

## **Supplementary Material for**

# **Activation Volumes for the Hydration Reactions of Carbon Dioxide**

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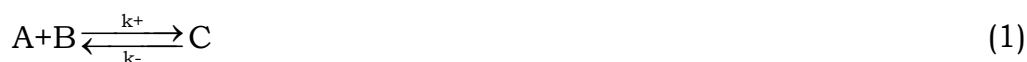
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## Activity based data analysis

Consider the reversible reaction



The law of mass action for equilibria states

$$K = \frac{\{C\}}{\{A\}\{B\}} = \frac{\gamma_C [C]}{\gamma_A \gamma_B [A][B]} \quad (2)$$

The equivalent for kinetics states

$$\frac{d[A]}{dt} = -k_+ \{A\}\{B\} + k_- \{C\} = -k_+ \gamma_A \gamma_B [A][B] + k_- \gamma_C [C] \text{ etc.} \quad (3)$$

Where  $\{A\}$  represents the activity of A. It is the product of its activity coefficient  $\gamma_A$  with the concentration  $[A]$ .

According to Debye-Hückel the activity coefficient of an ion is can be approximated by the equation.

$$\log \gamma_i = \frac{-A z_i^2 \sqrt{\mu}}{1 + \sqrt{\mu}} \quad (4)$$

where  $\mu$  is the ionic strength,  $z_i$  the charge of the i-th ion, and  $A = 0.242$  for aqueous solutions at room temperature.

Activities or activity coefficients are notoriously difficult to determine and thus the thermodynamically correct application of the law or mass action is not commonly implemented. Instead, an excess of an inert salt is added, attempting to keep ionic strength and thus activity coefficients constant. Rate and equilibrium constants are then reported for the particular chosen ionic strength.

A modern approach is to base all calculations on the proper law of mass action, using estimations of all activity coefficients based on the Debye-Hückel equation; i.e. activities are used for all equilibrium as well as all kinetic calculations. Thus, all computations are based on the equivalents of equations (2) and (3). This requires the continuous calculation of the ionic

strength at any given time in a titration or kinetic experiment with concomitant calculation of all activity coefficients.

Beta versions of the ReactLab Equilibria and ReactLab Kinetics packages where the above ideas are implemented are available upon request via [www.jplusconsulting.com](http://www.jplusconsulting.com).

**Table S1.** Summary of kinetic and equilibrium data for the reversible reactions of CO<sub>2</sub>(aq) with H<sub>2</sub>O and OH<sup>-</sup> at 25°C and elevated pressures. Values in parenthesis represent the standard deviation in the last decimal point.

Pressure (Bar)	$k_1$	$k_{-1}$	$K_1$	$k_2$	$k_{-2}$	$K_2$	$\log K_3$	$\log K_4$
400	$5.9(3) \times 10^{-3}$	$1.1(2) \times 10^1$	$5(3) \times 10^{-4}$	$4.1(7) \times 10^3$	$3.9(7) \times 10^{-5}$	$1.06(1) \times 10^8$	10.38(5)	2.7(3)
600	$5.8(2) \times 10^{-3}$	$1.17(6) \times 10^1$	$5(1) \times 10^{-4}$	$3.8(3) \times 10^3$	$3.5(3) \times 10^{-5}$	$1.07(2) \times 10^8$	10.39(2)	2.7(1)
800	$7.7(2) \times 10^{-3}$	$1.18(9) \times 10^1$	$7(2) \times 10^{-4}$	$3.3(3) \times 10^3$	$3.0(2) \times 10^{-5}$	$1.10(0) \times 10^8$	10.3(1)	2.7(1)
1000	$8.7(1) \times 10^{-3}$	$1.2(1) \times 10^1$	$7(3) \times 10^{-4}$	$3.2(4) \times 10^3$	$2.8(3) \times 10^{-5}$	$1.13(0) \times 10^8$	10.33(7)	2.7(1)