

## DISSOCIATION OF CARBONIC ACID AND BICARBONATE

### 1. Equilibrium equation

In water, CO<sub>2</sub>(aq) is partially hydrated into carbonic acid according to the reaction:



The ratio of CO<sub>2</sub>(aq) to H<sub>2</sub>CO<sub>3</sub> is close to 400:1, but for analytical reasons, it is more convenient to consider both the hydrated and non-hydrated forms of CO<sub>2</sub> as a single entity which is commonly designated by CO<sub>2</sub><sup>\*</sup>, and equilibrium constants are generally expressed in terms of CO<sub>2</sub><sup>\*</sup> concentration (see the section devoted to [CO<sub>2</sub> transfer across the interface](#)).

The distribution of dissolved carbonate species is governed by the dissociation of carbonic acid according to the following equilibria:



The stoichiometric (or apparent) dissociation constant for the reaction (2), which includes the value of the various activity coefficients, is defined by the following relation:

$$K_1' = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2^*]} \quad (4)$$

In this expression, the terms between brackets [ ] are in mole/kg of solution (molality). Although it is easy to convert molarity (mole/l) into molality (mole/kg) by taking into account the density of water as a function of temperature and salinity, we have used the above expression with molarity instead of molality in CONTRASTE, because concentration are expressed in terms of mass per unit volume in the model. Density variations and their departure from the value of pure water are therefore neglected.

In a similar way, the stoichiometric (or apparent) dissociation constant of the reaction (3) is defined by the relation:

$$K_2' = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (5)$$

### 2. First dissociation constant of carbonic acid $[K_1']$

The expression used for the first dissociation constant is from Cai and Wang (1998). These authors have merged into a single expression the results of Mehrbach *et al.* (1973), Mooke and Koene (1975) and Harned and Davis (1943), in order to cover the entire salinity range from 0 to 40 between 2 and 30°C. This is because the dissociation constants of carbonic acid determined by Merbach *et al.* are not meant to be extrapolated to low-salinity water, *i.e.* outside a salinity range of 26-43. The general expression is given by:

$$\text{p}K_1'(T, S) = \text{p}K_1'(T) + f_1(T) \cdot S^{\frac{1}{2}} + f_2(T) \cdot S \quad (6)$$

where T refers to the absolute temperature and S to the salinity. It includes a function  $pK_1'(T)$  giving the value of the dissociation constant at zero salinity, and two temperature functions  $f_1(T)$  and  $f_2(T)$ . These 3 functions are detailed in the following table.

$pK_1'(T) = a_0 + \frac{a_1}{T} + a_2 T$	$a_0 = -1.48435 \cdot 10^1$
	$a_1 = 3.40471 \cdot 10^3$
	$a_2 = 3.2786 \cdot 10^{-2}$
$f_1(T) = b_0 + \frac{b_1}{T}$	$b_0 = -2.30848 \cdot 10^2$
	$b_1 = -1.43456 \cdot 10^1$
$f_2(T) = c_0 + \frac{c_1}{T}$	$c_0 = 6.91881 \cdot 10^{-4}$
	$c_1 = 4.29955 \cdot 10^{-1}$

Control values:

at 0°C (273.15 K), salinity 0:	$pK_1' = 6.57$	$K_1' = 2.65 \cdot 10^{-7}$
at 20°C (293.15 K), salinity 35:	$pK_1' = 6.03$	$K_1' = 9.30 \cdot 10^{-7}$

### 3. Second dissociation constant of carbonic acid $[K_2']$

The expression used for the second dissociation constant is again from Cai and Wang (1998). These authors have merged into a single expression the results of Mehrbach et al. (1973), Edmond and Gieskes (1970) and Harned and Davis (1943), in order to cover the entire salinity range from 0 to 40, between 0.2 and 35°C. The general expression is given by:

$$pK_2'(T,S) = pK_2'(T) + f_3(T)S^{\frac{1}{2}} + f_4(T)S \quad (7)$$

where T refers to the absolute temperature and S to the salinity. It includes a function  $pK_2'(T)$  giving the value of the dissociation constant at zero salinity, and two temperature functions  $f_3(T)$  and  $f_4(T)$ . These 3 functions are detailed in the following table.

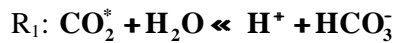
$pK_2'(T) = d_0 + \frac{d_1}{T} + d_2 T$	$d_0 = -6.4980$
	$d_1 = 2.90239 \cdot 10^3$
	$d_2 = 2.379 \cdot 10^{-2}$
$f_3(T) = e_0 + \frac{e_1}{T}$	$e_0 = -4.58898 \cdot 10^{-1}$
	$e_1 = 4.124048 \cdot 10^1$
$f_4(T) = g_0 + \frac{g_1}{T}$	$g_0 = 2.84743 \cdot 10^{-2}$
	$g_1 = -2.55895$

Control values:

at 0°C (273.15 K), salinity 0:	$pK_2' = 10.62$	$K_2' = 2.37 \cdot 10^{-11}$
at 20°C (293.15 K), salinity 35:	$pK_2' = 9.19$	$K_2' = 6.50 \cdot 10^{-10}$

#### 4. Model entries for computing the dissociation of carbonic acid and bicarbonate

1. Number of species: **4**
2. Number of kinetic reactions: **0**
3. Number of equilibrium conditions: **2**
4. Variables:  $\text{CO}_2^*$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$
5. Reactions:



6. Equilibria:

$$K_1 = K_1' \frac{[\text{CO}_2^*] \cdot [\text{H}^+]}{[\text{HCO}_3^-]}$$

$$K_2 = K_2' \frac{[\text{HCO}_3^-] \cdot [\text{H}^+]}{[\text{CO}_3^{2-}]}$$

7. Model parameters:  $K_1'$ ,  $K_2'$  (depend on temperature and salinity)

#### References

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