



Modelling equilibrium distribution of carbonaceous ions and molecules in a heterogeneous system of CaCO₃–water–gas

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Abstract. Equilibrium processes involving dissolved CO₂ play a vital role in many biological and technological systems. Dissolved CO₂ is an available carbon source for autotrophic organisms that have great natural and technological relevancy. In many places, including northern Estonia, the soil bedrock is limestone (CaCO₃), which has a relatively small ion product and hence low solubility. However, in the equilibrium system CaCO₃ ↔ CO₃²⁻ ↔ HCO₃⁻ ↔ H₂CO₃ ↔ CO₂ the solubility of CaCO₃ is elevated, which causes a relatively high alkalinity (pH > 8) of surface and ground water as a result of increased concentration of CO₃²⁻, HCO₃⁻, and OH⁻ ions. In this paper the equilibrium processes involving CaCO₃ (limestone) in liquid–gas–solid phase systems are described. The equilibrium distribution of ions and molecules in the system is described on the basis of a structural scheme. A mathematical model is presented for the calculation of pH and concentrations of ions and molecules in the equilibrium system CO₃²⁻, HCO₃⁻, CO₂, Ca²⁺, H⁺, and OH⁻ at different concentrations of CO₂ in its liquid phase using an iteration method. The developed model was experimentally validated.

Key words: calcium carbonate, carbon dioxide, water, equilibrium, ternary system.

INTRODUCTION

Carbon dioxide is an important component of Earth's atmosphere, constituting approximately 390–400 ppm [1,2]. Carbon dioxide is produced during many different oxidation and decomposition processes in both natural and engineered environments [3,4]. Either in free (CO₂) or bonded forms (HCO₃⁻ and CO₃²⁻), carbon dioxide is an essential component of the biosphere, lithosphere, atmosphere, and hydrosphere, with a continuous dynamic exchange of CO₂ taking place between these spheres [3,4]. For autotrophic organisms, inorganic carbon (CO₂) is the main carbon source for growth [5,6]. Carbon dioxide is used in photosynthesis by algae and plants. Microorganisms fixing CO₂ from archaeal and bacterial domains have a substantial role in a variety of biogeochemical cycles (e.g. the nitrogen

and carbon cycles) and ecosystems [7,8]. Technological applications of microbial processes based on autotrophic bacteria, for example autotrophic nitrogen removal that uses both aerobic and anaerobic ammonium-oxidizing bacteria, the so-called anammox bacteria, are growing rapidly [5,6,9]. Applications for photoautotrophic microalgae are also being developed [10,11].

Photosynthesis of algae in natural water bodies leads to an increase in pH [12]. When CO₂ (more precisely, (CO₂)_w) is removed from water by photosynthesis, some HCO₃⁻ is converted into (CO₂)_w over intermediate H₂CO₃ in order to maintain equilibrium. Consequently, some CO₃²⁻ will take up protons originating from dissociation of water and produce HCO₃⁻ in order to compensate for the decrease in the concentration of HCO₃⁻. These two processes combined result in a new equilibrium. However, due to the release of surplus OH⁻ ions the pH value of the water increases [12]. Inorganic carbon is taken up by microbial cells in the form of

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dissolved CO_2 , which permeates biological membranes by diffusion and results in a surplus of H^+ ions inside cells, causing a drop in intracellular pH [13]. The growth of autotrophic cells therefore depends on the availability of dissolved CO_2 . If however too much dissolved CO_2 enters the cytoplasm, causing acidification, the cells may be unable to expel the excess protons, resulting in the inhibition of cells' metabolism [14]. Additionally, this inhibitory effect of CO_2 may be linked to changes in the permeability and structure of cell membranes and enzymatic synthesis in the cytoplasm [15]. Relatively little attention appears to have been paid to studies concerning the CO_2 limitations and C/N ratio on autotrophic bacteria [9].

Limestone, which forms the soil bedrock in northern Estonia, causes relatively high alkalinity ($\text{pH} > 8$) of ground and surface water [16]. Equilibrium processes between carbonaceous ions and molecules dissolved in water from this solid phase (i.e. limestone bedrock, which mainly consists of CaCO_3) and the atmosphere (CO_2 in the gaseous phase) also affect treatment processes of potable water and wastewater [3,8]. This equilibrium system involves the ions and molecules CO_3^{2-} , HCO_3^- , CO_2 , Ca^{2+} , H^+ , OH^- , and H_2CO_3 .

Although CO_2 balance in aqueous mediums has been a subject of intensive kinetic and computational studies, a detailed mechanistic interpretation of CO_2 in water environments has yet to be established [17]. For practical purposes, an accurate mathematical model enabling the calculation of the concentrations of all dissolved ions and molecules is required.

In this paper the equilibrium system of an aqueous solution of CaCO_3 and the corresponding equilibrium

content of CO_2 in the gas and water phases is described in a structural scheme. A mathematical model applying the solution to an iterative series of equations for the calculation of the components in this three-phase system is presented. Our model also contains interfacial mass transfer in the formation of the equilibrium distribution of the components of the system.

COMPONENTS OF THEORETICAL MODEL FOR THE EQUILIBRIUM SYSTEM OF SOLID CaCO_3 -WATER- CO_2 IN THE GAS PHASE

The interfacial transfer of CO_3^{2-} between solid and liquid phases and CO_2 between gas and liquid phases occurs in the ways shown in Fig. 1.

The quantity of carbonaceous ions and molecules in the liquid phase is defined as the sum of the quantity of CO_2 transferred from the gas to the liquid phase and the amount of CO_3^{2-} transferred from the solid to the liquid phase. This transition is described by a mass transfer of matter:

$$m_{\Sigma}(\text{CO}_X)_W = \Delta m(\text{CO}_2) + \Delta m(\text{CO}_3^{2-}). \quad (1)$$

After reaching equilibrium, the total amount of carbonaceous ions and molecules $m_{\Sigma}(\text{CO}_X)_W$ in the liquid phase with the volume V_W is quantitatively distributed in accordance with the equilibrium constants based of the structural scheme shown in Fig. 2.

The structural scheme suggests that H^+ ions play a central role in the establishment of equilibrium in the system and form a link between all equilibrium

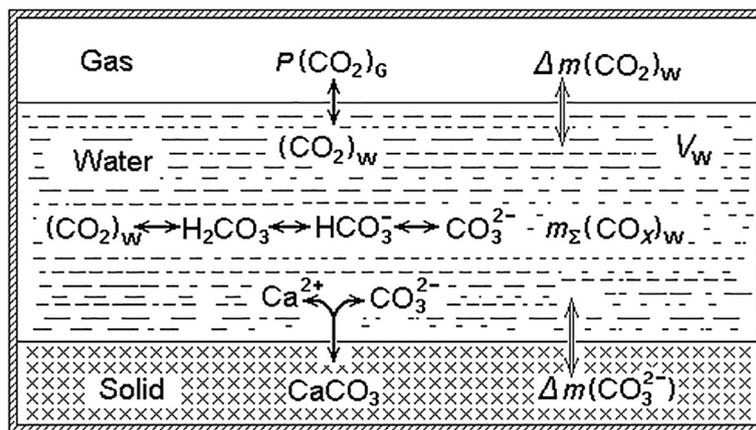


Fig. 1. Formation of an equilibrium state of ions and molecules in the ternary heterogeneous system CaCO_3 -water-gas. $P(\text{CO}_2)_G$ denotes the partial pressure of CO_2 in the gaseous phase; V_W is the volume of the liquid phase; $(\text{CO}_2)_W$ is the dissolved CO_2 in the liquid phase; H_2CO_3 , HCO_3^- , and CO_3^{2-} are the carbonaceous ions and molecules in the liquid phase; Ca^{2+} and CO_3^{2-} are the ions in the liquid phase and dissociation products of solid CaCO_3 ; $\Delta m(\text{CO}_2)$ is the amount of CO_2 transferred between the gas and liquid phases; $\Delta m(\text{CO}_3^{2-})$ is the amount of CO_3^{2-} ions transferred between the solid and liquid phases; $m_{\Sigma}(\text{CO}_X)_W$ is the total amount of carbonaceous ions and molecules in the liquid phase.

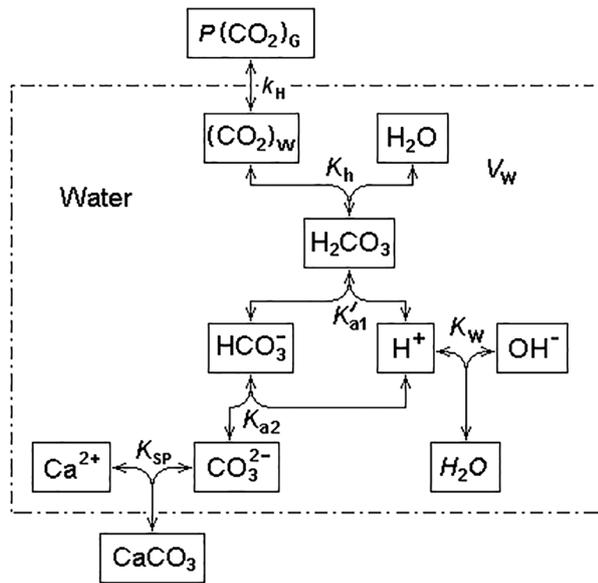


Fig. 2. Structural scheme of the equilibrium distribution of ions and molecules in the ternary heterogeneous system CaCO_3 –water–gas. k_H is Henry's constant, i.e. the distribution ratio of CO_2 between water and the gaseous phase; K_h is the coefficient of the equilibrium reaction of $(\text{CO}_2)_w + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$; K'_{a1} and K_{a2} are the acid dissociation constants of H_2CO_3 and HCO_3^- , respectively; K_{sp} is the solubility product of CaCO_3 ; K_w is the ion-product constant of water.

processes described in this theoretical model. In the model the dissociation of H_2CO_3 (the reaction product of CO_2 and H_2O) produces H^+ and HCO_3^- ions. The dissolution of CaCO_3 produces CO_3^{2-} and Ca^{2+} ions. The CO_3^{2-} ions take up H^+ ions and form HCO_3^- ions, leading to a decrease in the concentration of protons. These two processes produce a new equilibrium. Due to the release of OH^- ions by the dissociation of water molecules, pH rises. As the ion-product constant of water K_w must remain constant, the excess H^+ and OH^- ions combine, forming water molecules. The final pH of the equilibrium system depends on the concentration of CO_2 in the water phase.

Gaseous carbon dioxide dissolves in water with only a small fraction converted into carbonic acid (H_2CO_3), which is in complex equilibrium with CO_2 and its dissociated forms HCO_3^- and CO_3^{2-} . Based on the literature, the concentration of H_2CO_3 would form less than 0.3% [8,18–20] of the equilibrium concentration of $(\text{CO}_2)_w$ in the aqueous phase. Therefore, the concentration of the unionized species H_2CO_3 and $(\text{CO}_2)_w$ is often summed into a single hypothetical species $(\text{CO}_2)^*$, which effectively represents the concentration of all dissolved CO_2 . Thus, the first acid ionization constant K_{a1} is expressed as a product of both the constants K_h

and K'_{a1} , and the concentration of H_2CO_3 may be omitted from the calculations [8]. The constant K'_{a1} has a value of $10^{-3.5}$, thus H_2CO_3 is a fairly strong acid. However, as the product of K_h and K'_{a1} , K_{a1} has a much smaller value ($K_{a1} = 4.45 \times 10^{-7}$) [8]. Therefore, carbonic acid is usually considered a weak acid, although K_{a1} actually characterizes the acidity of the hypothetical species CO_2^* [20].

A characteristic feature of the heterogeneous ternary system CaCO_3 –water–gas is that hydrogen is not driven out from the liquid phase to the gas phase in any form, unlike in the aqueous solutions of CaS , where hydrogen is transferred to the gas phase in the form H_2S [21].

The total amount of carbonaceous ions and molecules in the liquid phase with the volume V_w is determined by the sum of their concentrations:

$$m_z(\text{CO}_x)_w = V_w ([\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2]_w). \quad (2)$$

The amount of CO_3^{2-} ions transferred from the solid phase to the liquid phase with the volume V_w equals the amount of Ca^{2+} ions simultaneously transferred from the solid phase of CaCO_3 to the water phase:

$$\Delta m(\text{CO}_3^{2-}) = V_w [\text{Ca}^{2+}]. \quad (3)$$

The amount of CO_2 molecules transferred from the gas phase to the liquid phase is determined by the specific amount ($\Delta[\text{CO}_2]_w$) of CO_2 molecules transferred from the gas phase per unit volume (V_w) of the water phase:

$$\Delta m(\text{CO}_2) = V_w \Delta[\text{CO}_2]_w. \quad (4)$$

By combining Eq. (1) with Eqs (2), (3), and (4), an equation expressing the molar balance in the water phase of the heterogeneous system is formed:

$$[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CO}_2]_w = \Delta[\text{CO}_2]_w + [\text{Ca}^{2+}]. \quad (5)$$

The physical essence of Eq. (5) is that a difference between the total quantity of carbonaceous ions and molecules and the amount of calcium in the liquid phase occurs due to a transfer of CO_2 from the gas phase to the liquid phase. The term $\Delta[\text{CO}_2]_w$ on the right hand side of Eq. (5) contains the dimension of concentration. If the system is at equilibrium, the concentrations of all species in the liquid phase can be calculated on the basis of the following equations.

Henry's constant:

$$k_H = \frac{[\text{CO}_2]_w}{P(\text{CO}_2)_G} = 3.39 \times 10^{-2}, \frac{\text{mol}}{\text{L} \times \text{atm}}; \quad [18] \quad (6)$$

the first acid ionization constant (the product of K_h and K'_{a1}):

$$K_{a1} = \frac{[H^+] \times [HCO_3^-]}{[CO_2]_w} = 4.30 \times 10^{-7}, \text{ mol/L}; [22] \quad (7)$$

acid dissociation constant of HCO_3^- :

$$K_{a2} = \frac{[H^+] \times [CO_3^{2-}]}{[HCO_3^-]} = 4.70 \times 10^{-11}, \text{ mol/L}; [22] \quad (8)$$

solubility product of $CaCO_3$:

$$K_{SP} = [Ca^{2+}] \times [CO_3^{2-}] \cong 2.80 \times 10^{-9}, \text{ (mol/L)}^2; [23] \quad (9)$$

ion-product constant of water:

$$K_W = [H^+] \times [OH^-] = 1.01 \times 10^{-14}, \text{ (mol/L)}^2. [23] \quad (10)$$

In the heterogeneous system $CaCO_3$ –water–gas, charge balance can be expressed as follows:

$$2[Ca^{2+}] + [H^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-]. \quad (11)$$

BASIC EQUATIONS FOR THE CHARACTERIZATION OF THE EQUILIBRIUM OF THE SYSTEM

In this paper the chemical characterization of the equilibrium distribution of carbonaceous ions and molecules in the liquid phase, as well as the dissociation products of $CaCO_3$ and water, is given as functions of the concentration of CO_2 in water:

$$([Ca^{2+}], [CO_3^{2-}], [HCO_3^-], [H^+], [OH^-]) = f[CO_2]_w. \quad (12)$$

These functions are defined by the five implicit equations given above (7–11) containing five variables of the concentrations of Ca^{2+} , CO_3^{2-} , HCO_3^- , H^+ , and OH^- , i.e. the necessary and sufficient number of equations to solve the system. The equilibrium concentration of dissolved CO_2 in the liquid phase at a given partial pressure of CO_2 in the gaseous phase is calculated using Eq. (6). The concentration of CO_2 molecules in the water phase at a defined partial pressure in the gas phase is a constant taken into consideration in the equations.

In order to calculate the concentrations of the ions Ca^{2+} , CO_3^{2-} , HCO_3^- , H^+ , and OH^- at a predetermined value of the concentration of $[CO_2]_w$, it is necessary to solve a series of equations (7–11) in relation to one of

the concentrations of this as a function of the $[CO_2]_w$ concentration in the liquid phase. In this function the selected parameter accounts for all the remaining parameters of the equilibrium system. The complete solution to the system of equations in relation to the concentration of H^+ ions is based on the following fourth-degree equation:

$$\begin{aligned} & 2 \frac{K_{SP}[H^+]^2}{K_{a1} \times K_{a2}[CO_2]_w} + [H^+] \\ & = 2K_{a1} \times K_{a2} \frac{[CO_2]_w}{[H^+]^2} + K_{a1} \frac{[CO_2]_w}{[H^+]} + \frac{K_W}{[H^+]}. \end{aligned} \quad (13)$$

The analytic solution of the given fourth-degree Eq. (13) is complicated. Therefore, in practice simplified solutions for specific individual cases under real conditions are used. For most applications in the pH range 6–9, determining the approximate concentration of $[H^+]_{apx}$ considering equilibrium distribution as a partial solution is proposed, simplifying Eq. (13) to Eq. (14):

$$[H^+]_{apx} \cong \sqrt[3]{\frac{(K_{a1}[CO_2]_w)^2 K_{a2}}{2K_{SP}}}. [22] \quad (14)$$

Our aim was to determine the parameters of the equilibrium distribution of ions and molecules in the liquid phase of the ternary heterogeneous system CO_2 – HCO_3^- – CO_3^{2-} for a wider range of pH, i.e. from 7 to 12. Therefore, we converted Eq. (13) to a form suitable for iterative Eq. (15). Using Eq. (15), accurate results should also be obtained for any values of pH within the range 9–12:

$$[H^+] = \sqrt[3]{\frac{K_{a1} \times K_{a2}[CO_2]_w}{2K_{SP}} \left\{ K_{a1}[CO_2]_w \left(2 \frac{K_{a2}}{[H^+]} + 1 \right) + K_W - [H^+]^2 \right\}}. \quad (15)$$

The calculation of the equilibrium concentrations of Ca^{2+} , CO_3^{2-} , and HCO_3^- and pH was performed on the basis of the value for the equilibrium concentration of H^+ ions obtained by an iterative method based on Eq. (15) using different values for constant concentrations of CO_2 in the range of $[CO_2]_w \cong (2.74 \times 10^{-11} \div 8.02 \times 10^{-1})$ mmol/L with respective equilibrium values of $P(CO_2)_G \cong (8.08 \times 10^{-7} \div 2.37 \times 10^4)$ ppm. Results of these calculations are presented in Table 1.

The data in Table 1 show that in the given range of concentrations of $[CO_2]_w \cong 2.74 \times 10^{-11}$ mmol/L to $[CO_2]_w \cong 8.02 \times 10^{-1}$ mmol/L, the concentration of HCO_3^- and pH have a monotonous dependence

Table 1. Equilibrium concentrations of $[\text{CO}_2]_w$, HCO_3^- , CO_3^{2-} , and Ca^{2+} and pH in the system of gas–water–solid CaCO_3 at $t = 25^\circ\text{C}$. Boldface designates extremal of Ca^{2+} and CO_3^{2-} at $[\text{CO}_2]_w \cong 2.35 \times 10^{-5}$ mmol/L

$P(\text{CO}_2)_G$, ppm	$[\text{CO}_2]_w$, mmol/L	$[\text{HCO}_3^-]$, mmol/L	$[\text{CO}_3^{2-}]$, mmol/L	$\Sigma[\text{CO}_X]_w$, mmol/L	$[\text{Ca}^{2+}]$, mmol/L	pH
8.08×10^{-7}	2.74×10^{-11}	1.18×10^{-5}	5.54×10^{-3}	5.66×10^{-4}	5.05	12.00
2.55×10^{-5}	8.66×10^{-10}	1.18×10^{-4}	1.75×10^{-3}	1.87×10^{-3}	1.60	11.50
2.95×10^{-4}	1.00×10^{-8}	6.01×10^{-4}	3.94×10^{-3}	4.55×10^{-3}	0.71	11.15
2.95×10^{-3}	1.00×10^{-7}	2.77×10^{-3}	8.37×10^{-3}	1.11×10^{-2}	0.33	10.81
2.95×10^{-2}	1.00×10^{-6}	1.24×10^{-2}	1.67×10^{-2}	2.90×10^{-2}	0.17	10.46
2.95×10^{-1}	1.00×10^{-5}	4.88×10^{-2}	2.60×10^{-2}	7.48×10^{-2}	0.11	10.06
6.92×10^{-1}	2.35×10^{-5}	7.63×10^{-2}	2.71×10^{-2}	1.03×10^{-1}	0.10	9.88
2.95×10^0	1.00×10^{-4}	1.49×10^{-1}	2.42×10^{-2}	1.73×10^{-1}	0.12	9.54
2.95×10^1	1.00×10^{-3}	3.60×10^{-1}	1.41×10^{-2}	3.75×10^{-1}	0.20	8.92
8.85×10^1	3.00×10^{-3}	5.28×10^{-1}	1.01×10^{-2}	5.41×10^{-1}	0.28	8.61
2.95×10^2	1.00×10^{-2}	7.95×10^{-1}	6.91×10^{-3}	8.12×10^{-1}	0.41	8.27
3.90×10^2	1.32×10^{-2}	8.74×10^{-1}	6.31×10^{-3}	8.93×10^{-1}	0.44	8.19
8.85×10^2	3.00×10^{-2}	1.15	4.82×10^{-3}	1.19	0.58	7.95
2.95×10^3	1.00×10^{-1}	1.72	3.24×10^{-3}	1.82	0.86	7.60
2.37×10^4	8.02×10^{-1}	3.45	1.62×10^{-3}	4.25	1.73	7.00

on the concentration of $[\text{CO}_2]_w$. The data were characterized by a minimum value for solubility of CaCO_3 $[\text{Ca}^{2+}]_{\min} \cong 10^{-1}$ mmol/L and a maximum value of $[\text{CO}_3^{2-}]_{\max} \cong 2.71 \times 10^{-2}$ mmol/L at the value of $[\text{CO}_2]_w \cong 2.35 \times 10^{-5}$ mmol/L. In the range of $[\text{CO}_2]_w \cong (2.35 \times 10^{-5} \div 2.74 \times 10^{-11})$ mmol/L the corresponding value for the solubility of CaCO_3 increases according to the equation for the solubility product of CaCO_3 (K_{SP}) due to a decrease in the concentration of CO_3^{2-} from $\cong 2.71 \times 10^{-2}$ mmol/L to $\cong 5.54 \times 10^{-3}$ mmol/L. The decrease in the concentration of CO_3^{2-} ions calculated using this model occurs due to the decrease in the concentration of all carbonaceous species in the water phase. A graphical expression of the dependence of pH and the solubility of CaCO_3 on the content of $[\text{CO}_2]_w$ in the liquid phase is presented in Fig. 3. A logarithmic scale was used for the values of $[\text{CO}_2]_w$ concentration.

The concentration of CO_2 in the ambient air also depends on the season, with an annual fluctuation of approximately 3–9 ppm [2]. The content of CO_2 in the ambient air is normally the highest in March–April and the lowest in September–October, roughly following the Northern Hemisphere’s growing season. There is a dynamic balance between the atmosphere and hydrosphere, which is affected by oscillations in meteorological conditions such as atmospheric pressure and temperature [2]. Where $P(\text{CO}_2)_G$ levels differ from normal atmospheric values, the solubility of CaCO_3 is correspondingly affected. This situation arises when biological respiration, aerobic or anaerobic, releases

large amounts of CO_2 , as for example in soil containing a substantial population of microorganisms or in water bodies with active algal growth.

The graph in Fig. 3 also shows the dependence of pH and the solubility of CaCO_3 on the content of CO_2 in the water phase (pH_{apx} and $[\text{Ca}^{2+}]_{\text{apx}}$), as calculated by the approximate method using Eq. (13). Simplification of Eq. (13) to give Eq. (14), with the goal of the elimination of some terms, is justified on the grounds that such elimination does not create a significant error [24]. The solubility of CaCO_3 calculated using Eq. (13) produces a significant error if $\text{pH} > 9$ (Fig. 3).

The approximate method has been mentioned in many sources [3,4,8,24]. In conformity with Eq. (13) the solubility of Ca^{2+} monotonously decreases along with decreasing CO_2 concentrations (as shown with a dashed line in Fig. 3) [4]. This is in contrast with our model, demonstrating that the solubility of Ca^{2+} passes through a minimum at $[\text{CO}_2]_w \cong 2.35 \times 10^{-5}$ mmol/L and increases again with decreasing $[\text{CO}_2]_w$.

Figure 3 shows the graph has a well-defined quasi-linear region dependence of $\text{pH} = f(\log[\text{CO}_2]_w)$ at $\text{pH} < 9$. This dependence is described by a linear equation following the approximate expression [22]:

$$\text{pH}_{\text{apx}} \cong \frac{1}{3} \{ \log(2K_{\text{SP}}) - \log K_{\text{a}2} - 2(\log K_{\text{a}1} + \log[\text{CO}_2]_w) \}. \quad (16)$$

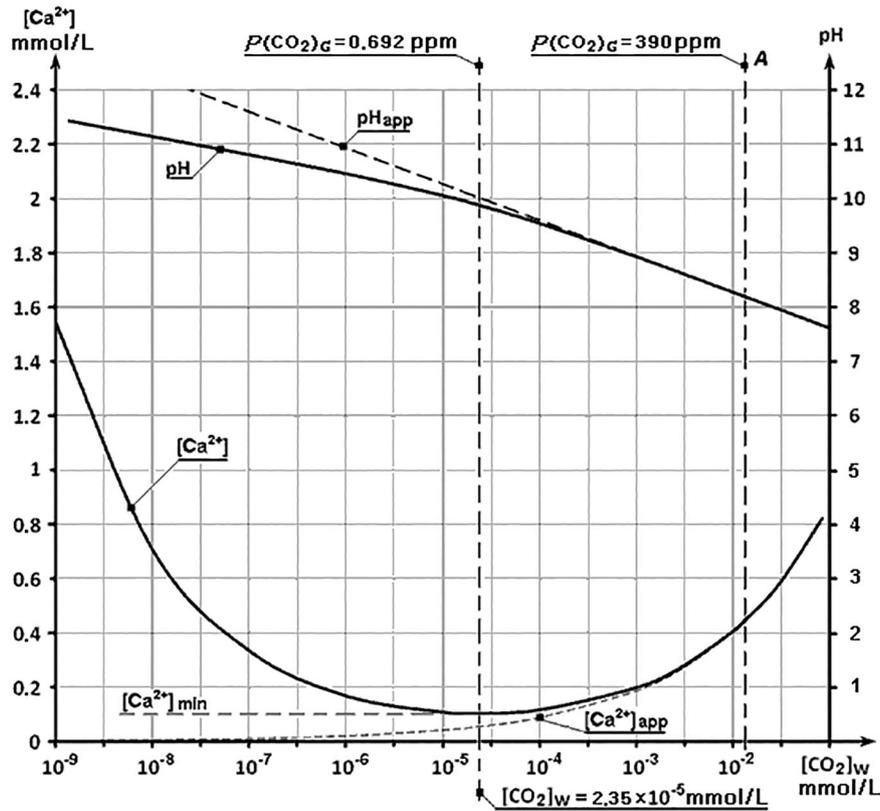


Fig. 3. Dependence of pH and $[Ca^{2+}]$ on $[CO_2]_w$. A refers to the content of $[CO_2]_w$ in the liquid phase at $P(CO_2)_G \cong 3.9 \times 10^2$ ppm [1] in the ambient air at standard conditions (25 °C, 100 kPa).

INTERFACIAL TRANSPORT OF SUBSTANCES IN A HETEROGENEOUS SYSTEM AT THE EQUILIBRIUM DISTRIBUTION OF $CaCO_3-CO_3^{2-}-HCO_3^--(CO_2)_w-(CO_2)_G$

During the formation of an equilibrium state, all transferred calcium ions remain in the liquid phase. Therefore, the transfer of CO_3^{2-} from the solid phase to the liquid phase is determined by the amount of Ca^{2+} ions in the liquid phase:

$$\Delta[CO_3^{2-}]_w = [Ca^{2+}], \tag{17}$$

where $\Delta[CO_3^{2-}]_w$ is the amount of CO_3^{2-} transferred from the solid ($CaCO_3$) to the liquid phase per unit volume of the liquid.

The amount of CO_2 transferred from the gas phase to the liquid phase per unit volume of the liquid during the formation of equilibrium in the system containing carbonaceous ions and molecules can be derived from Eqs (1) and (17) as:

$$\Delta[CO_2]_w = \Sigma[CO_X]_w - [Ca^{2+}], \tag{18}$$

where $\Delta[CO_2]_w$ is the amount of CO_2 transferred to the liquid phase per unit volume of the liquid and $\Sigma[CO_X]_w$ is the total amount of carbonaceous ions and molecules in the liquid phase at equilibrium.

The data in Table 1 and in Fig. 4 show that at a value of $[CO_2]_w \cong 2.35 \times 10^{-5}$ mmol/L, the total equilibrium concentration of carbonaceous ions and molecules in the liquid phase is nearly equal to the concentration of calcium ions:

$$\Sigma[CO_X]_w \cong [Ca^{2+}], \tag{19}$$

$$\Delta[CO_2]_w = \Sigma[CO_X]_w - [Ca^{2+}] \cong 0. \tag{20}$$

Consequently, there is no transfer of CO_2 from the gas phase, which corresponds to the case of equilibrium in a closed system without the gas phase. At the value $[CO_2]_w = 1.32 \times 10^{-2}$ mmol/L the total equilibrium

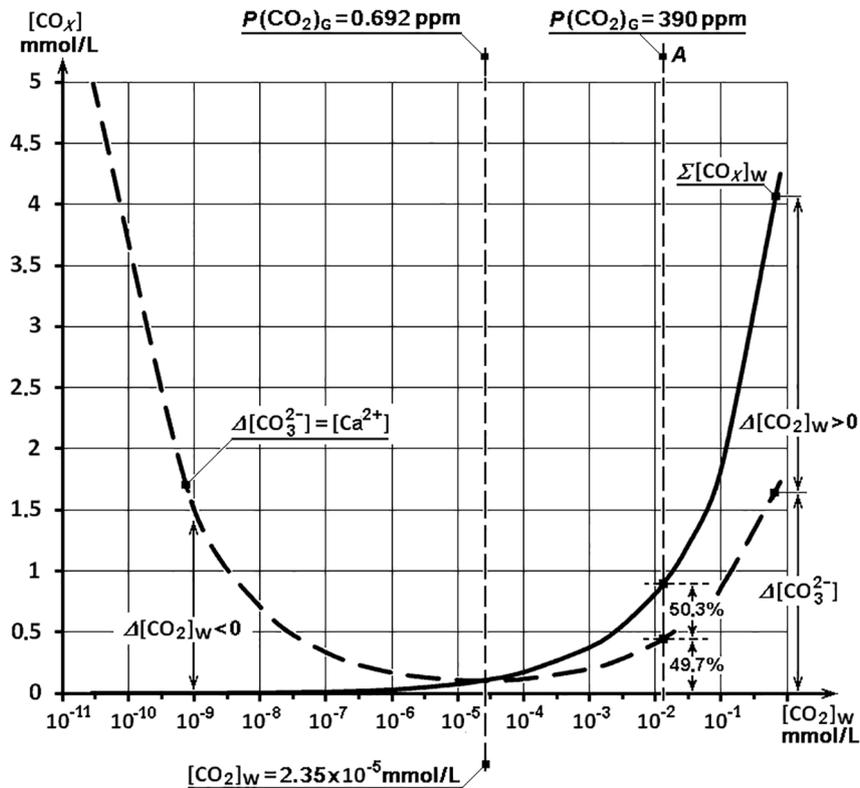


Fig. 4. Functions of the phase transfer of $\Delta[\text{CO}_3^{2-}] = f[\text{CO}_2]_w$ and $\Delta[\text{CO}_2]_w = f[\text{CO}_2]_w$.

concentration of calcium ions was approximately less than twice the sum of carbonaceous ions and molecules:

$$\Sigma[\text{CO}_X]_w \approx 2[\text{Ca}^{2+}]. \quad (21)$$

Thus, the transfer of CO_2 from the gas phase accounts for nearly half the amount of carbonaceous ions and molecules in the liquid phase, with the other half of the carbonaceous ions and molecules resulting from the transfer of CO_3^{2-} from the solid phase to the water phase (see Fig. 4).

The dependence of the phase transfer of carbonaceous ions and molecules on the concentration of dissolved carbon dioxide $\Delta[\text{CO}_3^{2-}] = f[\text{CO}_2]_w$ and $\Delta[\text{CO}_2]_w = f[\text{CO}_2]_w$ is shown in Fig. 4.

The region $[\text{CO}_2]_w > 2.35 \times 10^{-5}$ mmol/L was characterized by the condition $\Delta[\text{CO}_2]_w > 0$, i.e. transfer of CO_2 from the gas phase to the liquid phase, while the region $[\text{CO}_2]_w < 2.35 \times 10^{-5}$ mmol/L was characterized by the condition $\Delta[\text{CO}_2]_w < 0$, i.e. transfer of CO_2 from the liquid phase to the gas phase.

The value $[\text{CO}_2] \cong 2.35 \times 10^{-5}$ mmol is characterized by the condition $\Delta[\text{CO}_2]_w \cong 0$, i.e. lack of a transfer of

CO_2 between the liquid and the gaseous phase, which corresponded to the case of equilibrium in a closed system.

EXPERIMENTAL VALIDATION OF THE THEORETICAL MODEL

A series of experiments were performed in order to validate the theoretical model CaCO_3 –water–gas. A five-necked Simax 1 L glass bottle was used as a reaction cell and thermostatted to 25.0 ± 0.1 °C in a water bath (ELMI SkyLine). The reaction cell was equipped with a pH glass electrode (Mettler Toledo InLab[®] Routine, pH = 0–14), temperature sensors (Jenway model 027500), and two gas inlets enabling the channelling of the gas flow through the liquid phase using a disperger and the gas phase without dispersing the gas through the liquid phase. The gas outlet was equipped with a water lock in order to prevent penetration of ambient air into the reaction medium. The pH and temperature values were measured and recorded using a pH meter (Jenway type 3520) and Dataway software.

For the liquid phase, MilliQ water was used with added KCl (100 mg/800 mL) to ensure sufficient conductivity for accurate pH measurements at low concentrations of substrate. The gas mixtures used for purging the liquid phase are listed in Table 2. The gas mixtures and Argon 5.0 and 6.0 (argon containing <10 ppm or <1 ppm impurities, respectively) were purchased from AGA Eesti Ltd. For aeration the liquid phase was purged with ambient air until the pH value dropped below 6 in the liquid phase; then solid CaCO₃ (CAS # 471-34-1, 99.95%, obtained from Sigma-Aldrich) was added to the liquid phase with discontinued

aeration. Experiments of purging the liquid phase with argon containing small concentrations of CO₂ were also carried out (Table 2). In these experiments, purging was continued until a stable pH value was reached and then solid CaCO₃ was added. During the experiment the liquid phase was agitated at 200 rpm using a magnetic stirrer. At the end of the experiment, stirring was discontinued and solids were let to settle for 30 min.

From settled samples, total hardness and alkalinity were determined titrimetrically. In addition, from the filtrated samples (0.45 µm membrane filter), the concen-

Table 2. Experimentally measured and model-predicted values for the concentration of Ca²⁺

Composition of gas atmosphere	[Ca ²⁺] measured, mmol/L	[Ca ²⁺] theoretically predicted, mmol/L	<i>p</i> -value	pH value measured	pH value theoretically predicted	<i>p</i> -value
A. Ambient air, 390 ppm CO ₂	0.421 ± 0.005	0.444	0.24	8.09 ± 0.03	8.19	0.26
B. Ar 5.0, <1.7 ppm CO ₂	0.113 ± 0.012	<0.108	0.80	9.83 ± 0.03	9.67	0.62
C. Ar, 0.836 ppm CO ₂	0.100 ± 0.016	0.104	0.84	10.02 ± 0.03	9.88	0.24
D. Ar 6.0, <0.1 ppm CO ₂	0.120 ± 0.007	<0.126	0.52	10.06 ± 0.03	10.25	0.23
E. Ar, previously purified with 5 M NaOH	0.145 ± 0.009	Not calculated		10.24 ± 0.03	Not calculated	

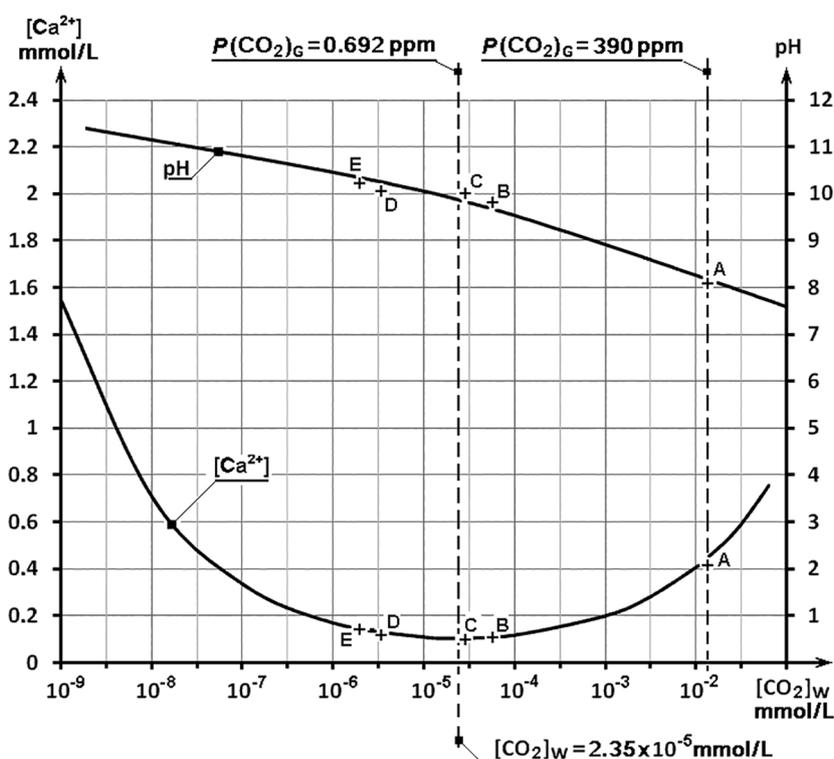


Fig. 5. Experimentally determined values for the concentration of soluble Ca²⁺ and pH. Experimental data points A–E are specified in Table 2.

tration of Ca^{2+} was determined using ion chromatography (type Dionex ICS-1000 ion chromatograph, suppressor Dionex CERS 500, 4 mm, column type Dionex IonPac CS12A, 4 mm, with a CG12A 4 mm guard column). Total hardness was determined by complexometrical titration of Ca^{2+} with 0.001 M EDTA solution. The experimental results are shown in Table 2 and Fig. 5. In order to evaluate statistical similarity of data from the experiments and theoretical model, p -values of two-way t -test for both data sets were calculated ($\alpha = 0.05$).

Experimentally determined values for the concentration of soluble Ca^{2+} , in accordance with the model developed in this study, showed a minimum value at a $P(\text{CO}_2)_G$ of 0.836 ppm and a $[\text{CO}_2]_W$ value of 2.82×10^{-5} mmol/L, thus providing evidence in favour of the efficacy of the theoretical model developed in this study. The statistical similarity between experimental data and calculated data obtained by the theoretical model was shown by the two-way t -test (Table 2).

CONCLUSIONS

The developed model for equilibrium distribution in the system solid CaCO_3 –water–gas containing CO_2 can be used for the determination of the concentrations of all components in the water phase over a wide range of natural and industrial conditions, based on the known content of CO_2 in the water phase in equilibrium with the gas phase. The developed model also describes interfacial mass transfer of CO_3^{2-} between the solid and liquid phases and CO_2 between the liquid and gas phases. Quantitative evaluation of the equilibrium distribution of ions and molecules in the system CaCO_3 – CO_3^{2-} – HCO_3^- – CO_2 at an equilibrium state showed a value of $\text{pH} \cong 8.2$, which is characteristic for a situation where limestone (mainly consisting of CaCO_3) bedrock is in contact with water and the atmosphere. The value $\text{pH} \cong 8.2$ corresponds to the content of CO_2 in water in equilibrium with atmospheric air (gas phase) containing $P(\text{CO}_2)_G \cong 390$ ppm at a temperature of $t \cong 25$ °C. Quantitative evaluation of the equilibrium distribution of the species CaCO_3 – CO_3^{2-} – HCO_3^- – CO_2 in a ternary heterogeneous system identified a relevant minimum solubility of $s[\text{CaCO}_3]_{\min} \cong 0.1$ mmol/L. The model allows for assessment of the impact of anthropogenic processes on the natural environment and could be usefully applied by environmental technologists, for instance in wastewater treatment, including nitrogen removal from reject water of biomethane production. The model is useful for developing innovative methods for the measurement of $[\text{CO}_2]_W$. This will be a topic for future research by our group.

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Süsinikku sisaldavate ioonide ja molekulide tasakaalulise jaotuse modelleerimine heterogeenses süsteemis CaCO_3 -vesi-gaasifaas

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Lahustunud CO_2 osalusel kulgevad tasakaalulised protsessid on paljudes bioloogilistes ja tehnoloogilistes süsteemides väga olulised. Lahustunud CO_2 on peamine süsinikuallikas autotroofsetele organismidele, kel on suur tähtsus looduslikes ökosüsteemides ja reoveepuhastuse tehnoloogias. Piirkondadele, kus pinnase aluskivim on lubjakivi (CaCO_3), sealhulgas Põhja-Eesti, on omane pinna- ja põhjavee suhteliselt kõrge leelisus ($\text{pH} > 8$) ning karedus. Kuigi CaCO_3 -le on iseloomulik madal lahustuvuskorrutise (K_{SP}) väärtus ja sellest tulenevalt vähene lahustuvus, toimub heterogeenses tasakaalulises süsteemis $\text{CaCO}_3 \leftrightarrow \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2$ lahustuvuse suurenemine, mis põhjustab pinna- ja põhjavees CO_3^{2-} , HCO_3^- ning OH^- ionide kontsentratsiooni tõusu.

Käesolevas artiklis on kirjeldatud CaCO_3 (lubjakivi) osalusel kulgevaid tasakaalulisi protsesse vedeliku-gaasitahtkise faasis. Ioonide ja molekulide tasakaalulist jaotust süsteemis on kirjeldatud struktuurskeemi abil. On esitatud matemaatiline mudel pH ja CO_3^{2-} , HCO_3^- , CO_2 , Ca^{2+} , H^+ ning OH^- kontsentratsioonide arvutamiseks tasakaalulises süsteemis vedelfaasi erinevate CO_2 kontsentratsioonide korral, kasutades iteratsioonimeetodit. Väljatöötatud mudel on leidnud katselist kinnitust. Mudelit saab kasutada vedelfaasi kõikide koostisosade kontsentratsioonide määramiseks erinevate looduslike ja tehnoloogiliste süsteemide iseloomulikel tingimustel, põhinedes teadaolevale CO_2 kontsentratsioonile gaasifaasiga tasakaalus olevas veefaasis. Mudel kirjeldab ka CO_3^{2-} massiülekannet tahke ja vedela faasi ning CO_2 massiülekannet vedela ja gaasilise faasi vahel. Ioonide ja molekulide õhuga tasakaalulise süsteemi jaotuse kvantitatiivne hindamine heterogeenses süsteemis $\text{CaCO}_3 \leftrightarrow \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2$ on iseloomustatav pH väärtusega 8,2, mis on iseloomulik olukorrale, kus lubjakivi (koosneb peamiselt CaCO_3 -st) pinnase aluskivimina on kokkupuutel vee ning atmosfääri õhuga. Väärtus $\text{pH} \cong 8,2$ vastab CO_2 sisaldusele vees temperatuuril $t \cong 25^\circ\text{C}$, mis on tasakaalus atmosfääriõhuga (gaasifaasis), CO_2 sisaldusel $P(\text{CO}_2)_G \cong 390$ ppm. Ioonide ja molekulide tasakaalulise jaotuse kvantitatiivne hindamine heterogeenses süsteemis $\text{CaCO}_3 \leftrightarrow \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2$ tuvastas iseloomuliku CaCO_3 lahustuvuse miinimumi $s[\text{CaCO}_3]_{\text{min}} \cong 0,1$ mmol/L. Mudel võimaldab hinnata inimtekkeliste protsesside mõju looduskeskonnale ja on rakendatav keskkonnatehnoloogias, näiteks reoveepuhastuses (sealhulgas lämmastikuärastusel biometaani tootmisel tekkiva vädu töötlemisel). Mudel võimaldab arendada innovaatilisi CO_2 kontsentratsiooni mõõtmise meetodeid, mis on uurimisgrupi üks tulevaste uuringute teemasid.