Using carbonic acid to explain pH changes in aqueous solutions is invalid due to its undetectability under normal temperature and pressure conditions. Instead, two reversible reactions involving the decomposition of HCO$_3^-$ ions into OH$^-$ and CO$_2$ or H$^+$ and CO$_3^{2-}$ should be employed. The second reaction (H-mechanism) is well known as the basis for the second dissociation constant of “carbonic acid”. For the first reaction (OH-mechanism), the formula has been derived from the first imaginary constant of the same acid. That is, the researchers experimentally determined the proposed constant based on the results of pH value, CO$_2$ and HCO$_3^-$ concentrations, but calculated the imaginary constant from these values. The pH increase observed following filtration on the cationic resin in Na$^+$ form is attributed to the weakened HCO$_3^-$ decomposition via the H-mechanism, resulting in decreased H$^+$ and CO$_3^{2-}$ concentrations. A significant decrease in Ca$^{2+}$ concentration (from 5.0 to 0.05 mmol/dm$^3$) is the main reason for the observed phenomenon, as it leads to a decrease in the driving force of calcium carbonate formation. The mechanism of bicarbonate ions decomposition based on two reactions has been confirmed experimentally. An increase in the pH of the mixture of CaCl$_2$ and NaHCO$_3$ solutions (both with the same pH and concentration) indicates the H-mechanism, while a decrease in the pH indicates the OH-mechanism decomposition of bicarbonate ions. The pH value at which the pH does not change indicates a change in the decomposition mechanism. The change in the HCO$_3^-$ dissociation mechanism depends on hardness and alkalinity, and the pH of this change decreases from softened water (pH 8.30) to seawater (pH 7.5).

Keywords: bicarbonate ions dissociation, carbonic acid, derivation of constant, dissociation mechanism, imaginary constant, pH changes
At the same time, the idea of carbonic acid as a source of $\text{H}^+$ ions continues to be used to describe various processes (Fig. 2).

![Diagram](image)

**Fig. 2.** Carbonic Acid Eluent Ion Chromatography (Sricharoen, 2019)

The same concepts are used to describe processes in fluids of biological objects (Aminov, 2019): “Here we argue-based on experimental observations described within-that a key role in this connection is played by a previously unappreciated major proton source: carbonic acid ($\text{CA}$) $\text{H}_2\text{CO}_3$. In particular, we focus on the protonation of biorelevant bases $\text{B}$ by $\text{CA}$

$$\text{B}^+ + \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ \text{B} + \text{HCO}_3^-.$$

While it deals with experiments on $\text{CA}$ in aqueous solution, this paper focuses on the issue of the significance of $\text{CA}$ in the blood plasma”. The decomposition reaction of bicarbonate ions in acid solution has been well-known since high school chemistry (the inverse reaction for the reaction at Fig. 2):

$$\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2. \quad (3)$$

The carbonic acid presented in this reaction looks quite logical, and its "rapid decomposition" does not allow it to be fixed analytically.

Earlier (Kontsevoi, 2022), we have presented an alternative approach for estimating scaling in water heat exchange systems, which includes “$\text{OH}^-$” and “$\text{H}^-$” mechanisms for bicarbonate ions' decomposition under nonequilibrium conditions:

$$\text{HCO}_3^- \rightleftharpoons \text{OH}^- + \text{CO}_2 \quad (4)$$
$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad (5)$$

Applying the right side of reaction (4) instead of $\text{HCO}_3^-$ to reaction (3), we get a logical mechanism that does not require the formation of the mythical carbonic acid:

$$\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{OH}^- + \text{CO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2 \quad (6)$$

It is quite logical that the presence of an excess of $\text{H}^+$ ion in the solution leads to the formation of products in reaction (4).

Moreover, it is known that the acid decomposition of sodium bicarbonate solution starts the formation of $\text{CO}_2$ at a pH of about 8.35, and at this pH the existence of carbonic acid seems quite unlikely.

Also, there is no convincing explanation for the known effect of increasing the pH of water softened on a Na-cationic filter from 5.0 to 0.05 mmol/dm$^3$. For tap water in Kyiv, the pH value changes from 7.4 to 7.9 with an alkalinity of about 3.5 mmol/dm$^3$.

The most well-known point of view is that the activity of ions in water changes as a result of changes in the ionic strength of the solution (replacement of divalent cations with a monovalent $\text{Na}^+$ ion). Thus, it is assumed that the activity of $\text{OH}^-$ increases in relation to the activity of $\text{H}^+$ under these conditions, although the activity coefficients of each are already close to 1.0.

From our point of view, it is logical to assume that the pH increases as a result of an increase in the concentration of $\text{OH}^-$ or a decrease in the concentration of $\text{H}^+$ ions. Therefore, it is necessary to determine which reaction occurs in this case and explain why.

Thus, it seems advisable to reconsider the existing approaches, and to do this:

- should determine the actual first dissociation constant of bicarbonate ions. The
second one is already known - it is the second dissociation constant of "carbonic acid";
- should be determined the pH at which bicarbonate ions (BCI) dissociate by the reaction (4) or (5) in real solutions depending on hardness and alkalinity. For sodium bicarbonate solution (0.1 mol/dm$^3$) this pH is already known - 8.35. At pH greater than 8.35 there is the reaction (5) by H-mechanism, and at pH less than 8.35 there is the reaction (4) by OH-mechanism;
- to use the new approach for phenomena that are not actually explained now. For example, the increase in pH of water after any Na-cationic exchange filter.

2. The calculating formula for the first constant dissociation of BCI

The reaction by which the first dissociation constant of carbonic acid was determined is actually the dissociation reaction of HCO$^-_3$ by the OH-mechanism in the reverse direction (formation reaction):

$$\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-,$$  \hspace{1cm} (7)

or in the ionic form:

$$\text{H}^+ + \text{OH}^- + \text{CO}_2 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-,$$  \hspace{1cm} (8)

and in the ionic reduced form:

$$\text{OH}^- + \text{CO}_2 \rightleftharpoons \text{HCO}_3^-.$$  \hspace{1cm} (9)

Indeed, the transition from dissolved CO$^2$ to HCO$^3-$ in reaction (7) is impossible without the OH$^-$ ion, and water is a natural source of hydroxide ions (as well as hydrogen ions) and therefore it is written in ionic form in reaction (8).

Thus, the first dissociation constant of BCI is defined as

$$K_1 = [\text{OH}^-][\text{CO}_2]/[\text{HCO}_3^-].$$  \hspace{1cm} (10)

To determine it we obtain the equation for the concentration of bicarbonate ions from the definition of the imaginary constant $K^{*1}_1$:

$$[\text{HCO}_3^-] = K^{*1}_1[\text{CO}_2]/[\text{H}^+].$$  \hspace{1cm} (11)

Let's substitute the right-hand side of equation (11) into the denominator of equation (10), and after reducing [CO$^2$] and taking into account the ionic product of water ($K_w$), we get the final formula:

$$K_1 = [\text{OH}^-][\text{CO}_2]/(K^{*1}_1[\text{CO}_2]),$$  \hspace{1cm} (12)

$$K_1 = [\text{OH}^-][\text{H}^+]/K^{*1}_1 = K_w/K^{*1}_1.$$  \hspace{1cm} (13)

Reference values for $K^{*1}_1$=4.05805·10$^{-7}$ and for $K_w$=6.46809·10$^{-15}$ at 20°C. So, $K_1$ at a temperature of 20°C:

$$K_1 = 6.468\cdot10^{-15}/4.058\cdot10^{-7} = 1.594\cdot10^{8}.$$  \hspace{1cm} (14)

Since the temperature dependence for $K^{*1}_1$ and $K_w$ up to 90°C is known, it is possible to calculate the first dissociation constant of BCI at the corresponding temperatures.

It should be noted that the results of calculations of the composition of aqueous solutions ([CO$^2$] and [HCO$^3$-]) according to the pH value do not differ when using the actual $K_1$ of BCI or $K^{*1}_1$ of CA. That is, the researchers experimentally determined $K_1$ based on the results of the analytical determination of CO$^2$, HCO$^3-$, and pH value, but calculated $K^{*1}_1$ from these values.

3. Materials and Methods

Standard solutions and techniques for determination of water hardness (WH) with EDTA and Alkalinity (Alk), NaOH (0.1 mol/dm$^3$), and H$_2$SO$_4$ (5\%\%) solutions for pH correction, CaCl$_2$ and NaHCO$_3$ solutions for modeling of natural water (raw and purified), tap water (Kyiv) in the Igor Sikorsky KPI laboratory, pH meter (Jenway, UK, accuracy 0.01 pH units), photocolorimeter for fixation of suspended solids in solutions.

Certain pH values were set in the working solutions (CaCl$_2$ and NaHCO$_3$) by adding a solution of sodium hydroxide or hydrochloric acid. After that, the solutions were mixed and the pH value of the resulting
mixture was measured. This value was used to determine the mechanism of the decomposition reaction: if the pH of the mixture was higher than the set value, the reaction proceeded by the OH-mechanism (with the formation of OH⁻ and CO₂); if the pH of the mixture was lower than the set value, the reaction proceeded by the H-mechanism (with the formation of H⁺ and CO₃²⁻ anions).

4. Results and Discussion

The results of studies by method 1 are presented in Table 1 (concentrations and pH of reagents are the same). The obtained data allows us to determine the pH value (pHₐ) at which the mechanism of HCO₃⁻ ions decomposition is changed (Table 2). It is significant that with decreasing pH no CaCO₃ suspended solid is formed. It was confirmed on the photocolorimeter: the optical density of the mixture did not increase relative to the initial solutions.

Obviously, the change in the mechanism of BCI decomposition depends on the values of water hardness and alkalinity: as they increase (from 1 to 100 mmol/dm³), the pHₐ decreases (from 8.30 to 7.25).

Table 1. pH of mixture and reagents (solutions of NaHCO₃ and CaCl₂ with the same pH)

<table>
<thead>
<tr>
<th>C, mmol/dm³</th>
<th>Samples</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>reagents</td>
<td>mixture</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>7.40</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>7.26</td>
</tr>
<tr>
<td>10</td>
<td>7.80</td>
<td>7.60</td>
</tr>
<tr>
<td></td>
<td>7.70</td>
<td>7.55</td>
</tr>
<tr>
<td>5</td>
<td>8.00</td>
<td>7.70</td>
</tr>
<tr>
<td></td>
<td>7.91</td>
<td>7.67</td>
</tr>
<tr>
<td>1</td>
<td>8.80</td>
<td>8.60</td>
</tr>
<tr>
<td></td>
<td>8.68</td>
<td>8.52</td>
</tr>
</tbody>
</table>

Table 2. Dependence of pHₐ on Alkalinity (NaHCO₃) and Hardness (CaCl₂)

<table>
<thead>
<tr>
<th>C, mmol/dm³</th>
<th>Modeled water</th>
<th>pHₐ</th>
<th>pHₐ️apr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>seawage</td>
<td>7.25</td>
<td>7.28</td>
</tr>
<tr>
<td></td>
<td>sea</td>
<td>7.50</td>
<td>7.49</td>
</tr>
<tr>
<td></td>
<td>tap</td>
<td>7.60</td>
<td>7.57</td>
</tr>
<tr>
<td></td>
<td>softened</td>
<td>8.30</td>
<td>8.31</td>
</tr>
</tbody>
</table>

The data presented above were approximated in different ways, and it is found that the data best approximate the logarithmic function. The equation of the approximating function (Excel, coefficient of determination R²=0.9965) is

\[ \text{pHₐ}=\ln(C-9.99\times10^{-4})+7.0714, \]

where C is the concentration of working solutions (C=Hardness=Alkalinity), mol/dm³ (not mmol/dm³ like in tables).

To finally check the correctness of the approximating function we calculated by the last equation the value of pHₐ️apr and compared them with the data pHₐ in Table 2. The deviations of these values do not significantly exceed the accuracy of the measurement (0.01 to 0.03 pH units).

Based on the results presented above, it can be argued that the concentration of Ca²⁺ cations affects the pH through the reaction of
the poorly soluble CaCO₃ formation as a factor that enhances the decomposition of BCI by the H-mechanism.

With a significant decrease in the Ca²⁺ concentration as a result of Na-cationization (hardness < 0.1 mmol/dm³), the H-mechanism of BCI decomposition is significantly weakened:

\[
\text{HCO}_3^- + \text{Ca}^{2+} \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{H}^+ + \text{CaCO}_3
\] (16)

The aqueous solution enters a new equilibrium state with a higher pH due to the reaction of BCI decomposition by the OH-mechanism, the intensity of which remains at the same level.

5. Conclusions

The use of carbonic acid to explain the processes with a change in pH in aqueous solutions is irrational, and the observed phenomena are logically considered using 2 reactions of bicarbonate ions’ decomposition (and formation in the opposite direction) by the H- or OH- mechanisms. For the reaction by the OH-mechanism, the dissociation constant has been derived from the first imaginary dissociation constant of carbonic acid. That is, the researchers experimentally determined the proposed constant based on the results of pH value, CO₂ and HCO₃⁻ concentrations, but calculated the imaginary constant of “carbonic acid” from these values.

The mechanism of bicarbonate ions decomposition based on two reactions has been confirmed experimentally. An increase in the pH of the mixture of CaCl₂ and NaHCO₃ solutions (both with the same pH and concentrations) indicates the formation of CO₂ and OH⁻, while a decrease in the pH indicates a reaction with the formation of H⁺ and CO₃²⁻. At higher pH values, there is a decrease in the pH of the mixture relative to the initial solutions, and at lower pH values, there is an increase in the pH. The change in the decomposition mechanism of bicarbonate ions depends on hardness and alkalinity, and the pH of this change decreases from softened water (pH 8.30) to seawater (pH 7.5).

The reason for the pH increase after filtration on the cationic resin in Na⁺ form is the decrease of HCO₃⁻ decomposition degree by H-mechanism and, as a consequence, the decrease of H⁺ and CO₃²⁻ ions concentration in filtered water. A significant decrease in Ca²⁺ concentration is the main reason for the observed phenomenon, as it leads to a decrease in the driving force of poorly soluble calcium carbonate formation.

References


Застосування вугільної кислоти для пояснення процесів зі зміною рН у водних розчинах нераціонально, оскільки ця кислота ніколи не була виявлена експериментально за звичайних умов (температура і тиск). Пропонується розглядати такі явища за допомогою двох оборотних реакцій розкладання іонів HCO$_3^-$ з утворенням OH$^-$ або H$^+$. Друга реакція (H-механізм) добре відома як основа другої константи дисоціації "вугільної кислоти". Для першої реакції (ОН-механізм) формулу було отримано з першої уявної константи тієї самої кислоти. Тобто раніше дослідники експериментально визначали запропоновану константу на основі результатів визначення рН, концентрації CO$_2$ і HCO$_3^-$, але розрахували уявну константу з цих значень. Причина підвищення рН після фільтрації на катіонній смолі у Na$^+$ формі (для водопровідної води у Києві значення рН змінюється від 7,4 до 7,9) визначається на основі такого підходу: це ослаблення розкладання HCO$_3^-$ за H-механізмом і, як наслідок, зниження концентрації іонів H$^+$ у фільтрованій воді. Значення зниження концентрації Ca$^{2+}$ (від 5,0 до 0,05 ммоль/дм$^3$) є основною причиною цього явища, оскільки призводить до зменшення рушійної сили утворення карбонату кальцію. Експериментально підтверджено механізм розкладання бікарбонатних іонів на основі двох реакцій. Підвищення рН суміші розчинів CaCl$_2$ і NaHCO$_3$ (обидва з однаковими рН і концентраціями) свідчить про утворення OH$^-$ і CO$_2$, а зниження рН свідчить про реакцію з утворенням H$^+$ і CO$_3^{2-}$. Зміна механізму дисоціації HCO$_3^-$ залежить від твердості та лужності, а рН цієї зміни зменшується від пом’якшеного (рН 8,30) до морської води (рН 7,5).

**Ключові слова:** виведення константи, дисоціація бікарбонатних іонів, зміна рН, карбонова кислота, механізм дисоціації, уявна константа