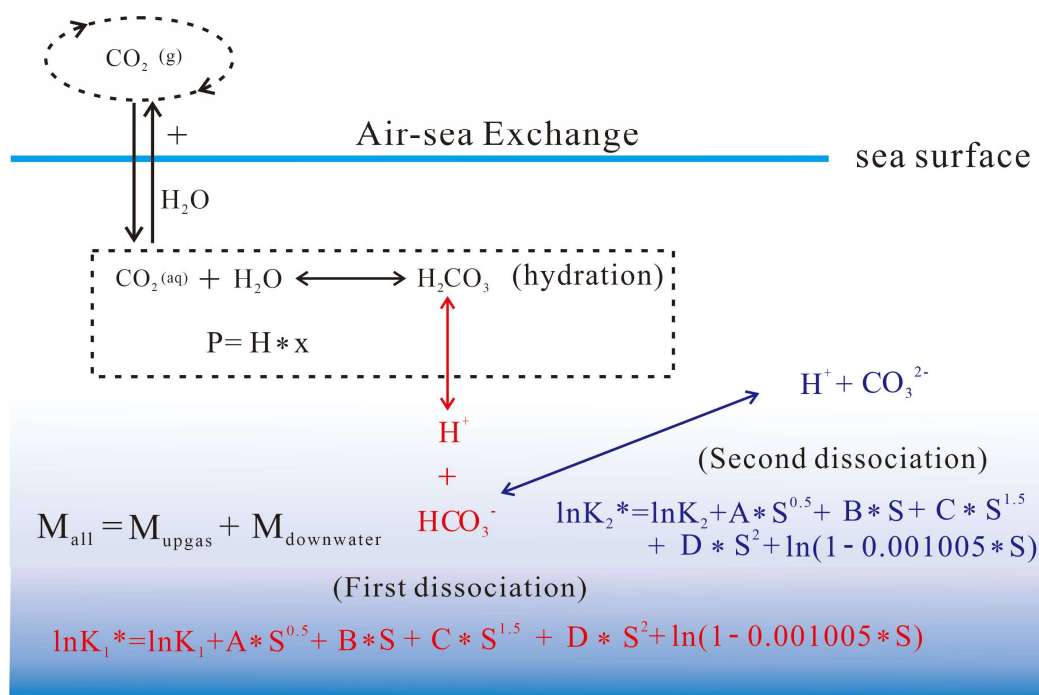


Figure 1. A series of chemical reactions where carbon dioxide dissolves in water.

According to the theory of the dissolution of gases in water [15], the concentration of free carbon dioxide in seawater conforms to the Henry's Law in a closed balance system. According to the D.B.S/Henry's Law, the Henry's law constant of carbon dioxide in artificial seawater in a closed system and the initial value M_0 of total carbon dioxide in the original system are determined, and then the concentration of free carbon dioxide in the liquid phase is calculated based on the concentration of carbon dioxide in the headspace gas phase in the balance system according to Henry's Law. In a constant temperature closed system, the partial vapor pressure P of the solute is proportional to the solution concentration x in dilute solutions, and the ratio is a constant value, i.e., Henry's law constant H , at the same temperature.

$$P = H * x \quad (1)$$

The solubility of free CO_2 in artificial seawater conforms to Henry's Law. In a balance system at 1 atm, the molar concentration of free CO_2 in artificial seawater is x mol/L, the concentration of CO_2 in the gas mixture is C_{upgas} , generally at 10^{-6} or 10^{-9} level and dimensionless, and the partial pressure of the CO_2 gas in the gas mixture is $P_{\text{upgasCO}_2} = C_{\text{upgas}} * 101325$;

The gas mixture in the balance system conforms to the ideal gas equation of state $PV = nRT$, and the amount of substance M_{upgas} of carbon dioxide in it is:

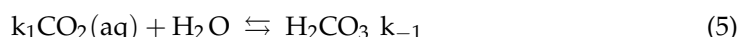
$$M_{\text{upgas}} = P_{\text{upgasCO}_2} * V_{\text{upgas}} / RT \quad (2)$$

where M_{upgas} represents the amount of substance of carbon dioxide in the gas mixture in the balance system, P_{upgasCO_2} represents the partial pressure of carbon dioxide in the gas mixture in the balance system, V_{upgas} represents the volume of the gas mixture in the balance system, R is the ideal gas constant and T represents the absolute temperature of the balance system.

Because $P_{\text{upgasCO}_2} = C_{\text{upgasCO}_2} * P_{\text{upgas}}$, Equation (2) can be transformed into:

$$M_{\text{upgas}} = C_{\text{upgasCO}_2} * P_{\text{upgas}} * V_{\text{upgas}} / RT \quad (3)$$

When CO_2 dissolves in water, chemical reactions occur to form carbonic acids:



where $\text{CO}_2(\text{g})$ represents gaseous CO_2 , $\text{CO}_2(\text{aq})$ represents hydrated gaseous CO_2 , K_1 and K_{-1} represents the balance constants for hydration and ionization reactions, respectively,

$$K = \frac{k_1}{k_{-1}} = \frac{0.03}{20} = \frac{1}{670}$$

that is, the concentration of $\text{CO}_2(\text{aq})$ in seawater is 670 times that of H_2CO_3 at balance, which can be neglected. Thus, Equation (6) can be used to express the first-stage ionization process of H_2CO_3 :



The thermodynamic apparent ionization balance constant K_1^* of the first-stage ionization process is:

$$K_1^* = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} \quad (7)$$

where

$$[\text{CO}_2] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3] \quad (8)$$

where $[\text{CO}_2(\text{aq})]$ represents the concentration of hydrated gaseous CO_2 in seawater; $[\text{H}_2\text{CO}_3]$ represents the concentration of H_2CO_3 in seawater; $[\text{CO}_2]$ represents the total concentration of free CO_2 in seawater, i.e., the sum of concentrations of hydrated gaseous CO_2 and H_2CO_3 . The solubility of free CO_2 in artificial seawater conforms to Henry's Law. Because the concentration of $[\text{H}_2\text{CO}_3]$ is only 1/670 of that of free CO_2 , which can be neglected,

$$X_{\text{downwaterco}_2} = [\text{CO}_2] \approx [\text{CO}_2(\text{aq})] = P_{\text{upgasco}_2} * H \quad (9)$$

where $X_{\text{downwaterco}_2}$ represents the concentration of free carbon dioxide in the liquid phase in the balance system.

The first-stage thermodynamic apparent ionization balance constant K_1^* can be calculated based on the first-stage apparent ionization balance constant K_1 , temperature T and salinity S of H_2CO_3 in fresh water [14]:

$$\ln K_1^* = \ln K_1 + A * S^{0.5} + B * S + C * S^{1.5} + D * S^2 + \ln(1 - 0.001005 * S) \quad (10)$$

$$A = -228.39774 + 9714.36839 * \frac{1}{T} + 34.485796 * \ln T \quad (11)$$

$$B = 54.20871 - 2310.48919 * \frac{1}{T} - 8.19516 * \ln T \quad (12)$$

$$C = -3.969101 + 170.22169 * \frac{1}{T} + 0.603627 * \ln T \quad (13)$$

$$D = -0.00258768 \quad (14)$$

$$\ln K_1 = 290.9097 - 14554.21 * \frac{1}{T} - 45.0575 * \ln T \quad (15)$$

Accordingly, the second-stage ionization process of H_2CO_3 can be expressed by Equation (16):



The thermodynamic apparent ionization balance constant K_2^* of the second-stage ionization process:

$$K_2^* = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (17)$$

where $[H^+]$ is the concentration of H^+ in seawater; $[CO_3^{2-}]$ is the concentration of CO_3^{2-} in seawater; $[HCO_3^-]$ is the concentration of HCO_3^- in seawater; the second-stage thermodynamic apparent ionization balance constant K_2^* can be calculated based on the second-stage apparent ionization balance constant K_2 , temperature T and salinity S of H_2CO_3 in fresh water (FENG, 1999):

$$\ln K_2^* = \ln K_2 + A * S^{0.5} + B * S + C * S^{1.5} + D * S^2 + \ln(1 - 0.001005 * S) \quad (18)$$

$$A = -167.69908 + 6551.35253 * \frac{1}{T} + 25.928788 * \ln T \quad (19)$$

$$B = 39.75854 - 1566.13883 * \frac{1}{T} - 6.171951 * \ln T \quad (20)$$

$$C = -2.892532 + 116.270079 * \frac{1}{T} + 0.45788501 * \ln T \quad (21)$$

$$D = -0.0061342 \quad (22)$$

$$\ln K_2 = 207.6548 - 11843.79 * \frac{1}{T} - 33.6485 * \ln T \quad (23)$$

In addition, the effect of pressure on the first and second apparent ionization balance constants K_1^* and K_2^* of H_2CO_3 meets Equation (24):

$$\ln \frac{K_i^P}{K_i^O} = -\frac{\Delta V_i}{RT} * P + 0.5 * \Delta K_i * P^2 \quad (24)$$

where

$$-\Delta V_1 = 25.50 + 0.151 * (S - 34.8) - 0.1271 * t \quad (25)$$

$$-10^3 \Delta K_1 = 3.08 + 0.578 * (S - 34.8) - 0.0877 * t \quad (26)$$

$$-\Delta V_2 = 15.82 - 0.321 * (S - 34.8) - 0.0219 * t \quad (27)$$

$$-10^3 \Delta K_2 = -1.13 + 0.314 * (S - 34.8) + 0.1475 * t \quad (28)$$

In the experiment, artificial seawater of the same composition in the stock solution barrel is used in all balance systems, and devices such as the thermostatic oscillator and system constant pressure equipment are used to keep the salinity, temperature and pressure of seawater in each balance system equal, so as to eliminate the effect of the changes in salinity, temperature, pressure and components on apparent ionization balance constants K_1^* and K_2^* .

In summary, CO_2 entering seawater exists mainly in the forms of $CO_2(aq)$, H_2CO_3 , HCO_3^- and CO_3^{2-} , where the concentration and amount of substance of free CO_2 can be expressed by a formula consisting of the Henry's law constant (H), the concentration of CO_2 in the gas mixture ($C_{upgasCO_2}$), the volume of the gas mixture (V_{upgas}) and the volume of lower seawater in the balance system ($V_{downwater}$); the concentration of CO_3^{2-} and the amount of substance of HCO_3^- in seawater can be expressed using the formula of the total amount of substance of CO_2 in each system or free CO_2 and K_1^* and K_2^* . Data, such as the

pressure of the gas mixture in the balance system (P_{upgas}), the volume of the gas mixture (V_{upgas}), the concentration of CO_2 in the gas mixture ($C_{upgasCO_2}$), the absolute temperature of the balance system (T), the salinity of the seawater (S), and the difference of total amount of substance of CO_2 among different balance systems, can be obtained through tests; the amount of substance of CO_2 in gas mixture (M_{upgas}) can be obtained by Equation (3), and the first- and second-stage ionization thermodynamic apparent balance constants K_1^* and K_2^* of H_2CO_3 in each balance system can be obtained by Equations (10) and (18). If the difference of the total amount of substance of CO_2 among different balance systems is known, the Henry's law constant H_0 of CO_2 and the amount of substance of free CO_2 in seawater are calculated using the combination of equations.

The internal medium in the closed system is 99.999% high purity argon. Artificial seawater of a certain volume is placed in the closed system, and the carbon dioxide in artificial seawater is the source of all carbon dioxide in the system; the total amount of the substance M_{all} of carbon dioxide in the closed system is the sum of the amount of substance of gaseous carbon dioxide, carbonic acids, carbonate radicals and bicarbonate radicals after hydration of gaseous carbon dioxide in the headspace gas mixture with seawater, namely

$$M_{all} = M_{upgas} + M_{downwater} \quad (29)$$

where M_{all} represents the total amount of substance of carbon dioxide in the system, M_{upgas} represents the amount of substance of gaseous carbon dioxide in the gas mixture and $M_{downwater}$ represents the total amount of substance of carbon dioxide in water, namely the sum of the amount of substance of gaseous carbon dioxide, carbonic acids, carbonate radicals and bicarbonate radicals after hydration.

Combining Equations (3) and (29), we obtain

$$M_{all} = C_{upgasCO_2} * P_{upgas} * V_{upgas}/RT + M_{downwater} \quad (30)$$

All balance systems 1, 2, 3, i in the experiment shall meet the above equation, namely:

$$M_{all-0} = C_{upgasCO_2-0} * P_{upgas-0} * V_{upgas-0}/RT + M_{downwater-0} \quad (31)$$

$$M_{all-1} = C_{upgasCO_2-1} * P_{upgas-1} * V_{upgas-1}/RT + M_{downwater-1} \quad (32)$$

$$M_{all-2} = C_{upgasCO_2-2} * P_{upgas-2} * V_{upgas-2}/RT + M_{downwater-2} \quad (33)$$

$$M_{all-i} = C_{upgasCO_2-i} * P_{upgas-i} * V_{upgas-i}/RT + M_{downwater-i} \quad (34)$$

The components, temperature, salinity and other aspects of artificial seawater imported in all balance systems are the same. Therefore, the total amount of substance M_{all} of carbon dioxide in each balance system should be proportional to the volume of artificial seawater V , namely:

$$M_{all-i}/M_{all-0} = V_i/V_0 \quad (35)$$

where M_{all-i} represents the total amount of substance of carbon dioxide in the system i, M_{all-0} represents the total amount of substance of carbon dioxide the original system 0, V_i represents the volume of artificial seawater in the system i, and V_0 represents the volume of artificial seawater in the original system 0.

Compared to the original balance system 0, the total amount of substance $M_{\Delta i-0}$ of the increased carbon dioxide in balance systems 1, 2, 3, . . . i is:

$$M_{\Delta i-0} = M_{iCO_2} - M_{0CO_2} = M_{upgas\Delta i-0} + M_{downwater\Delta i-0} \quad (36)$$

According to Equation (35),

$$M_{\Delta i-0} = M_{iCO_2} - M_{0CO_2} = M_{all-0} * (V_i - V_0)/V_0 \quad (37)$$

When $i = 1$ and $i = 2$, combining (36) and (37), we obtain

$$M_{\Delta 1-0} = (V_1 - V_0)/V_0 * M_{all-0} = M_{upgas\Delta 1-0} + M_{downwater\Delta 1-0} \quad (38)$$

$$M_{\Delta 2-0} = (V_2 - V_0)/V_0 * M_{all-0} = M_{upgas\Delta 2-0} + M_{downwater\Delta 2-0} \quad (39)$$

According to the law of conservation of mass and the solvency law of carbon dioxide in water,

$$M_{downwater} = M_{CO2aq} + M_{H2CO3} + M_{CO3^{2-}} + M_{HCO3^{-}} \approx M_{CO2aq} + M_{CO3^{2-}} + M_{HCO3^{-}} \quad (40)$$

where $M_{downwater}$ is the total amount of substance of carbon dioxide in seawater, M_{CO2aq} is the amount of substance of free carbon dioxide in seawater, M_{H2CO3} is the amount of substance of H_2CO_3 in seawater, $M_{CO3^{2-}}$ is the amount of substance of carbonate radicals in seawater and $M_{HCO3^{-}}$ is the amount of substance of bicarbonate radicals in seawater.

According to Equation (1), the concentration of free carbon dioxide in the liquid phase in the balance system $x_{downwaterco2}$:

$$x_{downwaterco2} = P_{upgasco2} * H_0 \quad (41)$$

Therefore, M_{CO2aq} in Equation (40) can be expressed by a formula consisting of P_{upgas} , the volume of the gas mixture (V_{upgas}), the concentration of carbon dioxide in the gas mixture (C_{upgas}) and the unknown number H_0 . Similarly, $M_{CO3^{2-}}$ and $M_{HCO3^{-}}$ can also be expressed through a formula consisting of the unknown number H_0 . Combining Equations (38) and (39), we obtain the series Equation (42):

$$\begin{aligned} (V_1 - V_0)/V_0 * M_{all-0} &= M_{upgas\Delta 1-0} + M_{downwater\Delta 1-0} \\ (V_2 - V_0)/V_0 * M_{all-0} &= M_{upgas\Delta 2-0} + M_{downwater\Delta 2-0} \\ (V_i - V_0)/V_0 * M_{all-0} &= M_{upgas\Delta i-0} + M_{downwater\Delta i-0} \end{aligned} \quad (42)$$

In series Equation (42), $V_1, V_0, V_2, \dots, V_i$ are known; $M_{upgas\Delta 1-0}, M_{upgas\Delta 2-0}, \dots, M_{upgas\Delta i-0}$ can be calculated using Equation (30); $M_{downwater\Delta 1-0}, M_{downwater\Delta 2-0}, \dots, M_{downwater\Delta i-0}$ can be expressed by a formula containing H_0 according to Equations (10)–(18) and (40). Therefore, there are only the two unknowns, M_{all-0} and H_0 , in series Equation (42), and they can be solved by combining any two equations. The concentration or amount of substance of free carbon dioxide in seawater in each system can be calculated through Equation (1).

When determining the concentration of free carbon dioxide in artificial seawater by D.B.S/Henry's Law, seawater samples with the same components and of different volumes should be placed in at least four calibrating standard solution preparers [21] or other closed devices. A.R.M can also be used—that is, seawater of the same volume is imported into all calibrating standard solution preparers, but standard gas of different volumes is added in order to construct a closed system where the total amount of substance of carbon dioxide is different. All closed systems are subjected to thermostatic oscillation to make them reach balance before measuring the partial pressure of carbon dioxide in the headspace gas mixture in the balance system, solving the Henry's law constant and calculating the concentration of free carbon dioxide. This method is suitable for thin water with a concentration of carbon dioxide below 4 mg/L. If the concentration of carbon dioxide in the headspace gas mixture is lower than the detection limit of the device, it can be increased to the limit by increasing the seawater volume and reducing the headspace volume in the closed system. In addition, if more than four balance systems are constructed in the experiment, different systems can be selected as the system 0 to solve the Henry's law constant. This method is also used to verify the results of the experiment for determining the Henry's law constant of carbon dioxide in seawater at a certain temperature.

3. Experiment

3.1. Experimental Design

The experiment consists of the gas source, vacuum system, balance system and analytical unit (Figure 2). The gas source, the source of the gas for the experimental system, mainly includes high purity argon and carbon dioxide standard gas. The vacuum system composed of the vacuum pump, vacuum line and control valve is connected to all devices, and can achieve the overall or partial vacuum of the system at any time. The balance system consists of the calibrating standard solution preparer, thermostatic oscillator, transfer gas bag, control valve, line and so on. The calibrating standard solution preparer, the main part of the closed system, is a space for gas and liquid, which is connected to the transfer gas bag via the control valve and line and used with an inflatable balloon placed in the chamber in advance to achieve the transfer of headspace gas under isobaric conditions in the system [21]. The thermostatic oscillator, a device that keeps the system at constant temperature and promotes the full mixture of gas and liquid, can make the system reach a gas–liquid balanced state quickly, and can accommodate, at most, four calibrating standard solution preparers at the same time. The analytical unit is composed of the carbon dioxide analyzer, vacuum pump, connecting line, control valve and so on. With its inlet connected to the outlet line for headspace gas from the calibrating standard solution preparer and controlled by the control valve, the concentration of carbon dioxide in the headspace gas can be determined in real time (Figure 2).

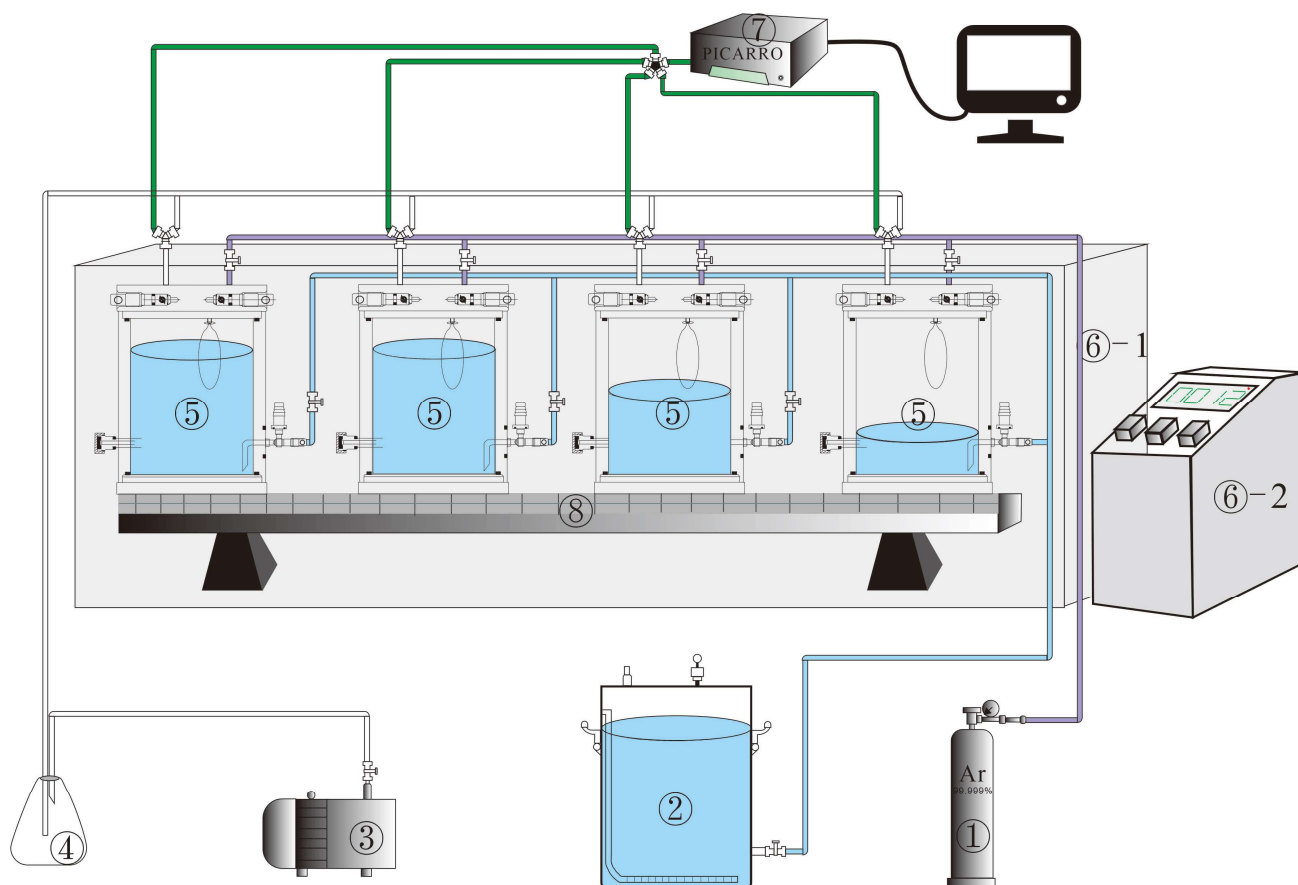


Figure 2. Schematic representation of experimental design process.

① gas source → ② stock solution barrel → ③ vacuum system–vacuum pump → ④ vacuum system–waterproof conical flask → ⑤ balance system–calibrating standard solution preparer → ⑥-1 balance system–thermostatic oscillator → ⑥-2 balance system–thermostatic oscillator controller → ⑦ analytical unit–carbon dioxide analyzer 8 oscillator

3.2. Apparatus

High precision carbon dioxide analyzer: USA, Picarro G2131-i. Main working conditions: ambient temperature 10–35 °C, sample flow < 0.4 SLM, Cavity Pressure 148 Torr, Cavity Temperature 45 °C, Warm Box Temp 45 °C, carbon dioxide measurement error < 200 ppbv within 30 s. The device is suitable for the gas mixture sample, which is continuously measured every 1–2 s on average. During measurement, the stable data is averaged as the measured value of the sample.

Calibrating standard solution preparer: independently developed, FZKJPYP-L4 (Figure 3). The volume is 5 L, and the pressure control range is 1–2 atm. The device has the following features: (1) it has very good tightness, (2) the inside of the chamber can be air-washed conveniently, (3) the target gas can be added conveniently, (4) the headspace pressure in the chamber can be monitored in real time, (5) the headspace gas can be transferred without changing the headspace gas pressure in the chamber and overall volume and destroying the gas–liquid balance in the closed system [22].

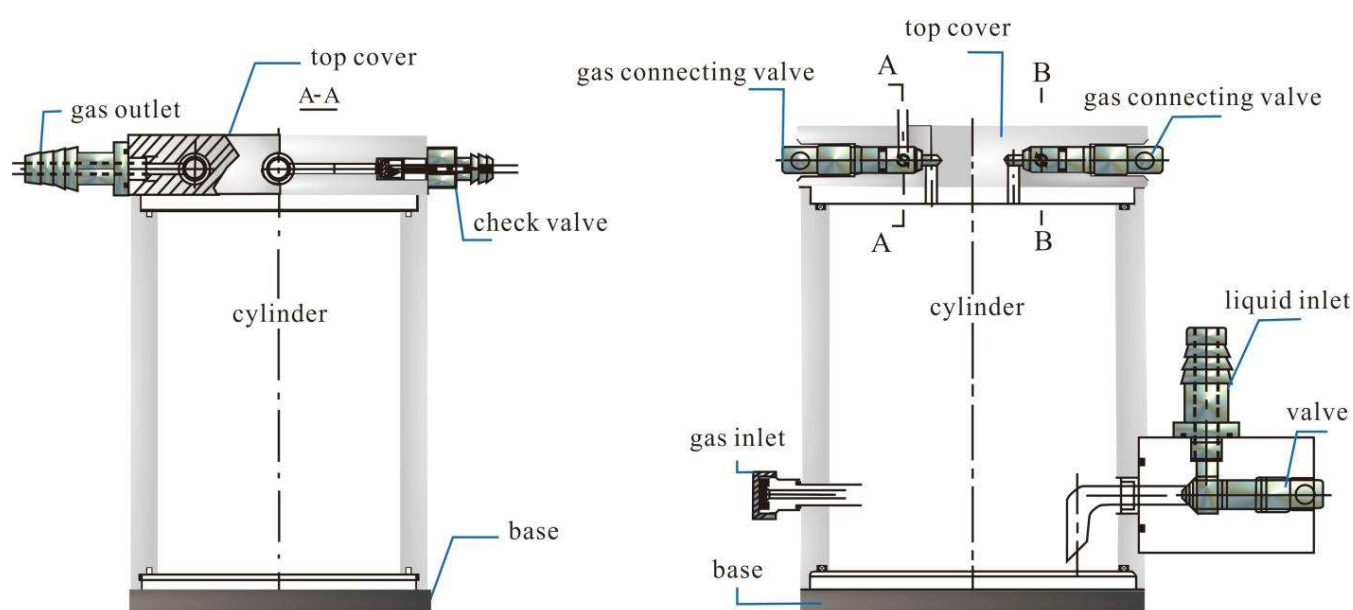


Figure 3. Schematic representation of the calibrating standard solution preparer.

Stock solution barrel: with a volume of 20 L and withstanding the pressure of 10 atm, the barrel is used to prepare, contain and transfer artificial seawater.

Thermostatic oscillator: independently developed, FZKJHWYC-P40, the device is mainly composed of the metal plate box, temperature probe, refrigerating system, heating system, circulation system, oscillator and control system, with the volume 40 L, temperature control range 4–50 °C (refrigerating), power 1500 w, and temperature resolution 0.1 °C; the oscillation mode is rotatory type, the rotary frequency is 30–400 rpm, and the timing range is 0–999 min.

Microsyringe: USA, HAMILTON, 825 RN, specification 22 s/2"/2, maximum range 250 µL, maximum tolerable temperature 115 °C, and maximum bearing pressure 2000 psig.

Vacuum pump: China, Flight, FY-4 C-N, ultimate pressure 2 Pa, power 550 w, and pumping rate 14.4 m³/h.

3.3. Experimental Materials and Reagents

Artificial seawater: prepared in laboratory, the salinity is 3.2–3.5%;

High purity argon: standard substance, 99.999%;

Carbon dioxide standard gas: standard substance, the balance gas is argon.

3.4. Calculation of $M_{\Delta i-0}$

The components of artificial seawater added in all closed systems during the experiment are the same, and carbon dioxide in seawater is the source of all carbon dioxide forms in the closed systems. Therefore, the total amount of substance ($M_{\Delta i-0} = M_{iCO_2} - M_{0CO_2}$) of the increased carbon dioxide in the balance system i relative to the balance system 0 can be calculated through the total amount of substance M_{all-0} of carbon dioxide in the balance system 0 and the volumes V_i and V_0 of artificial seawater in the two systems, that is: $M_{\Delta i-0} = (V_i - V_0) * M_{all-0}$. The volumes of seawater in balance systems 0, 1, 2, ... i are recorded, and $M_{\Delta i-0}$ is solved by combining Equation (42). The addition of an equal volume of standard gas can also be used in the experiment, where artificial seawater of the same volume is added in all closed systems, and then carbon dioxide standard gas with the volume of $V_{\Delta i-0}$ and the concentration of C_{sg} is added in systems 1.2.3 ... i using a microsyringe, with the balance system 0 as the original system. Then, the total amount of substance of the increased carbon dioxide in the balance system I relative to the balance system 0 can be calculated directly by the ideal gas equation of state: $M_{\Delta i-0} = M_{iCO_2} - M_{0CO_2} = PV_{\Delta i-0} * C_{sg}/RT$. In the experiment, the same microsyringe and the same vial of standard gas are used to reduce the possible error caused by the differences in standard gases and injectors.

3.5. Experimental Process

The experimental process roughly includes several parts, namely the preparation of artificial seawater, system vacuation, seawater import, injection of medium gas, system balance, headspace transfer, gas test, experimental verification and so on.

A total of 20 L artificial seawater is prepared (Yu-Bin Hu, 2014) for later use;

Three calibrating standard solution preparers ①, ② and ③ are washed with 99.999% high purity argon six times and vacuated using a vacuum pump until the pressure gauge reading of the system is 2 Pa;

Amounts of 1 L, 2 L and 3 L artificial seawater are imported into calibrating standard solution preparers ①, ② and ③, respectively, from the inlet valve at the bottom of the chamber;

Next, 99.999% high purity argon is injected into the chambers of preparers ①, ② and ③ from gas-connecting valves on the top cover, until the pressure gauge reading in the chamber is 101,325 Pa;

The calibrating standard solution preparers are oscillated in the thermostatic oscillator for 30 min and stand still at a constant temperature for 6 h to reach gas–liquid balance;

After balance, a 300 mL vacuum gas bag is connected to the outside through the gas connecting valve on the top cover;

Next, 99.999% high purity argon is injected into the volume transfer ball from the inlet on the top cover, and the vacuum gas bag inlet valve connected to the outside is opened to transfer the headspace gas to the gas bag;

The gas bag is connected to the Picarro G2131-I inlet, and the concentration of carbon dioxide in the gas mixture is measured and recorded. The standard gas is used for calibration at intervals of 5 samples before and during measurement.

4. Results and Discussion

4.1. Measurement of Henry's Law Constant of Carbon Dioxide in Artificial Seawater and Concentration of Free Carbon Dioxide

According to the experimental design scheme, the Henry's law constant of carbon dioxide in artificial seawater at different temperatures is measured based on the concentration of carbon dioxide in the headspace gas phase in each balance system and the $M_{\Delta i-0}$ between balance systems. In the experiment, two bags of 300 mL transferred headspace gas mixture are collected from each balance system to detect the concentration of carbon dioxide, or the headspace gas mixture is directly determined by opening the gas–liquid separator switch and connecting the outlet on the top cover of the calibrating standard

solution preparer to the Picarro inlet via the line. A gas mixture sample is tested every 1–2 s on average after entering Picarro G2131-I to form a test curve, and the stable near-straight line data are selected as the valid data of the headspace sample (Figure 4). The average of all valid data is taken as the carbon dioxide value of the headspace sample, with the standard deviation (Std dev) between valid data in the stable test curve less than 50 ppb. The data of the carbon dioxide concentration in the headspace sample is calculated using the method specified in the experimental design principle to obtain the Henry's law constant of carbon dioxide under the corresponding conditions (Table 1). Based on the data measured in the experiment, the concentration of free carbon dioxide in artificial seawater can be calculated using Equation (1).

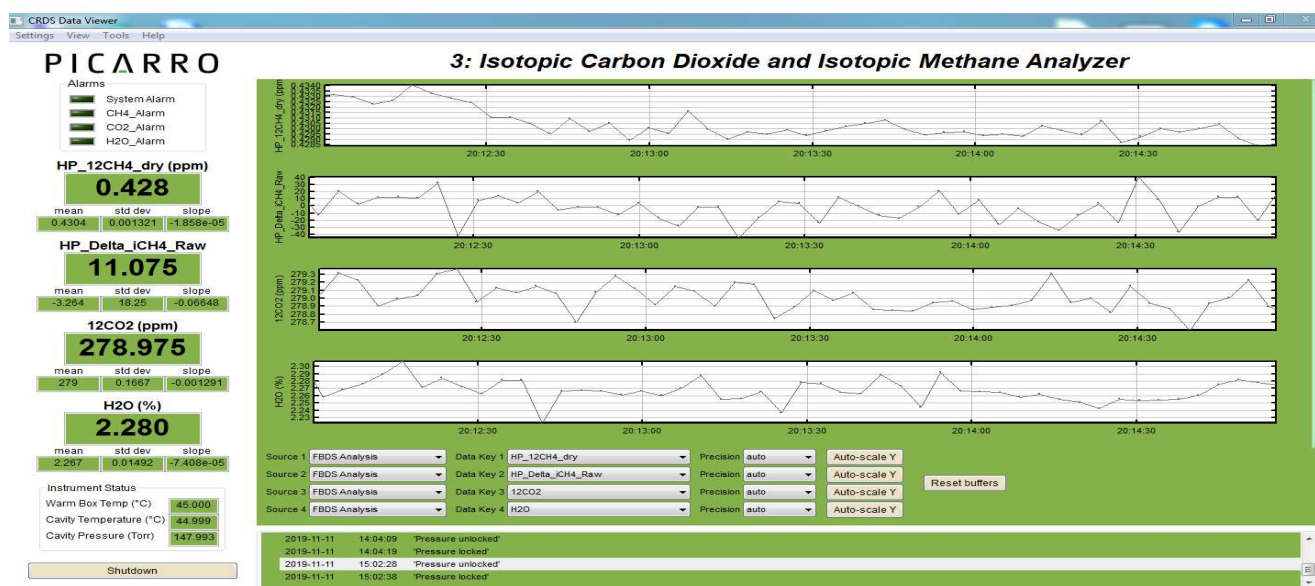


Figure 4. Test curve of carbon dioxide in the gas mixture in the balance system.

Table 1. Experimental data table of Henry's law constant of carbon dioxide in artificial seawater at different temperatures.

Seawater Temperature (°C)	Seawater Salinity (‰)	Henry's Law Constant of Carbon Dioxide in Seawater (kpa)	Seawater Salinity (‰)	Henry's Law Constant of Carbon Dioxide in Seawater (kpa)
20	35	139,741.4351	33	139,739.9233
18	35	131,725.6899	33	131,724.2447
16	35	124,068.3677	33	124,066.9884
14	35	116,496.1441	33	116,494.8329
12	35	109,265.7941	33	109,264.5501
10	35	102,177.1956	33	102,176.0197
8	35	95,433.44691	33	95,432.33758
6	35	88,858.37386	33	88,857.33137
4	35	82,642.78864	33	82,641.81077
3	35	79,587.6257	33	79,586.68021
20	34	139,740.6792	32	139,739.1674
18	34	131,724.9673	32	131,723.5221
16	34	124,067.678	32	124,066.2987
14	34	116,495.4885	32	116,494.1773
12	34	109,265.1721	32	109,263.928
10	34	102,176.6076	32	102,175.4317
8	34	95,432.89224	32	95,431.78292
6	34	88,857.85261	32	88,856.81013
4	34	82,642.2997	32	82,641.32184
3	34	79,587.15295	32	79,586.20747

4.2. Verification of Henry's Law Constant of Carbon Dioxide in Artificial Seawater—Systems Transformation Coincidence Experiment

The systems transformation coincidence experiment is that with systems 0 and 1 as the set original balance system, the Henry's law constant of carbon dioxide at different temperatures is determined based on system 0-1-2, system 0-1-3 and system 1-2-3, and their standard deviation is compared to evaluate the reliability of the method. In the systems transformation coincidence experiment, four balance systems are used in which the standard deviation between the Henry's law constant measured in each balance system and the average of the Henry's law constant measured in multiple balanced systems is only $(10\text{--}50) \times 10^{-6}$ kPa, the maximum relative standard deviation is 0.5‰, and the Henry's law constants repeatedly determined in the systems transformation almost coincide (Figure 5). The systems transformation coincidence experiment verifies the accuracy of this experiment and the scientificity and reliability of the D.B.S/Henry's Law design. D.B.S/Henry's Law, a scientific method for determining the Henry's law constant of carbon dioxide and the concentration of free carbon dioxide, is suitable for the determination of the Henry's law constant of carbon dioxide in artificial seawater. This method can be further used in the determination of the Henry's law constant of carbon dioxide and the concentration of free carbon dioxide in the natural seawater of different areas.

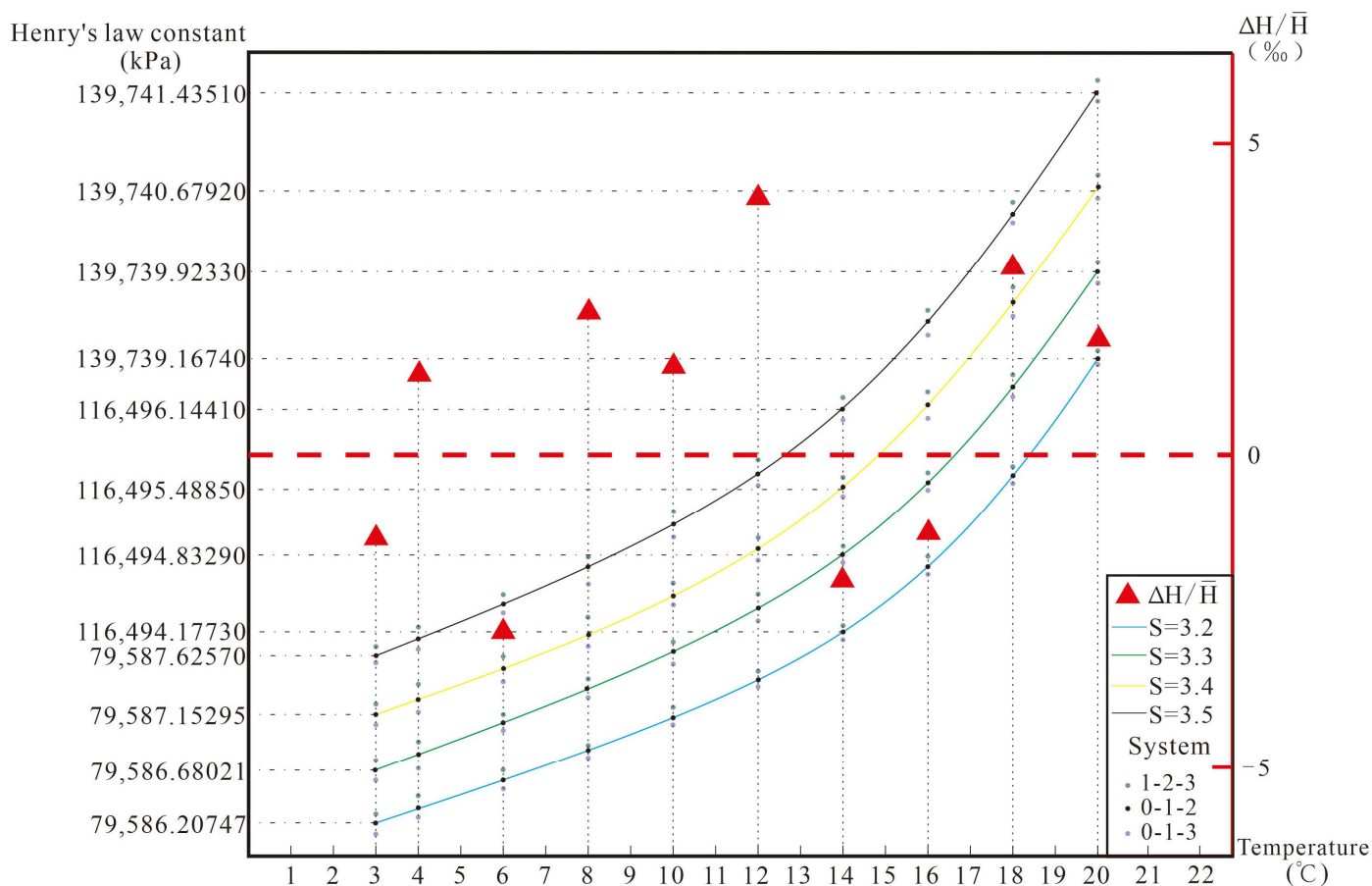


Figure 5. Changes in Henry's law constant of carbon dioxide in seawater at different temperatures based on systems transformations.

5. Conclusions

In this paper, the D.B.S/Henry's Law for determining the Henry's law constant of carbon dioxide and the concentration of free carbon dioxide is proposed and is used to measure the Henry's law constant of carbon dioxide in artificial seawater with salinities of 32, 33, 34 and 35‰ at 3–20 °C. Concurrently, a systems transformation coincidence

experiment is conducted to verify the accuracy of this experiment and the scientificity and reliability of the D.B.S/Henry's Law. The Henry's law constant of carbon dioxide in seawater measured in this experiment can be used as an important reference for the determination of the concentration of free carbon dioxide in seawater. In addition, it can also be used as a supplement of the methods specified in national and industrial standards, which are used to determine the free carbon dioxide content and are applied to the detection of the Henry's law constant of carbon dioxide and the concentration of free carbon dioxide.

Author Contributions: Methodology, G.-H.L. and L.-T.D.; Validation, H.-N.C. and C.-F.W.; Investigation, J.-Y.H., C.-P.W., T.-R.C. and H.-Y.Z.; Resources, M.-M.W. and J.-Y.H.; Writing—original draft, G.-H.L. and L.-T.D.; Writing—review & editing, M.-M.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by [National Key R&D Program of China] grant number [2016YFC0303902-04] and [National Natural Science Foundation of China], grant number [NSFC 42102259], And The APC was funded by [National Training Program of Innovation Entrepreneurship for Undergraduates] grant number [S202111775007].

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: My research data has been shared in article.

Acknowledgments: This study was supported by National Key R&D Program of China (No. 2016YFC0303902-04) and National Natural Science Foundation of China (NSFC 42102259) and National Training Program of Innovation Entrepreneurship for Undergraduates (S202111775007).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Chen, Y.R.; Zhao, D.L.; Lin, Z.K. Estimation of gas exchange rate and carbon dioxide gas flux at the sea-air interface. *Haiyang Xuebao* **2021**, *43*, 8–20.
- Qiu, S.; Ye, H.J.; Zhang, Y.H.; Tang, S.L. Multi-linear regression of partial pressure of sea-surface carbon dioxide in the South China Sea and its mechanism. *J. Trop. Oceanogr.* **2022**, *41*, 106–116.
- Ye, L.A.; Zhang, H.; Zhu, Z.; Liu, L.; Zhou, S. Distribution characteristics of $p(\text{CO}_2)$ in the sea-atmosphere interface in the East China Sea. *Environ. Sci. Technol.* **2019**, *42*, 121–127.
- Meng, G.X.; Lü, Q.T.; Yan, J.Y.; Deng, Z.; Qi, G.; Xue, R.H. The research and application of explorational technology of “penetrating” to geology and mineral investigation in overburden area. *Acta Geos. Sin.* **2019**, *40*, 637–650.
- Liu, T.Z.; Wang, B.L.; Liang, C.H.; Wang, X.D.; Yang, C. Spatiotemporal variation of CO_2 partial pressure and exchange flux at the air-water interface of the hongfeng reservoir. *Earth Environ.* **2019**, *47*, 851–856.
- Chen, F.; Lu, H.F.; Liu, J.; Zhuang, C.; Wu, C.; Cao, J.; Zhou, Y.; Liu, G.H. Sedimentary geochemical response to gas hydrate episodic release on the northeastern slope of the South China Sea. *Earth Sci.* **2016**, *41*, 1619–1629.
- Qu, B.X.; Song, J.M.; Yuan, H.M.; Li, X.; Li, N.; Duan, L.; Ma, Q.; Chen, X. Advances of seasonal variations and controlling factors of the sea-air CO_2 flux in the East China Sea. *Adv. Earth Sci.* **2013**, *28*, 783–793.
- ASTM D513-2006; Standard Test Methods for Total and Dissolved Carbon Dioxide in Water. American Society for Testing and Materials: West Conshohocken, PA, USA, 2006.
- Geological and Mineral Industrial Standard of the People's Republic of China, DZ/T 0064.47-1993; Method for Inspection of Underground Water Quality. Determination of Free Carbon Dioxide by Titration, Ministry of Geology and Mineral Resources of the PRC: Beijing, China, 1993.
- Geological and Mineral Industrial Standard of the People's Republic of China, DZ/T 0064.48-1993; Method for Inspection of Underground Water Quality. Determination of Erosive Carbon Dioxide by Titration, Ministry of Geology and Mineral Resources of the PRC: Beijing, China, 1993.
- Geological and Mineral Industrial Standard of the People's Republic of China, DZ/T 0064.49-1993; Method for Inspection of Underground Water Quality. Determination of Carbonate, Bicarbonate and Hydroxide by Titration, Ministry of Geology and Mineral Resources of the PRC: Beijing, China, 1993.
- Geological and Mineral Industrial Standard of the People's Republic of China, DZ/T 0064.74-1993; Method for Inspection of Underground Water Quality. Determination of Gases by Gas Chromatography, Ministry of Geology and Mineral Resources of the PRC: Beijing, China, 1993.
- Industry Standard of the People's Republic of China. SL 80-1994; Determination of Free Carbon Dioxide (Base Titration Method). Determination of Free Carbon Dioxide, Ministry of Water Resources of the PRC: Beijing, China, 1994.
- Feng, S.Z. *An Introduction to Marine Science*; Higher Education Press: Beijing, China, 1999.
- Fu, X.T.; Wang, Z.P.; Lu, S.T. Dissolving mechanism and equation of solubility of gas in water. *Sci. China Chem.* **1996**, *26*, 124–130.

16. Levy, J.B.; Hornack, F.M.; Levy, M.A. Simple determination of Henry's law constant for carbon dioxide. *J. Chem. Educ.* **1987**, *64*, 260. [[CrossRef](#)]
17. Wang, K.X.; Yao, M. A critical review of henry's law and its application in environmental science and engineering. *J. Zhejiang Shuren Univ.* **2004**, *4*, 90–94, 98.
18. Wang, Y.H.; Tao, S.; Li, X.Y.; Zhang, J.H.; Shi, J.; Shi, T.X.; Liu, R.H. Determination of volatile organohalides in water by twice phase equilibration/gc. *Environ. Chem.* **1997**, *16*, 68–72.
19. Robbins, G.A.; Wang, S.; Stuart, J.D. Using the static headspace method to determine henry's law constants. *Anal. Chem.* **1993**, *65*, 3113. [[CrossRef](#)]
20. Dukes, I.A.D. Measuring the henry's law constant for carbon dioxide and water with uv-visible absorption spectroscopy. *Anal. Sci.* **2020**, *36*, 971–975. [[CrossRef](#)] [[PubMed](#)]
21. Liu, G.H.; Wen, M.M.; Deng, L.T.; Cui, H.N.; Jia, Y.Y.; Cheng, S.H.; Cao, J.; Li, C. The determination of henry's law constant of methane in test water by a.r.m/headspace. *Acta Geos. Sin.* **2021**, *42*, 565–571.
22. Jia, Y.Y.; Liu, G.H.; Tan, T.; Wang, X.Y. Study on the preparation of standard solution of trace dissolved methane. *Sci. Technol. Innov. Her.* **2020**, *17*, 113–116.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.