

## 4. The Carbonate System in Seawater

To understand and to describe the desorption process of CO<sub>2</sub> in multiple-effect distillers, a detailed knowledge of the thermodynamics and the kinetics of the carbonate system in seawater is required.

The carbonate system is a weak acid-base system which exists in seawater as dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate ions and complexes of these ions. Basically the system is derived from the dissolution of carbon dioxide gas and carbonate minerals into the water. Addition of an acid or a base to an aqueous solution of carbonate species gives rise to changes in pH and changes in the concentrations of all the species that constitute the system.

A distinguishing feature of the carbonate system is that the gas phase forms an integral part of it. For a system initially in equilibrium, any change in the partial pressure of CO<sub>2</sub> in the gas phase induces a state of non-equilibrium between gas and aqueous phases. This causes, with time, an exchange of CO<sub>2</sub> between the phases resulting in a shift in pH and the species concentrations until equilibrium between the phases is re-established. A further feature is the relative insolubility of many carbonate minerals; the precipitation and dissolution of these minerals have a significant effect on the system's behaviour. As a consequence of these two features it is often necessary to consider all three phases, aqueous, gas and solid, in order to describe the response of the system to external influences [Loe84].

Seawater is an aqueous mixed electrolyte. It attains its chemical composition through a variety of chemical reactions and physicochemical processes. Among these are: acid-base reactions, gas absorption and desorption processes, precipitation and dissolution of solids and adsorption processes at interfaces. Characteristic for seawater is the high salinity that may vary between average limits of 7 g/kg (Baltic Sea) and 43 g/kg (Arabian Sea). The pH of seawater is usually in the range from 7.7 to 8.3 in surface waters. The pH is buffered by a set of reactions that take place between CO<sub>2</sub> and water. **Table 4.1** shows the composition of standard seawater with a salinity of 35 g/kg.

An overview of the carbonate system in seawater is given by Millero [Mil00] and Glade [Gla01a]. In the following, the solubility of CO<sub>2</sub> in seawater, the chemical equilibria, the mechanisms, the orders and the rates of reactions involved in CO<sub>2</sub> release are summarized. The effects of temperature, pressure and ionic strength on the solubility, the chemical equilibria and the reaction rates are described.

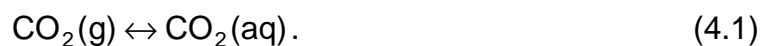
Species	Concentration		Specific concentration
	[g/kg seawater]	[mol/kg seawater]	[g/kg] / S
Na <sup>+</sup>	10.7838	0.46907	0.30811
Mg <sup>2+</sup>	1.2837	0.05282	0.036678
Ca <sup>2+</sup>	0.4121	0.01028	0.01177
K <sup>+</sup>	0.3991	0.01021	0.01140
Sr <sup>2+</sup>	0.0079	0.00009	0.000227
Cl <sup>-</sup>	19.3529	0.54588	0.55294
SO <sub>4</sub> <sup>2-</sup>	2.7124	0.02824	0.07750
HCO <sub>3</sub> <sup>-</sup>	0.1070	0.00175	0.00306
Br <sup>-</sup>	0.0672	0.00084	0.00192
CO <sub>3</sub> <sup>2-</sup>	0.0161	0.00027	0.000459
B(OH) <sub>4</sub> <sup>-</sup>	0.0079	0.00010	0.000225
F <sup>-</sup>	0.0013	0.000068	0.000037
B(OH) <sub>3</sub>	0.0193	0.00031	0.000551
Σ	35.1707	1.1199	1.004877

**Table 4.1:** The composition of standard seawater with S = 35 g/kg, TA =  $2.3 \cdot 10^{-3}$  mol/kg and pH = 8.1 at 25°C [Mil96]

#### 4.1 Thermodynamics of the Carbonate System

Atmospheric gases dissolve in seawater and are distributed to all depths by mixing processes and currents. The most abundant gases in atmosphere and in seawater are nitrogen, oxygen, carbon dioxide and argon. The gases dissolved in seawater can be divided into two types: the first type is molecularly dissolved and does not react chemically such as N<sub>2</sub>, O<sub>2</sub> and Ar, while the other type chemically reacts in seawater such as CO<sub>2</sub>.

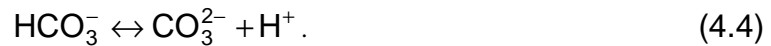
Carbon dioxide in seawater is governed by the following equilibria:



Subsequently, the dissolved gas combines with water to form carbonic acid  $\text{H}_2\text{CO}_3$ :



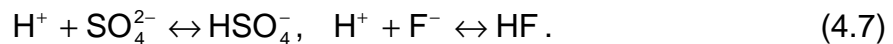
The carbonic acid dissociates to form bicarbonate  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$ :



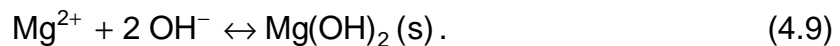
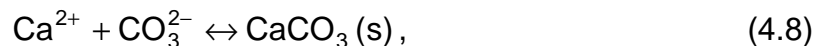
The water itself dissociates to form  $\text{H}^+$  and  $\text{OH}^-$  ions:



The carbonate system in seawater is characterised by the interaction of major cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$ ) and major anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ). These interactions can be described in terms of an ion association formalism and, more recently, in terms of a specific interaction theory [Mil96, Stu81].



Additionally insoluble calcium carbonate and magnesium hydroxide can be formed:



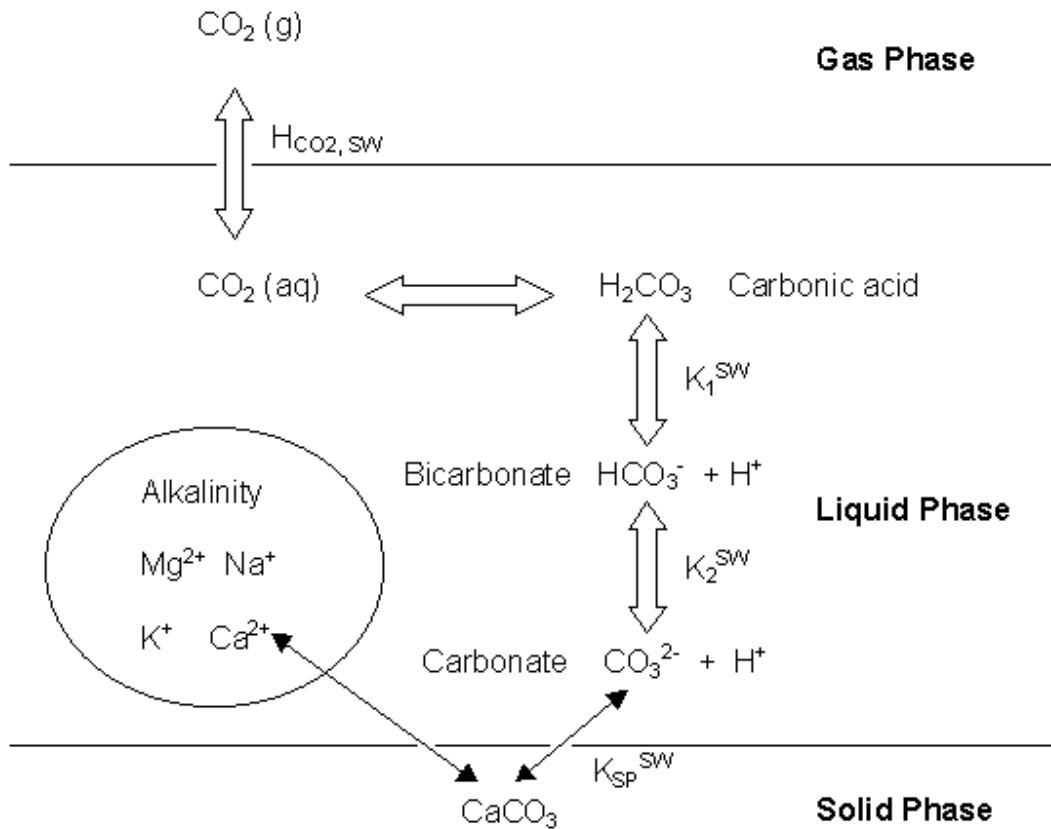
A schematic representation of the carbonate system in gas, liquid and solid phases is shown in **Figure 4.1**.

#### 4.1.1 Solubility of $\text{CO}_2$ in Seawater

Since the partial pressure and the concentration of  $\text{CO}_2$  dissolved in seawater are sufficiently small, the solubility can be described using Henry's law:

$$C_{\text{CO}_2} = H_{\text{CO}_2, \text{SW}} P_{\text{CO}_2} \quad (4.10)$$

where  $C_{\text{CO}_2}$  is the concentration of the dissolved  $\text{CO}_2$ ,  $p_{\text{CO}_2}$  is the partial pressure of  $\text{CO}_2$  and  $H_{\text{CO}_2, \text{SW}}$  is the Henry's law coefficient of  $\text{CO}_2$  in seawater.



**Figure 4.1:** A schematic representation of the carbonate system.

Henry's law describes only the physical equilibrium between the phases and may only be applied to the fraction of the gas that is molecularly dissolved and not chemically bound [Pra69, Dan70, Wil77]. Henry's law coefficient depends on the type of the gas and the solvent, the temperature, the total pressure and in the case of salt solutions it also depends on the ionic strength of the solution. The ionic strength  $I$  of a solution is defined as:

$$I = \frac{1}{2} \sum_i z_i^2 m_i \quad (4.11)$$

where  $z_i$  is the charge of the ion  $i$  and  $m_i$  is the molality of the ion.

The ionic strength can be related to salinity  $S$  as follows [Mil95]:

$$I = \frac{19.92 S}{1000 - 1.005 S} \quad (4.12)$$

with  $S$  in g/kg and  $I$  in mol/kg. The ionic strength of standard seawater with  $S = 35$  g/kg is 0.72 mol/kg.

For small and moderate pressures  $p < 5$  bar, the pressure dependence of Henry's law coefficient can be neglected [Fal92]. The influence of the other gases is negligible, if their concentrations are small.

The solubility of a gas is actually lowered in presence of salts in the solution. This effect is called salting out. Danckwerts [Dan70] proposed to relate Henry's law coefficient in the salt solution to that in water at the same temperature on the basis of a method originally proposed by Sechenov [Sec1889]. Furthermore, the activity coefficient of  $\text{CO}_2$  in seawater can be considered as the ratio of its solubility in water to the solubility in seawater [Mil96]. The application to  $\text{CO}_2$  in seawater yields

$$\log \left( \frac{H_{\text{CO}_2, \text{W}}}{H_{\text{CO}_2, \text{SW}}} \right) = \log \gamma_{\text{CO}_2, \text{SW}} = h I \quad (4.13)$$

where  $H_{\text{CO}_2, \text{W}}$  and  $H_{\text{CO}_2, \text{SW}}$  are the Henry's law coefficients of  $\text{CO}_2$  in water and seawater, respectively.  $\gamma_{\text{CO}_2, \text{SW}}$  is the activity coefficient of carbon dioxide,  $I$  is the ionic strength expressed in equation (4.12) and  $h$  is the summation of ion specific parameters of the positive ions ( $h_+$ ), negative ions ( $h_-$ ) and the gas specific parameter ( $h_G$ ):

$$h = h_+ + h_- + h_G. \quad (4.14)$$

Ion and gas specific parameters were experimentally determined for various ions and gases [Her95]. It is assumed that the temperature dependence of  $h$  is confined to the change in  $h_G$ . The ion specific parameters are considered to be independent of temperature.

Because the main constituent of seawater is NaCl (73% of seawater ionic strength), the ion specific parameters of  $\text{Na}^+$  and  $\text{Cl}^-$  are the only considered parameters. The values indicated by Dankwerts [Dan70] are  $h_+ = 0.091$  L/mol and  $h_- = 0.021$  L/mol. The  $\text{CO}_2$  specific parameter  $h_G$  between 0 and 50°C given by Danckwerts [Dan70] was correlated with temperature by Glade [Gla01a] as follows:

$$h_G = -5 \cdot 10^{-3} - 5.3 \cdot 10^{-4} \cdot \vartheta \quad (4.15)$$

where  $h_G$  is in L/mol and  $\vartheta$  is in °C.

Henry's law coefficient of CO<sub>2</sub> in pure water is given by Plummer and Busenberg [Plu82]:

$$\log H_{\text{CO}_2, \text{W}} = 108.3865 + 0.01985076 \cdot T - \frac{6919.53}{T} - 40.45154 \cdot \log T + \frac{669365}{T^2} \quad (4.16)$$

with  $H_{\text{CO}_2, \text{W}}$  in mol/(kg atm) and T in K.

The Henry's law coefficient of CO<sub>2</sub> decreases with increasing temperature, passes through a minimum at 170°C and increases again. The Henry's law coefficient also decreases with increasing salinity. The effect of salinity is less pronounced at high temperatures.

CO<sub>2</sub> is more soluble than O<sub>2</sub>, N<sub>2</sub> and Ar. The concentrations of the gases dissolved in seawater with a salinity of 35 g/kg in equilibrium with the atmosphere at 25°C are summarised in **Table 4.2**.

Gas	Partial pressure in atmosphere [bar]	Henry's law coefficient [mol/(m <sup>3</sup> bar)]	Concentration in seawater	
			[μmol/kg SW]	[mg/kg SW]
CO <sub>2</sub>	0.00033	29.3	9.45	0.4
N <sub>2</sub>	0.7808	0.5	383.4	10.7
O <sub>2</sub>	0.2095	1.0	206.3	6.6
Ar	0.00934	1.1	10.11	0.4

**Table 4.2:** Solubility data of the gases dissolved in seawater with S = 35 g/kg in equilibrium with the atmosphere at 25°C [Mil96, Gla01a]

#### 4.1.2 Equilibrium Constants in Seawater

##### Dissociation Constant of Water

The stoichiometric equilibrium constant of water in seawater  $K_w^{\text{SW}}$  can be expressed as

$$K_W^{SW} = K_W \frac{1}{\gamma_{H^+}^{SW} \gamma_{OH^-}^{SW}} = [H^+]^{SW} [OH^-]^{SW}, \quad (4.17)$$

where  $K_W$  is the thermodynamic equilibrium constant and  $[i]^{SW}$  and  $\gamma_i^{SW}$  are the concentration and the activity coefficient of the component  $i$ , respectively.

The equilibrium constant of water in seawater was measured for temperatures up to 35°C and salinities up to 44 g/kg [Dic79, Meh73, Cul73]. Dickson and Riley [Dic79] proposed the following correlation:

$$\log K_W^{SW} = - \left( \frac{3441}{T} + 2.241 - 0.09415 S^{0.5} \right) \quad (4.18)$$

where  $K_W^{SW}$  is on the basis mol/kg seawater,  $T$  is in K and  $S$  is in g/kg.

### **Dissociation Constants of Carbonic Acid**

Applying the law of mass action to the first dissociation of carbonic acid  $H_2CO_3 \leftrightarrow HCO_3^- + H^+$  yields

$$K_1^{SW} = K_1 \frac{\gamma_{CO_2}^{SW}}{\gamma_{H^+}^{SW} \gamma_{HCO_3^-}^{SW}} = \frac{[H^+]^{SW} [HCO_3^-]^{SW}}{[CO_2]^{SW}} \quad (4.19)$$

where  $K_1$  is the thermodynamic equilibrium constant and  $[i]^{SW}$  and  $\gamma_i^{SW}$  are the concentration and the activity coefficient of the component  $i$  that is free or involved in ion pairing, respectively.  $[CO_2]^{SW}$  is the sum of the concentrations of  $CO_2$  and  $H_2CO_3$ .

The second dissociation constant of the reaction  $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$  can be written as

$$K_2^{SW} = K_2 \frac{\gamma_{HCO_3^-}^{SW}}{\gamma_{H^+}^{SW} \gamma_{CO_3^{2-}}^{SW}} = \frac{[H^+]^{SW} [CO_3^{2-}]^{SW}}{[HCO_3^-]^{SW}} \quad (4.20)$$

where  $K_2$  is the thermodynamic equilibrium constant and  $[i]^{SW}$  and  $\gamma_i^{SW}$  are the concentration and the activity coefficient of the component  $i$ , respectively.

Various correlations of the dissociation constants  $K_1^{SW}$  and  $K_2^{SW}$  of carbonic acid in seawater are available in the literature [Han73, Meh73, Dic79, Goy89, Roy93].

They were experimentally determined for temperatures up to 45°C and for salinities up to 50 g/kg.

In this work, correlations are used which were suggested by Millero [Mil95] and are based on the experimental data of Goyet and Poisson [Goy89] and Roy et al. [Roy93]:

$$\ln K_1^{\text{SW}} = 2.18867 - \frac{2275.036}{T} - 1.468591 \ln T + \left( -0.138681 - \frac{9.33291}{T} \right) S^{0.5} + 0.0726483 S - 0.00574938 S^{1.5}, \quad (4.21)$$

$$\ln K_2^{\text{SW}} = -0.84226 - \frac{3741.1288}{T} - 1.437139 \ln T + \left( -0.128417 - \frac{24.41239}{T} \right) S^{0.5} + 0.1195308 S - 0.00912840 S^{1.5} \quad (4.22)$$

where  $K_1^{\text{SW}}$  and  $K_2^{\text{SW}}$  are on the basis mol/kg seawater, T is in K and S is in g/kg.

### **Solubility Product of Calcium Carbonate**

Calcium carbonate  $\text{CaCO}_3$  dissolves according to the following equation:



The solubility product of calcium carbonate is given by

$$K_{\text{SP}}^{\text{SW}} = K_{\text{SP}} \frac{1}{\gamma_{\text{Ca}^{2+}}^{\text{SW}} \gamma_{\text{CO}_3^{2-}}^{\text{SW}}} = [\text{Ca}^{2+}]^{\text{SW}} [\text{CO}_3^{2-}]^{\text{SW}}. \quad (4.24)$$

where  $K_{\text{SP}}$  is the thermodynamic solubility product and  $[i]^{\text{SW}}$  and  $\gamma_i^{\text{SW}}$  are the concentration and the activity coefficient of the component i, respectively.

$K_{\text{SP}}^{\text{SW}}$  of calcite and aragonite, respectively, can be calculated from correlations reported by Mucci [Muc83] for a salinity between 5 and 45 g/kg and a temperature between 5 and 40°C at 1 atm total pressure:

$$\begin{aligned} \log K_{\text{SP,ca}} = & -171.9450 - 0.077993 T + 2903.293/T + 71.595 \log T \\ & + \left( -0.77712 + 0.0028426 T + 178.34/T \right) S^{0.5}, \quad (4.25) \\ & - 0.07711 S + 0.0041249 S^{1.5} \end{aligned}$$



$$\begin{aligned} \log K_{\text{SP,ar}} = & -171.9450 - 0.077993 T + 2903.293/T + 71.595 \log T \\ & + (-0.068393 + 0.0017276 T + 88.135/T) S^{0.5} \\ & - 0.10018 S + 0.0059415 S^{1.5} \end{aligned} \quad (4.26)$$

with T in K and S in g/kg.

Increasing the temperature, pressure and ionic strength (salinity) results in an increase of  $K_1^{\text{SW}}$ ,  $K_2^{\text{SW}}$  and  $K_w^{\text{SW}}$ .  $K_{\text{SP}}^{\text{SW}}$  values increase with pressure and salinity but decrease with temperature. At  $\vartheta = 30^\circ\text{C}$ ,  $S = 60$  g/kg and  $p = 10$  bar, the values of  $K_1^{\text{SW}}$ ,  $K_2^{\text{SW}}$  and  $K_w^{\text{SW}}$  differ from the values at 1 bar by 1%, 0.3% and 0.3%, respectively [Gla01a].  $K_{\text{SP}}^{\text{SW}}$  differs from the values at 1 bar by 0.3%. Thus, for small and moderate pressures, the pressure dependence of the equilibrium constants can be neglected.

### 4.1.3 Activity Coefficients

Theoretical expressions for the activity coefficients are given in **Table 4.3**.

Approximation	Equation	Applicability
Debye-Hückel	$\log \gamma_i = -A z_i^2 \sqrt{I}$	$I < 0.005$ mol/kg
Extended Debye-Hückel	$\log \gamma_i = -A z_i^2 \frac{\sqrt{I}}{1 + B a_i \sqrt{I}}$	$I < 0.1$ mol/kg
“WATEQ”-Debye-Hückel	$\log \gamma_i = -A z_i^2 \frac{\sqrt{I}}{1 + B a_i \sqrt{I}} + b_i I$	$I < 1$ mol/kg
Davies	$\log \gamma_i = -A z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 I \right)$	$I < 0.5$ mol/kg
Güntelberg	$\log \gamma_i = -A z_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$	$I < 0.1$ mol/kg useful for mixed electrolytes

**Table 4.3:** Expressions for activity coefficients with  $z_i$  as the charge of the ion, A as the Debye-Hückel parameter which depends on the dielectric constant of the solvent and on the temperature; for water at  $25^\circ\text{C}$   $A = 0.509 \text{ kg}^{1/2}\text{mol}^{-1/2}$ ; B as temperature-dependent parameter;  $a_i$  and  $b_i$  as ion specific parameters

Davies equation [Dav38]

$$\log \gamma_i = -A z_i^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (4.27)$$

with  $z_i$  as the charge of the ion and  $A$  as the Debye-Hückel constant obtained by means of the interpolation formula [Hel74]

$$A = 0.4819 + 0.0011 \vartheta, \quad (4.28)$$

where  $\vartheta$  is the temperature in °C, which is valid for  $I < 0.5$  mol/kg, has the advantage that it needs no adjustable ion size parameter.

Because of its simplicity it is used in many of the chemical equilibrium systems. In this version of Debye-Hückel equation a simple term, linear in  $I$ , was added at the end of the equation. This term improves the empirical fit to higher ionic strength but it has no theoretical justification [Dav38]. The activity coefficients for seawater ( $I = 0.72$  mol/kg) are for monovalent ions  $\gamma_i = 0.69$ , for divalent ions  $\gamma_i = 0.23$  and for trivalent ions  $\gamma_i = 0.04$  (**Table 4.4**). Loewenthal [Loe84] found that these are realistic values even though seawater ionic strength is outside the valid range of this equation.

The activity coefficient of  $\text{CO}_2$  in seawater  $\gamma_{\text{CO}_2, \text{SW}}$  is the ratio of its solubility in water to the solubility in seawater [Mil96]. It can be calculated from equation (4.13).

Species	Activity coefficient in seawater ( $I = 0.72$ mol/kg)	
	Loewenthal and Marias [Loe84]	Davies Equation [Dav38]
$\text{Na}^+$	0.693	0.69
$\text{Ca}^{2+}$	0.248	0.23
$\text{HCO}_3^-$	0.669	0.69
$\text{Cl}^-$	0.649	0.69
$\text{CO}_3^{2-}$	0.203	0.23
$\text{CO}_2$	1.17 [Mil96]	
	1.167 (Equation 4.13)	

**Table 4.4:** Activity coefficients for some species in seawater ( $S = 35$  g/kg) at 25°C

Pitzer [Pit73] proposed a frequently used activity coefficient model for multi-component electrolyte solutions. The Pitzer model was applied to seawater by Millero [Mil96]. The problem of this model is the large number of needed temperature-dependent parameters. For electrolyte solutions of  $I \leq 6$  mol/kg, Bromley [Bro73] derived a half-empirical approach which contains only one interaction parameter for each electrolyte.

#### 4.1.4 Description of the Carbonate System

The carbonate system in seawater can be described by the following six quantities:

1. Concentration of dissolved  $\text{CO}_2$  [ $\text{CO}_2$ ]
2. Concentration of bicarbonate ions [ $\text{HCO}_3^-$ ]
3. Concentration of carbonate ions [ $\text{CO}_3^{2-}$ ]
4. pH value or concentration of  $\text{H}^+$  ions [ $\text{H}^+$ ] or concentration of  $\text{OH}^-$  ions [ $\text{OH}^-$ ]
5. Total carbon dioxide content TC:

$$\text{TC} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CO}_2] + [\text{H}_2\text{CO}_3]. \quad (4.29)$$

The concentration of  $\text{H}_2\text{CO}_3$  is so small that it can be neglected in equation (4.29).

6. Total alkalinity TA

The concentration of all bases that can accept a proton when seawater is titrated to the pH end point of carbonic acid:

$$\text{TA} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]. \quad (4.30)$$

TA and TC are independent of temperature, pressure and ionic strength if expressed in concentration units mol/kg seawater [UNE87]. The total alkalinity remains constant with absorption or desorption of  $\text{CO}_2$  [Dic84, Dic92, Mil95].

In chemical equilibrium the carbonate system is completely characterized by two of these six quantities. The remaining four quantities can be calculated by applying the law of mass action with the dissociation constants of carbonic acid and water in seawater. Given the measurable total alkalinity and the pH value, the remaining quantities can be determined as follows:

$$[\text{H}^+] = 10^{-\text{pH}^{\text{SW}}}, \quad (4.31)$$

$$[\text{CO}_2] = \frac{[\text{HCO}_3^-][\text{H}^+]}{K_1^{\text{SW}}}, \quad (4.32)$$

$$[\text{CO}_3^{2-}] = \frac{K_2^{\text{SW}}[\text{HCO}_3^-]}{[\text{H}^+]}, \quad (4.33)$$

$$[\text{OH}^-] = \frac{K_W^{\text{SW}}}{[\text{H}^+]}. \quad (4.34)$$

Inserting equations (4.33) and (4.34) into equation (4.30) gives

$$[\text{HCO}_3^-] = \frac{\text{TA} [\text{H}^+] + [\text{H}^+]^2 - K_W^{\text{SW}}}{[\text{H}^+] + 2 K_2^{\text{SW}}}. \quad (4.35)$$

TC can be calculated due to equation (4.29).

When a certain total carbon dioxide content TC is dissolved in seawater, it is important to know which fraction thereof is present as  $\text{CO}_2$ , which as  $\text{HCO}_3^-$  ions and which as  $\text{CO}_3^{2-}$  ions. The distribution of the species depends on the pH value, the temperature and the ionic strength.

**Figure 4.2** shows the mole fractions of  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  as a function of pH for different temperatures at constant salinity. At constant pH, the mole fraction of  $\text{CO}_2$  decreases with increasing temperature, while the mole fraction of  $\text{CO}_3^{2-}$  rises. With increasing temperature the mole fraction of  $\text{HCO}_3^-$  rises at  $\text{pH} < 7$ . At higher pH values the mole fraction of  $\text{HCO}_3^-$  decreases.

At  $\vartheta = 30^\circ\text{C}$  and  $S = 35 \text{ g/kg}$  more than 87 % of the total carbon dioxide content is dissolved as  $\text{CO}_2$  at pH values lower than 5. With increasing pH value the mole fraction of  $\text{CO}_2$  decreases, while the  $\text{HCO}_3^-$  concentration increases and reaches a maximum of 94.5 % at  $\text{pH} = 7.4$ . A further increase of pH causes a decrease of  $\text{HCO}_3^-$  and an increase of  $\text{CO}_3^{2-}$ . At pH values higher than 10, more than 92 % of the total carbon dioxide is present as  $\text{CO}_3^{2-}$ .

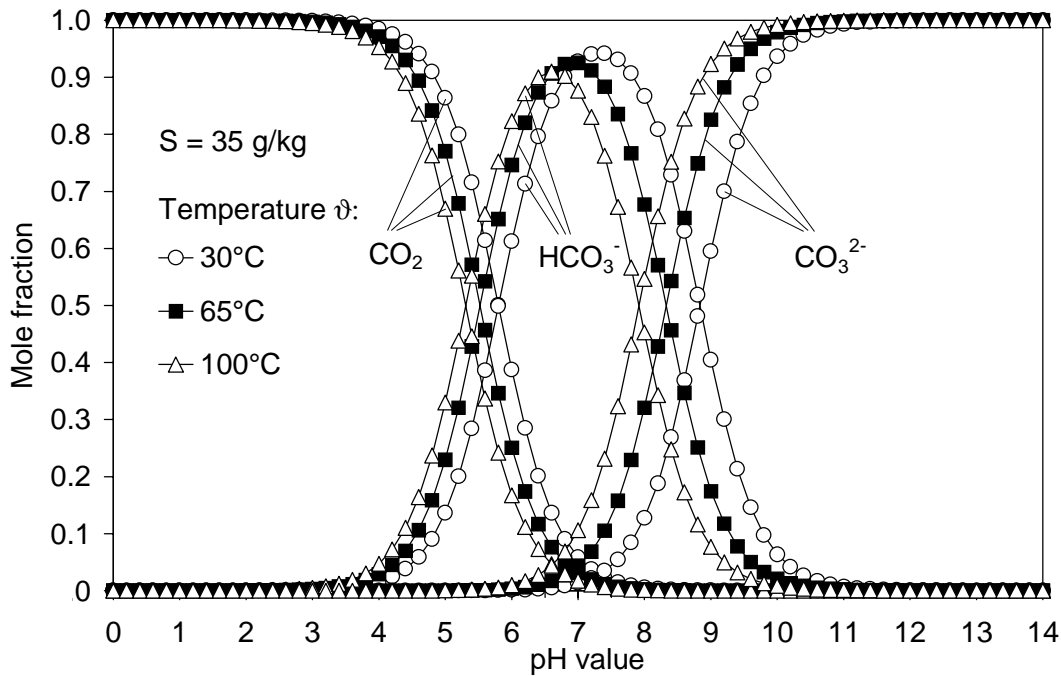
Total alkalinity TA can be related to chlorinity Cl according to the following relation [Stu81]

$$TA = 0.0001185 \text{ Cl} \quad (4.36)$$

where chlorinity can be expressed as

$$Cl = \frac{S}{1.80655} \quad (4.37)$$

with TA in mol/kg, Cl in g/kg and S in g/kg.



**Figure 4.2:** Mole fractions of  $\text{CO}_2$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  as a function of pH value for different temperatures at  $S = 35 \text{ g/kg}$  [Mil00, Gla01a].

To remove the variations in TA and TC due to changes in salinity due to mixing, evaporation or dilution, normalized values NTA and NTC are defined as follows [Mil98]:

$$NTA = TA \times \frac{35}{S} \quad (4.38)$$

and

$$NTC = TC \times \frac{35}{S} \quad (4.39)$$

with NTA, NTC, TA and TC in mol/kg and S in g/kg.

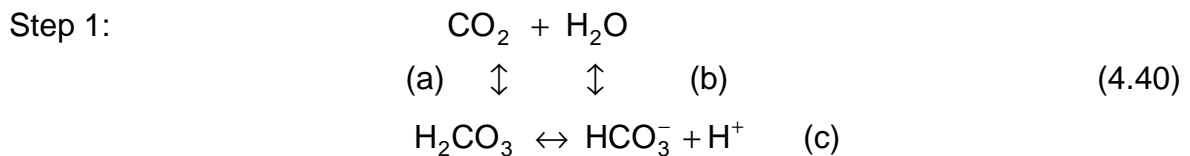
The carbonate system in the Arabian Sea was studied over an annual cycle by Millero et al. [Mil98]. The surface measurements (0–30 m) of pH, NTA and NTC were quite uniform through the year ( $\text{pH} = 8.1 \pm 0.05$ ,  $\text{NTA} = 2290 \pm 5 \mu\text{mol/kg}$  and  $\text{NTC} = 1950 \pm 20 \mu\text{mol/kg}$ ). Consequently, changes in the normalized TA and TC can be attributed to the production and oxidation of plants material and formation and precipitation of  $\text{CaCO}_3$ .

## 4.2 Chemical Kinetics in the Carbonate System

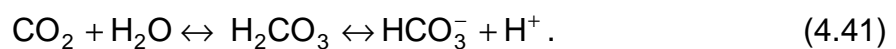
### 4.2.1 Reaction Mechanisms and Reaction Rates

The hydration and dehydration of  $\text{CO}_2$  in aqueous bicarbonate-carbonate solutions occur by the following reaction mechanisms in parallel [Her60, Wal66, Ast67, Dan70, Ast81, Gla01a].

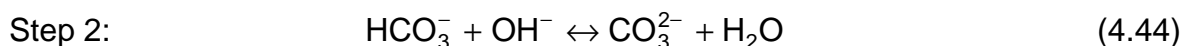
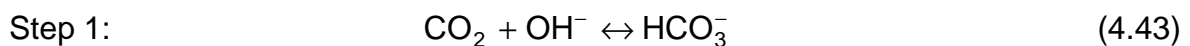
Reaction mechanism I (acidic mechanism):



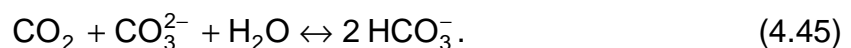
The reaction scheme (4.40) describes the conversion paths quite properly. By combining the rate constants, the reactions (4.40a), (4.40b) and (4.40c) can be summarised in a simplified scheme



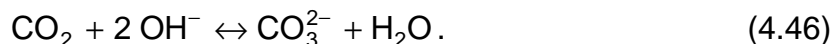
Reaction mechanism II (alkaline mechanism):



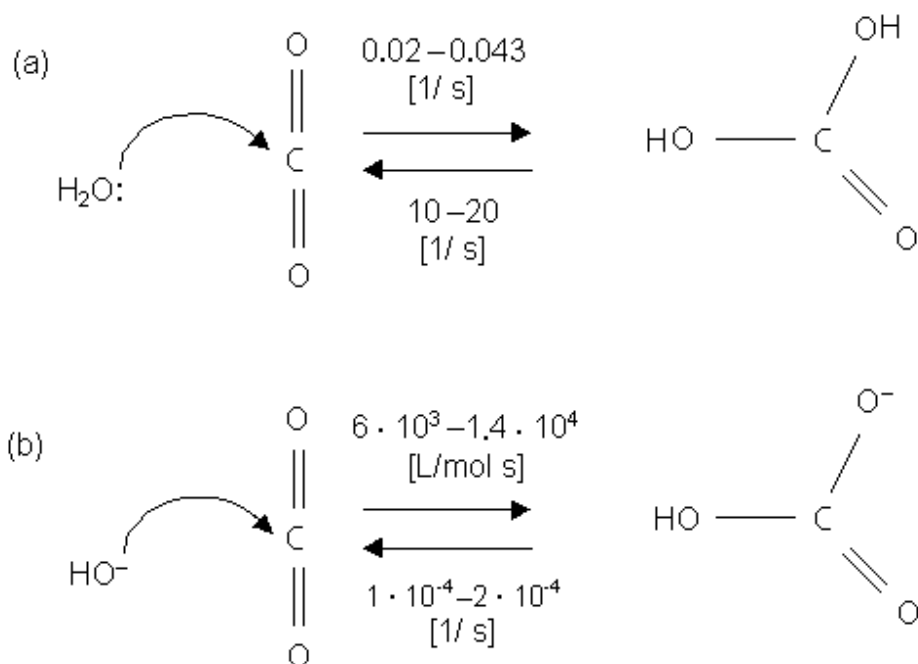
The net reaction of each reaction mechanism is



When a substantial amount of  $\text{OH}^-$  ions is present, the alkaline mechanism predominates and reaction (4.44) is completely shifted to the right. Thus the overall reaction, which is assumed to occur when  $\text{CO}_2$  is released from a strong alkaline aqueous solution, can be expressed as follows



The reactions (4.40c), (4.42) and (4.44) can be considered as instantaneous and thus in equilibrium at all times, because they only involve a proton exchange. The reactions (4.40a), (4.40b) and (4.43) between  $\text{CO}_2$  and  $\text{HCO}_3^-$ , however, are relatively slow, because they involve a rearrangement of the chemical structure in addition to the proton exchange [Ast67, Pra69, Hag71, Stu81, Ast83b]. The linear  $\text{CO}_2$  molecule must be rearranged into the trigonal  $\text{HCO}_3^-$  ion, as shown in **Figure 4.3**. Thus, reactions (4.40a), (4.40b) and (4.43) are the rate-determining steps in the reaction mechanisms.



**Figure 4.3:** Schematic representation of the rate-determining steps in (a) the acidic mechanism and (b) the alkaline mechanism.

The rate constants given in Figure 4.3 are taken from [Pin56, Ker60, Dan70, Hag71, Ski75, Stu81, Con90].

### 4.2.2 Rate Constants

The reaction rate depends on the temperature, the pressure and the ionic strength.

Pohorecki and Moniuk [Poh88] proposed a correlation between the reaction rate constant and the ionic strength as described in the following.

According to the absolute reaction rate theory, for a reaction between an ion B having a charge  $z$  and a neutral molecule A, one can write  $A + B^z \leftrightarrow [(AB)^z]^* \rightarrow \text{products}$ . According to the Brönsted-Bjerrum equation the rate constant of this reaction is as follows

$$k = k^o \frac{\gamma_A \gamma_B}{\gamma_{(AB)^*}} \quad (4.47)$$

where  $k^o$  is the rate constant of the reaction in ideal solution and  $\gamma_i$  is the activity coefficient of the reactants A and B and the activated complex  $(AB)^*$ .

The activity coefficient of an ion in the liquid phase can be determined from the Debye-Hückel-Brönsted equation

$$\log \gamma_{\text{ion}} = -A z_{\text{ion}}^2 \sqrt{I} + \beta_{\text{ion}} I \quad (4.48)$$

with  $z_{\text{ion}}$  as the charge of the ion, A as the Debye-Hückel parameter and  $\beta_{\text{ion}}$  as an ion specific parameter.

The Debye-McAulay equation yields for a neutral molecule

$$\log \gamma_A = \beta_A I. \quad (4.49)$$

Inserting equations (4.48) and (4.49) into equation (4.47) yields

$$\log \frac{k}{k^o} = [\beta_A + \beta_B - \beta_{(AB)^*}] I = b I. \quad (4.50)$$

Experimental results [Poh88] obtained for the rate constant  $k_{\text{OH}^-}$  of reaction (4.43) in KOH, NaOH and LiOH solutions in the concentration range 0.5 – 4 kmol/m<sup>3</sup> show that equation (4.50) describes fairly well the results of the experiments,



provided that the apparent value of  $k_{\text{OH}^-}^{\circ}$  determined by the linear extrapolation of the results obtained for  $I > 0.5 \text{ kmol/m}^3$  is used instead of the real value for  $k_{\text{OH}^-}^{\circ}$ .

For solutions containing several electrolytes equation (4.50) gives

$$\log \frac{k}{k^{\circ}} = \sum_i b_i I_i \quad (4.51)$$

with  $b_i = b_{+i} + b_{-i} + b_{gi}$ .  $b_{+i}$  and  $b_{-i}$  are the contributions of cations and anions and  $b_{gi}$  is the contribution of the gas in equation (4.51).

Pohorecki and Moniuk [Poh88] proposed to use equation (4.51) for determining the rate constant  $k_{\text{OH}^-}$  of reaction (4.43) in aqueous electrolyte solutions and to neglect the small value obtained for the gas contribution  $b_g$ . For the contributions of  $\text{Na}^+$  ions they found  $b_+ = 0.120 \text{ m}^3/\text{kmol}$  and for the contribution of  $\text{Cl}^-$  ions they found  $b_- = -0.061 \text{ m}^3/\text{kmol}$ .

The effect of the concentrations of other ions on the activity coefficients of the reacting components and thus on the rate constants is called primary salt effect. If the rate law of the considered reaction contains components involved in other reactions, their concentrations can depend on the ionic strength, since the equilibrium constant may depend on the ionic strength. The variation of the reaction rate due to this is called secondary salt effect.

### **Correlations for the rate constants**

An overview of correlations for the rate constants is given by Glade [Gla01a].

The rate constant of the reaction  $\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$  was measured by Pinsent et al. [Pin56] at temperatures between 0 and 40°C in diluted solutions. The rate constant was correlated with the temperature according to the Arrhenius equation with  $E_A = 55.439 \text{ kJ/mol}$  and  $A = 4.2 \cdot 10^{13} \text{ L/(mol s)}$ :

$$\log k_{\text{OH}^-} = 13.635 - \frac{2895}{T} \quad (4.52)$$

where  $k_{\text{OH}^-}$  is in  $\text{L/(mol s)}$  and  $T$  is in  $\text{K}$ .

The experiments of Pinsent et al. [Pin56] and Nijsing et al. [Nij59] in concentrated solutions with  $I < 5 \text{ mol/kg}$  at 20°C showed that the rate constant increases with

increasing ionic strength. The increase depends on the type of the electrolyte solution. For example, the effect of ionic strength in a KCl solution is stronger than in a NaCl solution of the same ionic strength. No experimental data are available for the rate of the reaction (4.43) in seawater. Astarita et al. [Ast83b] suggested a correlation for solutions with ionic strengths up to 7.75 mol/kg and temperatures between 0 and 110°C. Astarita et al. confirmed the influence of temperature on the rate constant which was found by Pinsent et al. [Pin56], but they neglected the effect of the type of the electrolyte solution:

$$\log k_{\text{OH}^-} = 13.635 - \frac{2895}{T} + 0.08 I \quad (4.53)$$

with  $k_{\text{OH}^-}$  in L/(mol s) and T in K.

The rate of the reaction  $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$  was experimentally examined by Pinsent et al. [Pin56] between 0 and 38°C:

$$\log k_{\text{H}_2\text{O}} = 329.85 - 110.541 \cdot \log T - \frac{17265.4}{T} \quad (4.54)$$

with  $k_{\text{H}_2\text{O}}$  in 1/s and T in K.

Since the extrapolation of correlation (4.54) does not yield reasonable results for higher temperatures, Glade [Gla01a] recorrelated the data of Pinsent et al. [Pin56] and proposed the following expression:

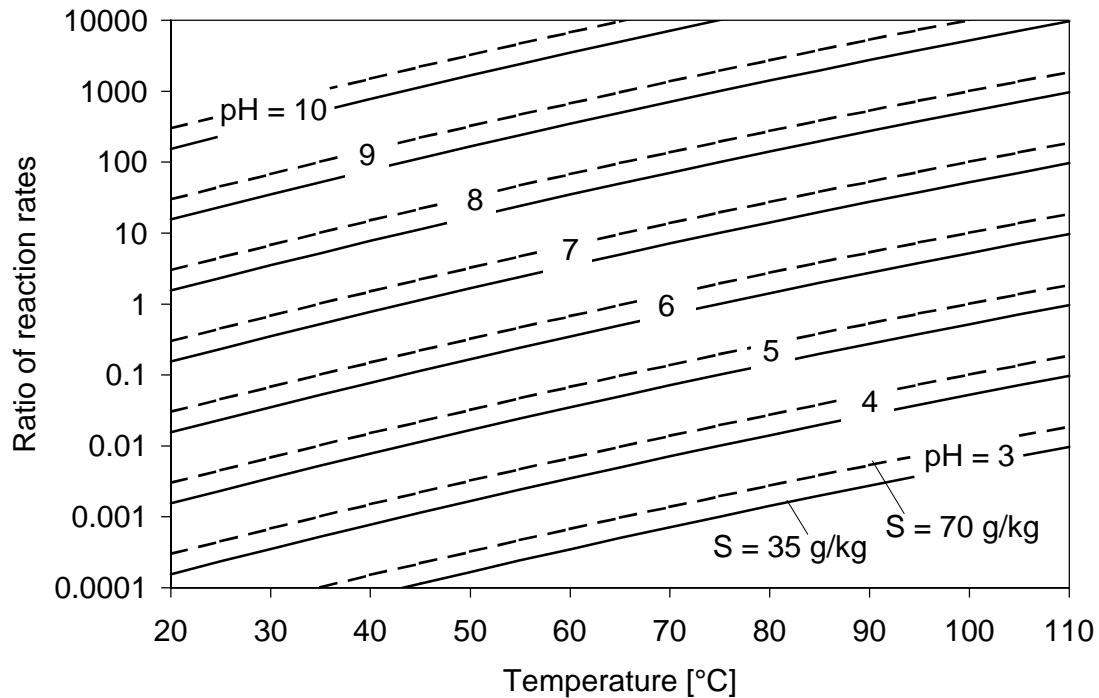
$$\log k_{\text{H}_2\text{O}} = 3.71 - \frac{472808}{T^2} \quad (4.55)$$

with  $k_{\text{H}_2\text{O}}$  in 1/s and T in K.

**Figure 4.4** shows the ratio of the rate of reaction  $\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$  to that of reaction  $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$  as a function of temperature at different pH values and different salinities.

As shown in Figure 4.4, both reactions are important in the pH range from 6.5 to 8.5 at 20°C. Reaction (4.40) predominates at lower pH values and reaction (4.43) becomes more important at higher pH values. The pH range in which both reactions must be considered shifts to lower pH values with increasing temperature. At constant temperature and pH value, the ratio of the reaction rates

risers with increasing salinity, i.e. the influence of the alkaline mechanism becomes stronger [Gla01a].

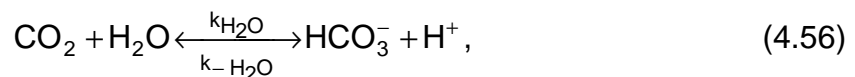


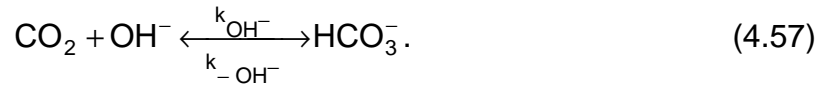
**Figure 4.4:** Ratio of the rate of reaction  $\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$  to that of reaction  $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$  as a function of temperature at different pH values and different salinities [Gla01a].

The reaction (4.43) predominates at the operating conditions in ME distillers which have been investigated in this work. For instance, for standard seawater with a salinity of 35 g/kg and a pH of 8.1, the pH values of the brine were found to be in the range of 7.8 and 7.6 at brine temperatures up to 70°C in the first evaporator stage and between 8.1 and 7.9 at temperatures down to 40°C in the last evaporator stage. Thus, the alkaline reaction mechanism with the rate-determining step  $\text{CO}_2 + \text{OH}^- \leftrightarrow \text{HCO}_3^-$  predominates, particularly at high temperatures.

#### 4.2.3 Reaction Time

The rate-determining steps of the acidic and the alkaline mechanisms are as follows:





The average reaction time of reaction (4.56) is given by

$$t_{\text{R,H}_2\text{O}} = \frac{1}{k_{\text{H}_2\text{O}} + k_{-\text{H}_2\text{O}} \left( [\text{HCO}_3^-] + [\text{H}^+] \right)} \quad (4.58)$$

The average reaction time of reaction (4.57) can be expressed as

$$t_{\text{R,OH}^-} = \frac{1}{k_{\text{OH}^-} \left( [\text{CO}_2] + [\text{OH}^-] \right) + k_{-\text{OH}^-}} \quad (4.59)$$

It was expected that for higher pH values the time of the reaction (4.56) would be in the order of the slower reaction. However, Zeebe et al. [Zee99] showed that the reaction (4.56) should be coupled with the dissociation reaction of water (4.5). The time constant of the coupled system is about 500 times larger than the estimated reaction time of the hydration of  $\text{CO}_2$ . Simplified formulae for the reaction times of the reactions (4.56) and (4.57) have been suggested as follows [Zee99]

$$t_{\text{R,H}_2\text{O}} = \frac{1}{k_{\text{H}_2\text{O}} + k_{-\text{H}_2\text{O}} [\text{H}^+]}, \quad (4.60)$$

$$t_{\text{R,OH}^-} = \frac{1}{k_{\text{OH}^-} [\text{OH}^-] + k_{-\text{OH}^-}} \quad (4.61)$$

The rate constant of the backward reaction (4.56) can be written as

$$k_{-\text{H}_2\text{O}} = \frac{k_{\text{H}_2\text{O}}}{K_1^{\text{SW}}} \quad (4.62)$$

Inserting equation (4.62) into equation (4.60) yields

$$t_{\text{R,H}_2\text{O}} = \frac{1}{k_{\text{H}_2\text{O}} \left( \frac{K_1^{\text{SW}} + [\text{H}^+]}{K_1^{\text{SW}}} \right)} \quad (4.63)$$

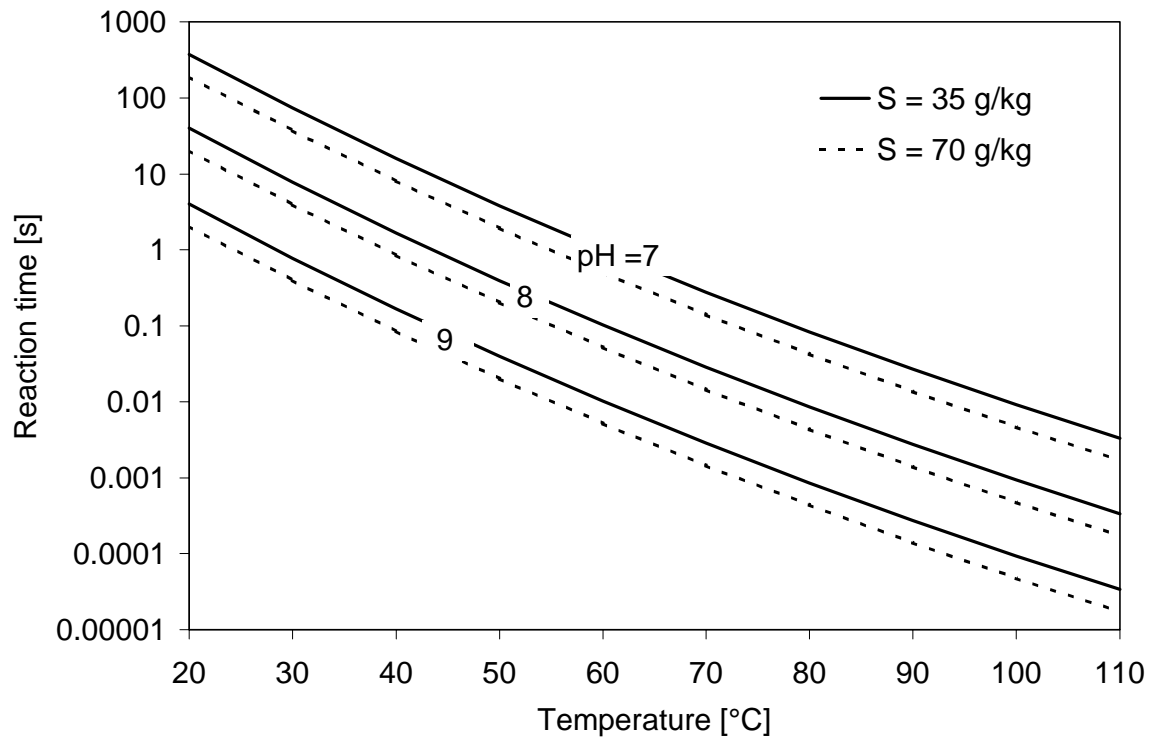
The rate constant of the backward reaction (4.57) is given by

$$k_{-\text{OH}^-} = \frac{k_{\text{OH}^-}}{K} = k_{\text{OH}^-} \cdot \frac{K_W^{\text{SW}}}{K_1^{\text{SW}}} \quad (4.64)$$

Inserting equation (4.64) into equation (4.61) yields

$$t_{\text{R,OH}^-} = \frac{1}{k_{\text{OH}^-} \left( \frac{K_W^{\text{SW}}}{K_1^{\text{SW}}} + [\text{OH}^-] \right)} \quad (4.65)$$

**Figure 4.5** shows the reaction time of reaction (4.57). The reaction time decreases with increasing temperature, pH and salinity.



**Figure 4.5:** Reaction time of reaction  $\text{CO}_2 + \text{OH}^- \xrightleftharpoons[k_{-\text{OH}^-}]{k_{\text{OH}^-}} \text{HCO}_3^-$ .