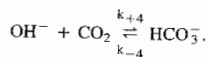
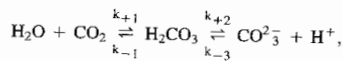


TABLE 5.1 Some Attributes of Carbon Dioxide and Oxygen Relevant to Their Interaction With Aquatic Photolithotrophs

Parameter	Value in Freshwater	Value in Seawater (35‰ salinity)	Value in Dead Sea water (330‰ salinity)	Reference
CO ₂ in equilibrium with 35Pa CO ₂ in the gas phase/mmole m ⁻³	22.43 (5°C)	18.75 (5°C)		Skirrow [1975]
	15.95 (15°C)	13.46 (15°C)		
	11.90 (25°C)	10.18 (25°C)		
	9.27 (35°C)	8.06 (35°C)		
O ₂ in equilibrium with 20.95kPa O ₂ in the gas phase/mmole m ⁻³	391.5 (5°C)	310.8 (5°C)		Riley and Skirrow [1975]
	298.3 (15°C)	240.8 (15°C)		
	236.0 (25°C)	193.5 (25°C)		
pK _{a1} of carbonic acid ^b	6.52 (5°C)	6.11 (5°C)		Skirrow [1975] Sas and Ben-Yaakov [1977]
	6.42 (15°C)	6.05 (15°C)	5.09 (30°C)	
	6.35 (25°C)	6.00 (25°C)		
	6.31 (35°C)	5.97 (35°C)		
pK _{a2} of carbonic acid ^b	10.55 (5°C)	9.34 (5°C)		Skirrow [1975] Sas and Ben-Yaakov [1977]
	10.43 (15°C)	9.23 (15°C)	6.23 (30°C)	
	10.33 (25°C)	9.10 (25°C)		
	10.25 (35°C)	8.95 (35°C)		
D _{CO₂} /m ² s ⁻¹ ^c	0.953 · 10 ⁻⁹ (0°C)			Kigoshi and Hashitani [1963]
	1.94 · 10 ⁻⁹ (25°C)			
	2.8 · 10 ⁻⁹ (30°C)			
	0.521 · 10 ⁻⁹ (0°C)			
D ^b HCO ₃ ⁻ m ² s ⁻¹	1.09 · 10 ⁻⁹ (25°C)			Kigoshi and Hashitani [1963]
	1.28 · 10 ⁻⁹ (30°C)			
	0.414 · 10 ⁻⁹ (0°C)			
	0.804 · 10 ⁻⁹ (25°C)			
D _{CO₃²⁻} /m ² s ⁻¹	0.974 · 10 ⁻⁹ (30°C)			Battino et al. [1968]
	0.575 (CO ₂ , 25°C)			
	0.227 (O ₂ , 25°C)			
	1.77 · 10 ⁻⁹ (18°C)			
[Gas] in equilibrium with 1 mmole m ⁻³ [gas] in olive oil mmole m ⁻³				Radford [1964] Edsall [1969]
D _{O₂} /m ² s ⁻¹ ^c				
Rate constant for hydration of CO ₂ ^a (CO ₂ +H ₂ O→H ₂ CO ₃)/s ⁻¹	0.037 (25°C)	0.037 (25°C)		
Rate constant for hydration of CO ₂ ^a (CO ₂ +H ₂ O→H ₂ CO ₃)/m ³ mol ⁻¹ s ⁻¹	9.4 · 10 ⁻⁷ (25°C)	9.4 · 10 ⁻⁷ (25°C)		Gutknecht et al. [1977], Johnson [1982], Walker et al. [1980]
Rate constant for hydration of CO ₂ ^a (CO ₂ +OH ⁻ →HCO ₃ ⁻)/m ³ mol ⁻¹ s ⁻¹	8.5 (25°C)	14.1 (25°C)		
Rate constant for dehydration of H ₂ CO ₃ ^a (H ₂ CO ₃ →CO ₂ +H ₂ O)/s ⁻¹	14 (25°C)	8 (25°C)		
Rate constant for dehydroxylation of HCO ₃ ⁻ (HCO ₃ ⁻ →CO ₂ +OH ⁻)/s ⁻¹	19 · 10 ⁻⁴ (25°C)	15 · 10 ⁻⁴ (25°C)		

^aThe reactions of carbonic acid in solution are



The ionic reactions with rate constants k_{+2} , k_{-2} , k_{+3} , and k_{-3} are very rapid (diffusion-limited). The reactions denoted by k_{+1} , k_{-1} , k_{+4} , and k_{-4} have rate constants which are shown in the table; note that the reaction with rate constant k_{+1} can have rate constants in units of s⁻¹ or of m³ mol⁻¹ s⁻¹ depending on the view adopted concerning the units of water activity [compare Gutknecht et al., 1977; with Walker et al., 1980].

^bThe pK_a values quoted are

$$\text{pK}_{a1} = -\log_{10} \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\text{pK}_{a1} = -\log_{10} \frac{[\text{HCO}_3^-]}{[\text{CO}_2 + \text{H}_2\text{CO}_3]}$$

^cThe self-diffusion coefficient of CO₂ in the gas phase 1.04 · 10⁻⁵ m² s⁻¹ at 0°C; that of O₂ in the gas phase is 1.89 · 10⁻⁵ m² s⁻¹ at 0°C [Radford, 1964]. These values are some four orders of magnitude greater than those in aqueous solution. Alternative approaches to the aqueous-phase diffusion coefficients of HCO₃⁻ and CO₃²⁻ (and of H₂CO₃) may be found in Rackham [1966] and in Walker et al. [1980]. The influence of the isotopic composition of inorganic carbon on diffusion coefficients of inorganic carbon species in the aqueous phase and (for carbon dioxide) in the gas phase has been discussed by O'Leary [1981] and Farquhar et al. [1982]. The diffusion coefficient of carbon dioxide in solution is slightly decreased in salt solutions as compared to pure water: Table 16 of Danckwerts and Sharma [1966] shows that D_{CO₂} at 25°C is 1.92 · 10⁻⁹ m² s⁻¹ in pure water; 1.73 · 10⁻⁹ m² s⁻¹ in 1.04 kmol m⁻³ NaCl (60.84‰); and 1.30 · 10⁻⁹ m² s⁻¹ in 3.78 kmol m⁻³ NaCl (221.13‰).