

# IS “THERMODYNAMIC CONSISTENCY” A USEFUL MEASURE OF OUR UNDERSTANDING OF SEAWATER CARBONATE CHEMISTRY?

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## ABSTRACT

An accurate knowledge of the thermodynamics of the carbonic acid system in seawater is crucial to our understanding of the behavior of carbon dioxide in seawater. In particular, this knowledge is needed whenever a particular property needs to be calculated from measurements of other related properties; *e.g.*, the estimation of the partial pressure of CO<sub>2</sub> in air that is in equilibrium with a sample of sea water,  $p(\text{CO}_2)$ , from measurements of the total dissolved inorganic carbon,  $C_T$ , and of the total alkalinity,  $A_T$ , of a water sample. This calculation is particularly important for ocean models, which transport  $C_T$  and  $A_T$ , but which need to calculate  $p(\text{CO}_2)$  at the sea surface so as to represent air-sea exchange processes. Numerous determinations of dissociation constants for carbon dioxide in seawater media have been published over the years. In each case the authors have recommended “best” values for the dissociation constants, and often the constants are represented in these papers by interpolating equations or tables. Furthermore, a number of investigators have attempted to assess the thermodynamic consistency of the various published values for these dissociation constants with analytical measurements made on natural seawater. Despite all this work, the results of these efforts are, as yet, not conclusive. I shall present a review of the situation and will try to provide a clear description of the magnitude of the problems, their possible sources, and their importance to understanding the behavior of CO<sub>2</sub> in seawater.

## BACKGROUND TO THE PROBLEM

Numerous determinations of these dissociation constants in seawater media have been published over the years. Furthermore, a number of evaluations of these measurements have been published. In each case the authors have recommended “best” values for the dissociation constants, and often the constants are represented in these papers by interpolating equations or tables. The differences between the various sets of measurements made over the past thirty years are not very large, about 0.01–0.02 in  $pK_1$  (Fig. 1) and up to 0.04–0.06 in  $pK_2$  (Fig. 2). However, the uncertainty introduced by such discrepancies is meaningful when compared with the present uncertainties in the analytical measurements of the carbonate system. In particular, the estimation of  $p(\text{CO}_2)$  from  $A_T$  and  $C_T$  is affected significantly by these uncertainties. A number of investigators have used this sensitivity to assess the *thermodynamic consistency* of the various published values for these dissociation constants with analytical measure-

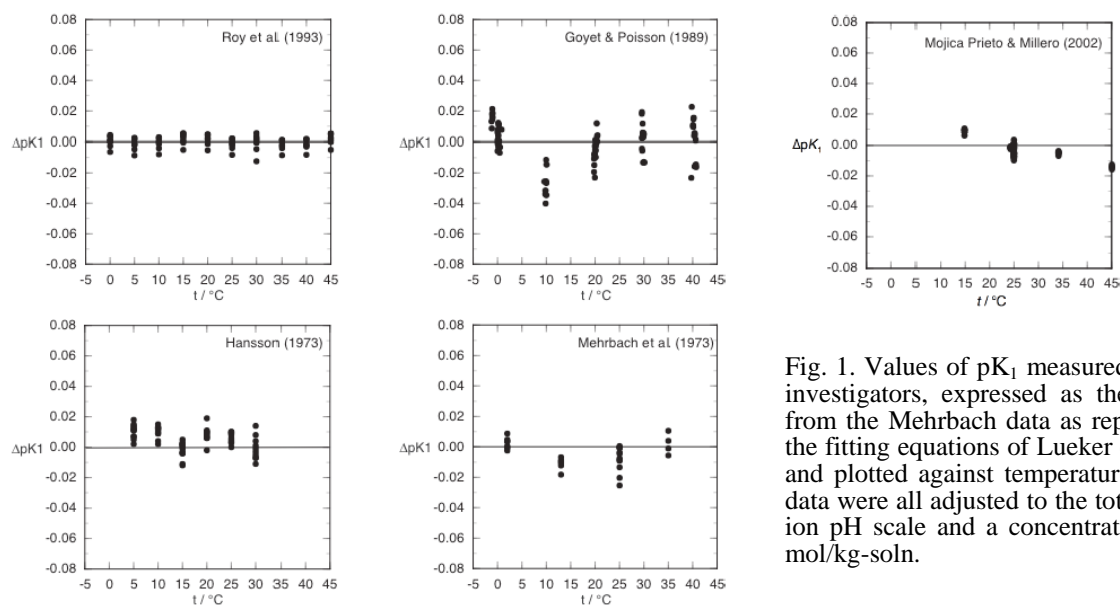


Fig. 1. Values of  $pK_1$  measured by various investigators, expressed as the difference from the Mehrbach data as represented by the fitting equations of Lueker et al. [2000] and plotted against temperature. Note: the data were all adjusted to the total hydrogen ion pH scale and a concentration scale of mol/kg-soln.

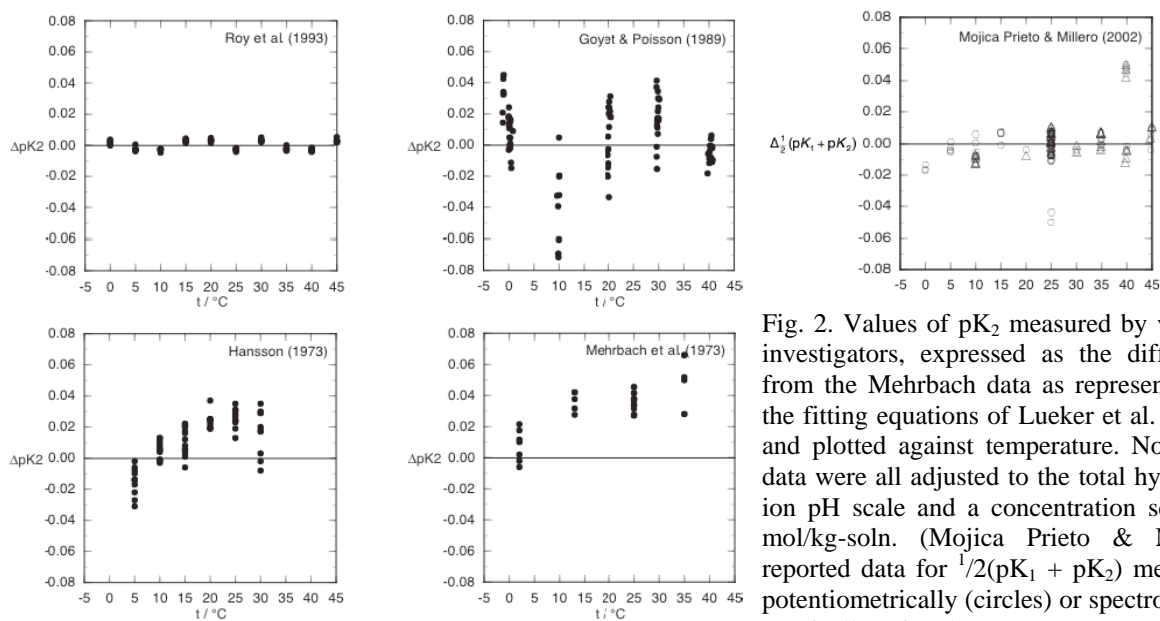


Fig. 2. Values of  $pK_2$  measured by various investigators, expressed as the difference from the Mehrbach data as represented by the fitting equations of Lueker et al. [2000] and plotted against temperature. Note: the data were all adjusted to the total hydrogen ion pH scale and a concentration scale of mol/kg-soln. (Mojica Prieto & Millero reported data for  $1/2(pK_1 + pK_2)$  measured potentiometrically (circles) or spectrophotometrically (triangles).

ments made on natural seawater samples. Despite all this effort, the results of these examinations are, as yet, not conclusive. Current opinion favors the use of the “Mehrbach” constants for the calculation of the  $p(\text{CO}_2)$  of surface seawater samples from measurements of  $C_T$  and  $A_T$  (*i.e.* for  $p(\text{CO}_2)$  values below about 500–600  $\mu\text{atm}$ ). This opinion is based on a number of studies over the past few years that concluded that at low  $p(\text{CO}_2)$  the equilibrium constants of Mehrbach *et al.* were consistent with the data; however, deviations were found at higher  $p(\text{CO}_2)$  values, particularly when  $p(\text{CO}_2)$  was estimated from  $A_T$  and  $A_T$ . Similar discrepancies have been found in laboratory experiments — see Fig. 3.

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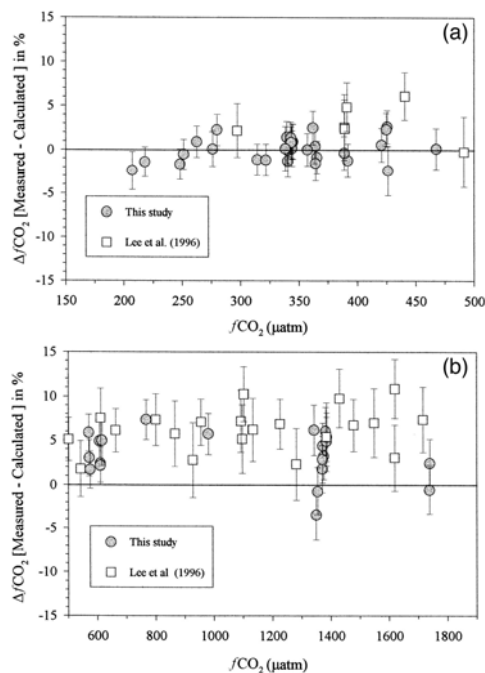


Fig. 3. Fractional deviation in  $f(\text{CO}_2)$  between measured values of  $f(\text{CO}_2)$  and values calculated from measurements of  $A_T$  and  $C_T$ : (a) for  $f(\text{CO}_2)$  values less than 500  $\mu\text{atm}$ ; (b) for  $f(\text{CO}_2)$  values greater than 500  $\mu\text{atm}$  [Figure 6 from Lueker *et al.*, 2000].