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Current estimates of K_1^* and K_2^* appear inconsistent with measured CO_2 system parameters in cold oceanic regions

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S1 Overview of past studies and derivations of the carbonic acid dissociation constants

Table S1. Overview of most commonly used (i.e. included in most popular carbonate system calculation software) and recently published stoichiometric equilibrium constants at atmospheric pressure, and some of their properties and methodological details. Studies in italic indicate refits of previous studies.

Reference	**T range (°C)**	**S_P range**	**pH scale**	**σ of fit**	**Medium**	**Method**
Mehrbach et al., 1973	2 to 35	19 to 43	NBS	$\ln K_1$	Natural seawater (filtered at 0.45 µm)	Electrochemical cell with glass electrode and $Hg–Hg_2Cl_2$ (calomel) reference electrode
M1973 refit by Dickson and Millero, 1987			*SWS*			*Recalculation of K_2; reformulation on SWS scale*
M1973 refit by Lueker et al., 2000			*T*			*K_2 determined as by Dickson and Millero (1987); reformulated to total scale*
Hansson, 1973	5 to 30	20 to 40	SWS		Artificial seawater (no Na_2CO_3)	Electrochemical cell with glass electrode and Ag–AgCl reference electrode
H1973 refit by Dickson and Millero, 1987			*SWS*			*Corrected for deviations of the sulfate concentration and lack of fluoride in medium*
M1973 and H1973 refit by Dickson and Millero, 1987	*2 to 35*	*0 to 40*	*SWS*			*Pooling of 1973 and H1973 data sets at SWS scale*
Goyet and Poisson, 1989	–1 to 40	10 to 50	SWS		Artificial seawater (incl. Na_2CO_3)	Electrochemical cell with glass electrode and $Hg–Hg_2Cl_2$ (calomel) reference electrode
Roy et al., 1993	0 to 45	5 to 45	T	±0.0048 ($\ln K_1^*$) ±0.0070 ($\ln K_2^*$)	Artificial seawater (no Na_2CO_3)	Electrochemical cell (no liquid junction) with $Pt–H_2$ and Ag–AgCl electrodes
Cai and Wang, 1998	*0.2 to 35*	*0 to 40*	*NBS*			*Refit of K_1 based on M1973 for $S_P > 15$ and Mook and Koene (1975) for $S_P < 15$, and refit of K_2 based on M1973 for $S_P > 20$ and Edmond and Gieskes (1970) for $S_P < 20$. T dependency as in M1973.*
Mojica Prieto and Millero, 2002	0 to 45	5 to 42	SWS		Artificial seawater (incl. Na_2CO_3); natural seawater (filtered at 0.45 µm)	Electrochemical cell with glass electrode and Ag–AgCl reference electrode; spectrophotometer

Table S1. (continued)

Reference	**T range**	**S range**	**pH scale**	**σ of fit**	**Medium**	**Method**
Millero et al., 2002	–1.6 to 35	34 to 37	SWS		Natural seawater	Concurrent measurements of TA, DIC, pH and pCO_2
Millero et al., 2006	0 to 50	1 to 50	SWS		Natural seawater (filtered at 0.45 µm)	Electrochemical cell with glass electrode and Ag–AgCl reference electrode
Millero, 2010	*0 to 50*	*1 to 50*	*SWS, T, F*			*Pooling of M1973, MPM2002 and M2006 data, recalculations on three different pH scales*
Waters et al., 2013, 2014	*0 to 45*	*5 to 45*	*SWS, T, F*			*Update from M2010 using a Pitzer ion-interaction model*
Tishchenko et al., 2013	0 to 30	1.5 to 40	T		Artificial seawater (incl. $NaHCO_3$)	Electrochemical cell (no liquid junction) with pH-glass and Ag–AgCl electrodes
Papadimitriou et al, 2018	–6 to 25	33 to 100	T		Natural seawater, seawater-derived brines (filtered at 0.2 µm)	Concurrent measurements of TA, DIC, pH and pCO_2

S2 Additional derivation of expressions for K_1^* and K_2^*

The following section describes expressions for K_1^* and K_2^* as functions of any three variables of the set carbonate alkalinity (*CA*), dissolved inorganic carbon (*DIC*), partial pressure of CO_2 (pCO_2) and proton concentration ($[H^+]$), and K_1^* (for K_2^*) or K_2^* (for K_1^*). These expressions were derived based on equations given by Dickson et al. (2007), who provide a comprehensive overview of carbonate system equations, based on *CA*, *DIC*, pCO_2 and $[H^+]$, in their Chapter 2. Here, for brevity, their equations are not repeated, but are referred to as Eq. (*D*#), where # represents the equation number used in their chapter. Note that, in comparison to Dickson et al. (2007), we use $H_2CO_3^*$ instead of CO_2^* to represent the sum of H_2CO_3 and solvated CO_2. We also use pCO_2 instead of fCO_2; this difference is accounted for in the calculation of K_0.

Recall that K_1^* and $K_2^*$are normally defined in terms of $[H^+]$, and the acid-base species for which equilibrium they describe:

$$K_1^* = \frac{[HCO_3^-][H^+]}{[H_2CO_3^*]} \tag{S1}$$

$$K_2^* = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \tag{S2}$$

S2.1 Expressions for K_1^* *and* K_2^* *as a function of DIC, CA and* $[H^+]$

To derive K_1^* as a function of this set of variables, we use Eq. (*S*1) and express $[HCO_3^-]$ and $[H_2CO_3^*]$ in terms of *DIC, CA,* $[H^+]$ and K_2^*. For this, we use Eq. (*D*58) and Eq. (*D*87) for $[HCO_3^-]$ and$[H_2CO_3^*]$, respectively. Upon substituting these equations into Eq. (*S*1) and multiplying the numerator and denominator by $([H^+] + 2K_2^*)$, we obtain the final expression for K_1^*:

$$K_1^* = \frac{CA[H^+]^2}{([H^+] + 2K_2^*)DIC - CA([H^+] + K_2^*)} \tag{S3}$$

The derivation of K_2^* is done in a similar manner. We use Eq. (*S*2) and replace $[CO_3^{2-}]$ and $[HCO_3^-]$ by Eq. (*D*85) and Eq. (*D*84), respectively. Both the numerator and denominator were then multiplied by $(2[H^+] + K_1^*)$, and the expression for K_2^* becomes:

$$K_2^* = \frac{[H^+]([H^+]CA + K_1^*CA - K_1^*DIC)}{K_1^*(2DIC - CA)} \tag{S4}$$

S2.2 Expressions for K_1^* *and* K_2^* *as a function of CA,* $[H^+]$ *and* pCO_2

Here, we again use Eq. (*S*1) to express K_1^* and replace $[HCO_3^-]$ with Eq. (*D*58) and $[H_2CO_3^*]$ with Eq. (*D*61). Upon multiplying the numerator and denominator by $([H^+] + 2K_2^*)$, we obtain:

$$K_1^* = \frac{CA[H^+]^2}{K_0pCO_2([H^+] + 2K_2^*)} \tag{S5}$$

In case of K_2^*, in Eq. (*S*2) $[CO_3^{2-}]$ and $[HCO_3^-]$ were replaced with Eq. (*D*90) and Eq. (*D*89), respectively. The numerator and denominator were then multiplied by $2[H^+]$, resulting in:

$$K_2^* = \frac{[H^+](CA[H^+] - K_0 K_1^* pCO_2)}{2K_0 K_1^* pCO_2} \qquad (S6)$$

S2.3 Expressions for K_1^* and K_2^* as a function of DIC, $[H^+]$ and pCO_2

In this variable set, to derive an equation for K_1^*, $[HCO_3^-]$ can be expressed by Eq. (*D*93), while $[H_2CO_3^*]$ is again replaced with Eq. (*D*61). Upon substituting this into Eq. (*S*1) and multiplying both the numerator and denominator by $([H^+] + K_2^*)$ we obtain:

$$K_1 = \frac{[H^+]^2(DIC - K_0 pCO_2)}{K_0 fCO_2([H^+] + K_1^*)} \qquad (S7)$$

For K_2^*, we replace $[CO_3^{2-}]$ by Eq. (*D*94) and $[HCO_3^-]$ by Eq. (*D*92). Upon multiplying the numerator and denominator by $[H^+]$, we obtain:

$$K_2^* = \frac{[H^+](DIC[H^+] - K_0 pCO_2[H^+] - K_0 K_1^* pCO_2)}{K_0 K_1^* pCO_2} \qquad (S8)$$

S2.4 Expressions for K_1^* and K_2^* as a function of DIC, CA and pCO_2

This set of variables does not allow for separate expressions for K_1^* and K_2^*. Rather, a single equation is derived, which should be solved for K_1^* and K_2^* sequentially using a Newton-Raphson technique. This single equation is derived by combining Eq. (*D*17) and Eq. (*D*53), the respective definitions of *DIC* and *CA*, into:

$$2DIC - CA = 2[H_2CO_3^*] + [HCO_3^-] \qquad (S9)$$

Then, we subtract $(2DIC - CA)$ from both the left- and right-hand sides of Eq. (*S*9), replace $[HCO_3^-]$ by Eq. (*D*79) and express $[H_2CO_3^*]$ again through Eq. (*D*61), leading to:

$$2K_0 pCO_2 + \tfrac{1}{2}\left(-\tfrac{K_1^*}{K_2^*}K_0 pCO_2 + \sqrt{\left(\tfrac{K_{1_1}^*}{K_2^*}K_0 pCO_2\right)^2 - 4\tfrac{K_1^*}{K_2^*}K_0 pCO_2(K_0 pCO_2 - DIC)}\right) - 2DIC + CA = 0 \ (S10)$$

S3 Reasons for discarding cruises #33AT20120419 and #49NZ20010828

In Fig. S1, we show $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ as a function of temperature and salinity as computed using the Lueker et al. (2000) dissociation constants and with six different carbonate variable pairs, to study carbonate system interconsistency in the different cruises that constitute our dataset. All data are from the top 5 meters of the water column, quality-controlled, and associated with a WOCE flag of 2 (i.e., “acceptable”). From Fig. S1, we see that for cruises #33AT20120419 and #49NZ20010828, the computed concentration of carbonate species can be very different depending on the input pair.

For cruise #49NZ20010828, the three pairs involving *pH* (*pCO_2-pH*, *DIC-pH* and *TA-pH*) yield very different results, while the three pairs that do not include *pH* appear to be interconsistent. Cruise #49NZ20010828 (GLODAP code #478) was not considered for carbon interconsistency checks, as seen in the GLODAP adjustment table (accessible on https://glodapv2.geomar.de/adjustments/list), because according to the adjustment table, there were only a few shallow profiles to compare. The quality controller for this cruise noted that there "seem to be an offset" in the *pH* data and that perhaps the correct flag should be "poor data".

For cruise #33AT20120419, we see in Fig. S1 that the three pairs that include *pCO₂* as a variable yield very different $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^{2-}]$ values than the three pairs without *pCO₂* data. This would go in the sense of an erroneous *pCO₂* dataset for this cruise. During carbon interconsistency checks, the *pH* from cruise #33AT20120419 (GLODAP code #330) was corrected by adding a constant value of 0.012. This procedure is quite common for GLODAP data and we did not see any particular comment or warming for this dataset in the GLODAP adjustment table. Given the apparent inconsistency of the carbonate system highlighted here for this cruise, it was not included in the dataset that we used to derive the dissociation constants.

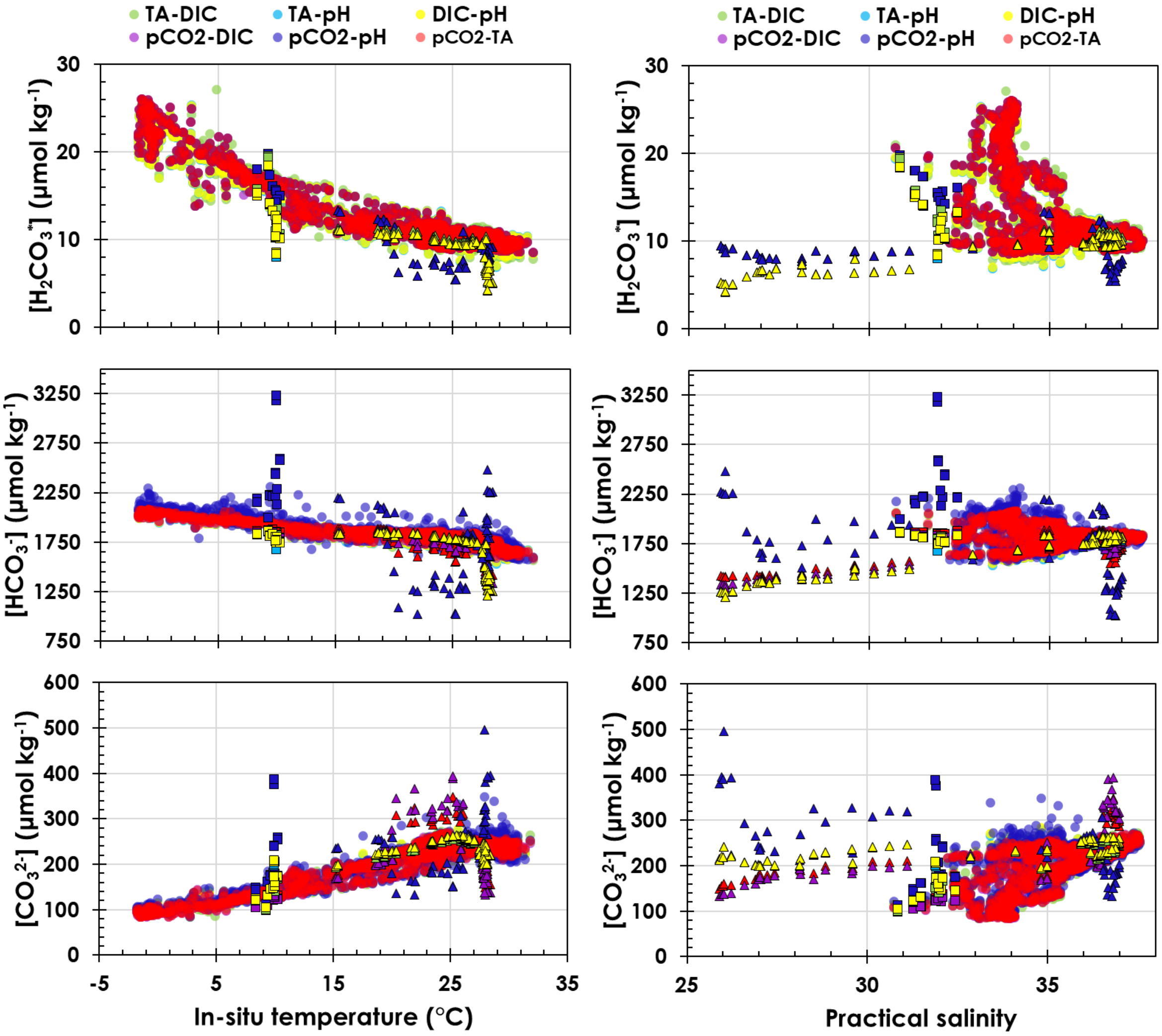

Figure S1. $[H_2CO_3^*]$, $[HCO_3^-]$ *and* $[CO_3^{2-}]$ *as a function of (left) in-situ temperature and (right) practical salinity, as computed with 6 different carbonate system variable pairs: TA-DIC (light green), TA-pH (light blue), DIC-pH (yellow), pCO₂-DIC (purple), pCO₂-pH (dark blue) and pCO₂-TA (red). Circles represents the 948 data points used for our analysis, squares are data from cruise #33AT20120419 (GLODAP code #330) and triangles are data from cruise #49NZ20010828 (GLODAP code #478).*

S4 Alternative iterative procedure

Since there are only two pH-independent parameters (*DIC*, pCO_2), we can use these two parameters and one pH-dependent parameter (either *pH* itself or *CA*) to initialise the iterative procedure. This implies that either K_1^* or K_2^* must be assigned an initial value, before starting the iterations. Here, we present an alternative iterative fitting procedure, in which in situ K_1^* rather than K_2^{*-} was initially set to Lueker et al. (2000). Again, each iteration consisted of four different steps.

(1) First, K_2^* was computed from in situ *DIC*, *CA*, pCO_2 and K_1^* from Lueker et al. (2000) and subsequently fitted (see details in the main text) to a general expression as a function of temperature and salinity of the form:

$$pK_{1\ or\ 2}{}^* = a_1 + a_2 S_P + a_3 S_P{}^2 + \frac{a_4}{T} + a_5 \ln(T) \qquad (S11)$$

where pK_i^* corresponds to $-\log_{10}(K_i)$ and a_i are fitting coefficients determined using nonlinear least-squares estimates (function *nlsLM*).

(2) Second, this new expression for K_2^*, and *CA* and the expression for K_1^* used in step 1 were used to compute *pH* at in situ temperature, see details for this procedure in the main text.

(3) Third, *CA* – that is dependent on *pH* – is updated based on the new $[H^+]$, as per Eq. (6) of the main text and the method outlined for the initial calculation of *CA*.

(4) Fourth, we use Eq. (8) of the main text to calculate K_1^* as a function of pCO_2, *DIC*, and the new *pH* and *CA*, and fit these in-situ computed constants to an equation of the form of Eq. (S11).

These four steps are repeated and at each iteration, K_1^*, *CA*, and *pH* from the previous iteration are used as initial values.

The coefficients a_n for pK_1^* and pK_2^* obtained with this procedure, in an equation of the form of Eq. (S11), and after 30 iterations, are reported in Table S2, along with their respective confidence intervals. In both expressions, all coefficients were significantly different from zero (p values < 0.001).

Table S2. *Coefficients for pK_1^* and pK_2^* using an equation of the form of Eq. (S11), for a situation where K_1^* is initially set to the Lueker et al. (2000) value. Coefficients are given as value ± 95% confidence interval*

	pK_1^*	pK_2^*
a_1	**- 170.233 ± 8.898**	**- 47.191 ± 14.308**
a_2	- 0.011555	- 0.01781
a_3	0.0001152	0.0001122
a_4	**8421.155 ± 388.159**	**3693.155 ± 626.060**
a_5	**25.994 ± 1.333**	**7.768 ± 2.143**

In Fig. S2, we show a comparison of our pK values when K_2^* is initially set to the value of Lueker et al. (2000) (as presented in the main text of this manuscript, see Table 1) with our pK values when K_1^* is initially set to the value of Lueker et al. (2000) (as presented in this section, see Table S2). Regardless of the K value that is initially set to the value of Lueker et al. (2000), both our pK fits are statistically indistinguishable, and higher than the Lueker et al. (2000) values at low temperatures.

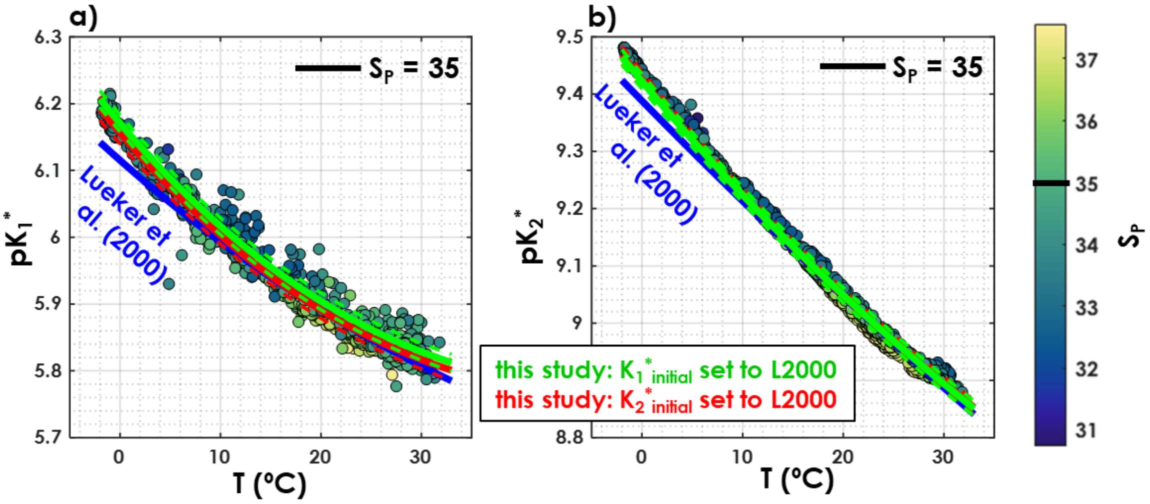

Figure S2. (**a**) *pK_1^* and* (**b**) *pK_2^* as a function of temperature where the colour represents practical salinity (S_P), and the fits are fixed for a S_P of 35. The solid blue line represents the pK^* fits from Lueker et al. (2000), the solid red line the pK^* from this study computed with the coefficients presented in Table 1, the solid green line the pK^* from this study computed with the coefficients presented in Table S2. Dashed lines are overall uncertainties for each of our pK fits, as defined in section 2.4.*

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