argo data management

Processing BGC-Argo pH data at the DAC level
Version 1.2
December 11, 2023

ARGO
part of the integrated global observation strategy

Argo data management
Processing BGC-Argo pH data at the DAC level

Authors: Kenneth S. Johnson, Joshua N. Plant, Tanya L. Maurer, Yuichiro Takeshita

How to cite this document

Kenneth S. Johnson, Joshua N. Plant, Tanya L. Maurer, Yuichiro Takeshita (2023). **Processing BGC-Argo pH data at the DAC level,** https://doi.org/10.13155/57195

Table of contents

History of the document

Version	Date	Authors	Modification
1.0	September 2017	Kenneth S. Johnson, Joshua N. Plant, Tanya L. Maurer	Initial version
1.1	December 2022	Kenneth S. Johnson, Joshua N. Plant, Tanya L. Maurer, Yui Takeshita	Splitting of the initial version into separate processing and QC documents. Incorporation of the GDF sensor type, as well as specification of the temperature coefficient, k2, as a function of pressure.
1.2	December 2023	Kenneth S. Johnson, Joshua N. Plant, Tanya L. Maurer, Yui Takeshita	Small update to the k2(PRES) format specification. v1.1 had an error in the polynomial expansion specification of this calibration term (Eqn 22).

<u>Preamble:</u>

This document was produced in response to action item 21 from the 5th Bio-Argo Data Management meeting in Tianjin, China (Oct., 2016).

"Few would [dispute] that pH is truly a master variable that permeates just about any area of study of living organisms and extends into the physical and chemical world in which living organisms come about, grow, develop, reproduce and die. There is arguably no other master variable that captures the complexities of the interactions between biological, physical and chemical aspects of the world to a similar extent" (Rengel, 2002)

1   Introduction

1.1   A Note on Chemical and Thermodynamic Units

In the text and equations of this document, a variety of concentration units are used to maintain consistency with underlying experimental determinations of required thermodynamic quantities. These units include measurements on the molality scale (mol of solute kg^{-1} solvent, in this case pure water) and the informally named molinity scale (mol of solute kg-seawater^{-1}). There is not consistency in their usage through the seawater thermodynamics that underlie pH measurements so diligence is required to produce a final result which is accurate. The differences in scales are significant and correspond to variations in pH of 0.015. To further compound matters, the pH of seawater can be reported on several scales which are discussed in more detail below.

Additionally, pressure and temperature are used to compute thermodynamic properties that have been fitted to empirical equations. These equations often use different units than reported by Argo floats (i.e. T °K vs T °C and pressure reported in bar vs dbar). Table 1 defines the mapping between Argo physical parameter names and those used in the following document. The usage of the "Document Variables" versus the "Argo Variables" throughout the text minimizes the need for conversion factors within the equations themselves, thus aiding readability. The remainder of this document steps the user through the calculation of pH from Argo profiling float data in a consistent manner, accounting for all of these nuances.

Document Variable	Units	Argo Variable
T	°K	TEMP + 273.15
t	°C	TEMP
S	Practical Salinity	PSAL
P	bar	PRES/10
pH	dimensionless	PH_IN_SITU_TOTAL or PH_IN_SITU_FREE (dependent upon pH scale)

Table 1 Mapping between variable names used in equations and the text, and Argo physical parameter names.

1.2   pH Sensor Theory

Seawater proton concentration is a master variable that controls the air-sea gas exchange of CO_2, the ability of organisms to produce calcium carbonate shells, and that tracks the production and respiration of organic carbon as CO_2 is removed or added to water by biological processes. The proton concentration in seawater [H^+] (mol kg-seawater^{-1}) is typically reported as the pH = -$\log_{10}$ [H^+]. The in situ proton concentration ranges from about 3 to 30 nmol kg-seawater^{-1} (7.5<pH<8.5).

Seawater pH is measured from profiling floats using a Deep-Sea DuraFET pH sensor that is manufactured at MBARI (Johnson et al., 2016) or at Sea-Bird Scientific, named the SeaFET. Note that the MBARI-manufactured sensors can be one of two designs. These are the original Deep-Sea DuraFET described in Johnson et al. (2016) and a new version with improved mechanical seals termed the Gasket DuraFET (GDF). The operating principle and data processing are identical for all of these instruments. The core of each sensor is an Ion Sensitive Field Effect Transistor (ISFET), produced by Honeywell, that responds to proton activity and a Ag/AgCl reference electrode that responds to chloride ion activity. When properly calibrated, the sensor measures the activity of HCl, which is the product of the activities of the two ions $a_{H+} \times a_{Cl-}$ (Martz et al., 2010). These ion concentrations and activities are related through the activity coefficient (γ)

$$a_{H+} \times a_{Cl-} = m_{H+} \times m_{Cl-} \times \gamma_{H+} \times \gamma_{Cl-} = m_{H+} \times m_{Cl-} \times (\gamma_{\pm HCl})^2 \qquad (1)$$

where m signifies molality (mol kg-H_2O^{-1}). The activity coefficient is a thermodynamic property of neutral pairs of ions that can be determined by experiment. The mean activity coefficient of HCl in seawater ($\gamma_{\pm HCl} = (\gamma_{H+} \times \gamma_{Cl-})^{0.5}$) was measured by Khoo et al. (1977) as a function of temperature and salinity at atmospheric pressure.

The Deep-Sea DuraFET sensor is operated in a mode where the potential between the reference electrode and the transistor source of the ISFET (VRS_PH with units of volt) follows the Nernst equation (Martz et al., 2010; Takeshita et al., 2014; Johnson et al., 2016)

$$VRS\_PH = k_{T,P} - R \times T \ln(10)/F \times \log_{10}(a_{H+} \times a_{Cl-})$$

$$= k_{T,P} - R \times T \times \ln(10)/F \times \log_{10}(\gamma_{\pm HCl, T,P})^2 - R \times T \times \ln(10)/F \times \log_{10}(m_{H+} \times m_{Cl-}) \qquad (2)$$

where $k_{T,P}$ (volts) is the reference potential of the sensor at the in situ temperature and pressure, T is the temperature (°K), R is the gas constant (8.31446 J mol^{-1} °K^{-1}), and F is the Faraday constant (96485 Coulombs mol^{-1}). In equation (2), m_{H+} refers to the free protons only and not those bound by sulfate or fluoride ions. The term RT ln(10)/F is termed the Nernst slope. Laboratory experiments have demonstrated that the sensor response follows the Nernst slope with insignificant error from pH 2 to 10 (Takeshita et al., 2014). The mean activity coefficient of HCl is at the temperature and pressure of the measurement. The mapping between variable names used in equation (2), and following, and approved Argo physical parameter names is shown in Table 1.

Several different pH scales are in use for seawater measurements (Marion et al., 2011; Waters and Millero, 2013). As noted above, the Deep-Sea DuraFET responds to the free (unbound by other ions) proton activity and the molality of free protons can be computed from equation (2). However, it is more common in ocean sciences to report pH on the Total Proton scale, which includes binding of protons by the sulfate ion:

$$PH\_IN\_SITU\_TOTAL = -\log_{10}([H^+] + [HSO_4^-]) = -\log_{10}([H^+](1 + S_T / K_S)) =$$

$$PH\_IN\_SITU\_FREE - \log_{10}(1 + S_T / K_S) \qquad (3)$$

where S_T is the total sulfate concentration (mol kg-$seawater^{-1}$) and K_S is the dissociation constant of bisulfate, which is defined as (Dickson, 1990)

$$K_S = [H^+] \times S_T / [HSO_4^-]. \qquad (4)$$

The conversion of pH scales is discussed further in Section 3.

Also, note that there is considerable ambiguity in the literature as to whether the various pH scales are based on proton concentrations in units of molality (m_{H+}, mol kg-H_2O^{-1}) or units of molinity[1] ($[H^+]$, mol kg-$seawater^{-1}$). The concentrations of a species X on these two scales are related by the equation

$$m_X \text{ (mol kg } H_2O^{-1}) = [X] \text{ (mol kg seawater}^{-1}) /(1 - 0.001005 \times S) \qquad (5)$$

where the factor 0.001005 converts the practical salinity value (S, distinguished from the sulfate concentration S_T) to the approximate mass of salt (kg) in one kg of seawater (Dickson et al., 2007). The

---

[1] Note that molinity is not an officially (International Union of Pure and Applied Chemistry/IUPAC) recognized term, but is informally used to specify concentration as mol/kg-solution. These units are frequently used in ocean science and they are the base units used by Clayton and Byrne (1993) and Liu et al. (2011) for spectrophotometric pH measurements used to calibrate the sensors.

difference in concentration scales corresponds to a pH error of 0.015 at salinity 35, which is about double the sensor uncertainty (Johnson et al., 2017; Maurer et al., 2021). Here the practice of Clayton and Byrne (1993), Dickson et al. (2007), and Liu et al. (2011) of using [H^+] (mol kg-seawater^{-1}) for the proton concentration scale is adopted. This differs from the practice of Dickson (1993) or Waters and Millero (2012) to use m_{H+} (mol kg H_2O^{-1}). A careful assessment back through the literature ensures that each of the computations outlined below uses the concentration scale appropriate to the original measurements of each thermodynamic property (e.g., Khoo et al., 1977; Dickson, 1993; Millero, 1983) and pH measurement methods (Clayton and Byrne, 1993; Liu et al., 2011) used to calibrate the sensor (Johnson et al., 2016).

2   Computing pH

Computation of pH from the observed VRS_PH signal requires knowledge of the sensor reference potential at in situ temperature and pressure, the mean activity coefficient at in situ temperature, pressure, and salinity, and the chloride ion molality, which is estimated from salinity. The procedures used to compute the pH are described below. Seawater temperature is required in all of the calculations. As the sensor is in the pumped stream of the CTD, the CTD temperature is used. The MBARI-manufactured sensors do not have an auxiliary temperature sensor. Early Sea-Bird SEAFET sensors carried an auxiliary pH temperature, but that is no longer the case.

The reference potential of the sensor follows the relationship

$$k_{T,P} = k_0 + k_2(PRES) \times t + f(PRES) \tag{6}$$

where t is the temperature (°C) from the CTD (see Table 1), $k_2(PRES)$ is the temperature coefficient that varies slightly over pressure, and f(PRES) is the pressure coefficient and is described as a polynomial function of pressure (up to 12th order). PRES has units of dbar (see Table 1). The function f(PRES) is considered to be temperature independent over the oceanic range (-2 to 35 °C) (Johnson et al., 2016). $k_{T,P}$ is somewhat equivalent to the Standard Potential of a conventional electrochemical cell. Initially, k_2 was considered to be independent of pressure (Johnson et al. 2016), but more recently, several sensors have demonstrated a clear pressure-dependence on k_2. To take this effect into account, $k_2(PRES)$ is parameterized by a 0 to n^{th} order polynomial where 0 order would be a constant value. However, the k_0, $k_2(PRES)$, and f(PRES) values contain terms that are dependent on the ISFET design, semiconductor processing, mechanical design of the ISFET support, and electronic circuit design. As a result, $k_{T,P}$ will be different for every device and each sensor reference potential must be individually calibrated as a function of temperature and pressure. However, once determined, $k_2(PRES)$ and f(PRES) are stable. Any drift in the sensor output is assumed to be attributable to slight shifts in sensor k_0 which can be corrected in situ (see Johnson et al, 2022). So as not to imply that the $k_{T,P}$ is the same for each sensor, it is referred to as a reference potential instead of the Standard Potential, and it is designated with a k, rather than the typical symbol E° for an electrochemical cell. The values for k_0, $k_2(PRES)$, and f(PRES) of each sensor are stored in the pH sensor calibration file with units such that the final computed value of $k_{T,P}$ is in volts.

The mean activity coefficient of HCl in seawater ($\gamma_{\pm HCl}$) is a thermodynamic property of seawater that is a function of temperature, salinity, and pressure. The values at various temperatures and atmospheric pressure, ($\gamma_{\pm HCl}$)$_{T,1}$, were reported by Khoo et al. (1977)

$$\log_{10}(\gamma_{\pm HCl})_{T,1} = -A \times I^{0.5} / (1 + 1.394 \times I^{0.5}) + (0.08885 - 0.000111 \times t) \times I \tag{7}$$

where the subscript T, 1 refers to temperature and a pressure of 1 bar. A is the Debye-Huckel constant and I is seawater ionic strength. Ionic strength of seawater (mol kg-seawater^{-1}) is a function of salinity (Dickson et al., 2007)

$$I = 19.924 \times S / (1000 - 1.005 \times S). \tag{8}$$

The Debye-Huckel constant is a function of pure water density and dielectric constant. The values reported in Table 2 of Khoo et al. (1977) were fitted to the empirical function

$$A = 3.4286 \times 10^{-6} \times t^2 + 6.7524 \times 10^{-4} \times t + 0.49172143. \tag{9}$$

The activity coefficient is also a function of pressure as required by the Gibbs-Duhem equation

$$\log_{10}(\gamma_{\pm HCl}{}^2)_{T,P} = \log_{10}(\gamma_{\pm HCl}{}^2)_{T,1} + \triangledown\!\star_{Cl^-} \times P / (RT \ln 10) / 10 \tag{10}$$

where P is the pressure (bar) and $\Delta\underline{V}_{Cl^-}$ is the partial molar volume of HCl in seawater (Millero, 1983)

$$\triangledown\!\star_{Cl^-} (cm^3\ mol^{-1}) = 17.85 + 0.1044 \times t - 0.001316 \times t^2. \tag{11}$$

The factor 10 on the right hand side of equation (10) is required for the combined conversion of units in cm^3 to m^3 and bar to pascal. Note that, by convention, the proton has a partial molar volume of zero. A compressibility term would normally be added to the partial molar volume, but it has no significant impact at the 2000 dbar maximum depth of a profiling float.

The chloride ion molality required in equation (2) can be computed from salinity (Dickson et al., 2007)

$$m_{Cl^-} (mol\ kg\ H_2O^{-1}) = 0.99889 / 35.453 \times S / 1.80655 / (1 - 0.001005 \times S)$$

$$= 0.015596 \times S / (1 - 0.001005 \times S). \tag{12}$$

The molality of protons is then computed by rearranging equation (2) and substitution of equations (6) and (10)

$$-\log_{10}(m_{H^+}) = (VRS\_PH - k_0 - k_2(PRES) \times t - f(PRES)) \times F / (RT \ln(10)) + \log_{10}(m_{Cl^-}) +$$
$$\log_{10}(\gamma_{\pm HCl}{}^2)_{T,1} + \triangledown\!\star_{Cl^-} \times P / (RT \ln 10) / 10. \tag{13}$$

where, as mentioned in Section 1.2, F is the Faraday constant (96485 Coulombs mol^{-1}) and R is the universal gas constant (8.31446 J mol^{-1} $°K^{-1}$). The proton concentration obtained in this manner has units of molality, mol per kg-H_2O. Seawater pH is reported with units of mol kg-seawater^{-1}. Thus, this requires one additional conversion to obtain the pH of seawater on the Free proton scale

$$PH\_IN\_SITU\_FREE = -\log_{10}([H^+]) = -\log_{10}(m_{H^+}) - \log_{10}(1 - 0.001005 \times S) \tag{14}$$

where $[H^+]$ signifies mol kg-seawater^{-1}.

3 Conversion of pH scales

As noted above, the Deep-Sea DuraFET responds to the free ion concentration, but it is common practice to convert these measurements to the total proton concentration using equation (3). The conversion requires the total sulfate concentration, S_T, (mol kg-seawater^{-1}), which can be computed (Dickson et al., 2007)

$$S_T = (0.1400 / 96.062) \times S / 1.80655 = 2.3049 \times 10^{-4} \times S. \tag{15}$$

The bisulfate dissociation constant has been measured at atmospheric pressure (or summarized) in a number of studies (Khoo et al., 1977; Dickson et al., 1990; Campbell et al., 1993; Waters and Millero,

2012). Here, the equation reported by Dickson et al. (2007) is used for consistency with data sets such as GLODAPv2, but note that other alternatives are available

$$K_{S\,1} = \exp(-4276.1 / T + 141.328 - 23.093 \times \ln(T) +$$

$$(-13856 / T + 324.57 - 47.986 \times \ln(T)) \times I^{0.5} +$$

$$(35474 / T - 771.54 + 114.723 \times \ln(T)) \times I -$$

$$2698 / T \times I^{1.5} + 1776 / T \times I^2 + \ln(1 - 0.001005 \times S)). \tag{16}$$

The equilibrium constant is a function of pressure, as well. Correction for pressure requires the change in partial molar volume for the dissociation reaction. The partial molar volume of HSO_4^- has been measured in pure water, but the value in seawater has not been measured. Its value was estimated by Millero (1983) using the pure water value and the assumption that the effect of sea salt was the same as that found for HCO_3^-. The partial molar volume in seawater is then

$$\triangledown\!\star_{HSO4}\ (cm^3\ mol^{-1}) = -18.03 + 0.0466 \times t + 0.000316 \times t^2 \tag{17}$$

with a compressibility of

$$\kappa_{HSO4} = (-4.53 + 0.09 \times t) / 1000. \tag{18}$$

These terms are used to compute the ratio of K_S at in situ pressure to the value and atmospheric pressure

$$\ln (K_{S\,P}/K_{S\,1}) = (-\triangledown\!\star_{HSO4} + 0.5 \times \kappa_{HSO4} \times P) \times P / (R \times T \times 10). \tag{19}$$

The in situ equilibrium constant is then obtained from the ratio and the one atmosphere value. Finally, the pH on the Total Proton scale can be computed as

$$PH\_IN\_SITU\_TOTAL = PH\_IN\_SITU\_FREE - \log_{10} (1 + S_T / K_{S\,P}). \tag{20}$$

The total proton scale is used throughout the remainder of this document.

4 pH calibration file

The pH calibration sheet (example shown in Figure 1) supplies values for k_0, $k_2(PRES)$, and f(PRES). f(PRES) is a polynomial in pressure , ie

$$f(PRES) = f_1 \times (PRES) + f_2 \times (PRES)^2 \ldots + f_n \times (PRES)^n \tag{21}$$

The polynomial order for f(PRES) will vary depending on the sensor type. The f(PRES) from Sea-Bird Scientific may consist of a fourth order (as in Figure 1) or higher order polynomial, while MBARI-calibrated DuraFET sensors usually use a sixth to eighth order polynomial as in equation 21. Note that the f_0 coefficient on the Sea-Bird example calibration sheet is not used. Additionally, for newer Sea-Bird Scientific sensors, as well as the MBARI-manufactured GDF sensors, the temperature response, $k_2(PRES)$ of the sensor can be a polynomial function of pressure (in dbar) with polynomial order >= 0 (0 = constant value), ie

$$k_2 = k2_{f0} + k2_{f1} \times (PRES) + k2_{f2} \times (PRES)^2 \ldots + k2_{fn} \times (PRES)^n \tag{22}$$

SEA·BIRD
SCIENTIFIC

Sea-Bird Scientific
13431 NE 20th Street
Bellevue, WA 98005 USA

Phone: +1 425-643-9866
Fax: +1 425-643-9954
E-mail: seabird@seabird.com

SBS ISFET PH CALIBRATION SHEET

Date: July 07 2023

CTD Serial Number: 17682

FET Serial Number: 11764

REF Serial Number: 11773

K0 Calibration Date: June 14, 2022

f(P), Maximum 6th Order Polynomial (Ascending)
f0 = -1.3189
f1 = -8.453e-06
f2 = 6.5885e-08
f3 = -1.1179e-10
f4 = 8.713e-14
f5 = -3.2423e-17
f6 = 4.6608e-21
* f0 is not used in pH calculations.

K0, Constant
K0 = -1.3219590000228736

K2(P), Constant
K2f0 = -0.00086825

K2(P), 3rd Order Polynomial (Optional)
K2f0 = -0.00086825
K2f1 = 1.6881e-08
K2f2 = -2.9158e-11
K2f3 = 8.6709e-15

Figure 1. Example of pH calibration file from Seabird Scientific for NAVIS float 1473 (WMO 2903465). **NOTE: the f0 coefficient reported for f(PRES) is not used in the pH calculation**

5 Sensor, parameter and calibration metadata

Sensor, parameter and calibration metadata are summarized in Tables 2 - 4. Note that the intermediate parameters, IB_PH, IK_PH and VK_PH, are sensor diagnostic variables that represent the base current, counter electrode current, and counter electrode voltage, respectively, of the pH sensor. They are not used in the computation of pH.

Table 2. Sensor metadata.

SENSOR	TRANSISTOR_PH
SENSOR_MAKER	(a) MBARI (b) SBE
SENSOR_MODEL	(a) DURA or GDF (b) SEAFET
SENSOR_SERIAL_NO	To be filled

Table 3. Parameter metadata. Note, b-parameters are in bold. All other parameters are ib-parameters.

PARAMETER	PH_IN_SITU_TOTAL
PARAMETER_UNITS	**dimensionless**
PARAMETER_ACCURACY	**0.05**
PARAMETER_RESOLUTION	**0.0004**
PARAMETER	PH_IN_SITU_FREE
PARAMETER_UNITS	dimensionless
PARAMETER_ACCURACY	0.05
PARAMETER_RESOLUTION	0.0004
PARAMETER	VRS_PH
PARAMETER_UNITS	volt
PARAMETER_ACCURACY	0.000030
PARAMETER_RESOLUTION	0.000001
PARAMETER	PH_IN_SITU_SEAWATER
PARAMETER_UNITS	dimensionless
PARAMETER_ACCURACY	
PARAMETER_RESOLUTION	
PARAMETER	IB_PH
PARAMETER_UNITS	nanoampere
PARAMETER_ACCURACY	
PARAMETER_RESOLUTION	
PARAMETER	IK_PH
PARAMETER_UNITS	nanoampere
PARAMETER_ACCURACY	
PARAMETER_RESOLUTION	
PARAMETER	VK_PH
PARAMETER_UNITS	volt
PARAMETER_ACCURACY	
PARAMETER_RESOLUTION	
PARAMETER	TEMP_PH
PARAMETER_UNITS	degrees C
PARAMETER_ACCURACY	
PARAMETER_RESOLUTION	
PARAMETER	NB_SAMPLE_SFET
PARAMETER_UNITS	dimensionless
PARAMETER_ACCURACY	
PARAMETER_RESOLUTION	

Table 4. Calibration metadata. Note, b-parameters are listed in bold.

PARAMETER	PH_IN_SITU_TOTAL
PREDEPLOYMENT_CALIB_EQUATION	**Stotal=(0.14/96.062)*(PSAL/1.80655); Tk=273.15+TEMP; IonS=19.924*PSAL/(1000-1.005*PSAL); Khso4=exp(-4276.1/Tk+141.328-23.093*ln(Tk)+(-13856/Tk+324.57-47.986*ln(Tk))*IonS^0.5+(35474/Tk-771.54+114.723*ln(Tk))*IonS-2698/Tk*IonS^1.5+1776/Tk*IonS^2+ln(1-0.001005*PSAL)); deltaVHSO4=-18.03+0.0466*TEMP+0.000316*TEMP^2; KappaHSO4=(-4.53+0.09*TEMP)/1000; lnKhso4fac=(-deltaVHSO4+0.5*KappaHSO4*(PRES/10))*(PRES/10)/(R*10*Tk); Khso4TPS=Khso4*exp(lnKhso4fac); PH_IN_SITU_TOTAL=PH_IN_SITU_FREE-log10(1+Stotal/Khso4TPS)**
PREDEPLOYMENT_CALIB_COEFFICIENT	**R=8.31446**
PREDEPLOYMENT_CALIB_COMMENT	
PARAMETER	PH_IN_SITU_FREE
PREDEPLOYMENT_CALIB_EQUATION	k2cor=k2f0+k2f1*PRES+k2f2*PRES^2+k2f3*PRES^3;k0T=k0+k2cor*TEMP; pcorr=f1*PRES+f2*PRES^2+f3*PRES^3+f4*PRES^4+f5*PRES^5+f6*PRES^6+f7*PRES^7+f8*PRES^8+f9*PRES^9+f10*PRES^10+f11*PRES^11+f12*PRES^12; k0TP=k0T+pcorr; Tk=273.15+TEMP; Cltotal=(0.99889/35.453*PSAL/1.80655)/(1-0.001005*PSAL); ADH=3.4286e-6*TEMP^2+6.7524e-4*TEMP+0.49172143; IonS=19.924*PSAL/(1000-1.005*PSAL); log10gammaHCl=[-ADH*sqrt(IonS)/(1+1.394*sqrt(IonS))]+[(0.08885-0.000111*TEMP)*IonS]; deltaVHCl=17.85+0.1044*TEMP-0.001316*TEMP^2; log10gammaHCLtP=log10gammaHCl+[deltaVHCl*(PRES/10)/(R*Tk*ln(10))/2/10]; PH_IN_SITU_FREE=[(VRS_PH-k0TP)/(R*Tk/F*ln(10))]+[ln(Cltotal)/ln(10)]+2*log10gammaHCLtP-log10(1-0.001005*PSAL)
PREDEPLOYMENT_CALIB_COEFFICIENT	R=8.31446; F=96485; k2f0=-0.00091091, k2f1=-4.412e-08, k2f2=1.6691e-11, k2f3=-1.025e-15; k0=-1.3026; f1=9.77204e-06, f2=4.11226e-08, f3=-2.1644e-10, f4=4.68831e-13, f5=-5.73612e-16, f6=4.21598e-19, f7=-1.842e-22, f8=4.40703e-26, f9=-4.44504e-30, f10=0, f11=0, f12=0
PREDEPLOYMENT_CALIB_COMMENT	Voltage difference between reference and source from pH sensor (in volt).
PARAMETER	VRS_PH
PREDEPLOYMENT_CALIB_EQUATION	

PREDEPLOYMENT_CALIB_COEFFICIENT	
PREDEPLOYMENT_CALIB_COMMENT	Voltage difference between reference and source from pH sensor (in volt).
PARAMETER	VK_PH
PREDEPLOYMENT_CALIB_EQUATION	
PREDEPLOYMENT_CALIB_COEFFICIENT	
PREDEPLOYMENT_CALIB_COMMENT	Counter electrode voltage of pH sensor (in volt).
PARAMETER	IK_PH
PREDEPLOYMENT_CALIB_EQUATION	
PREDEPLOYMENT_CALIB_COEFFICIENT	
PREDEPLOYMENT_CALIB_COMMENT	Counter electrode current of pH sensor (in nanoampere).
PARAMETER	IB_PH
PREDEPLOYMENT_CALIB_EQUATION	
PREDEPLOYMENT_CALIB_COEFFICIENT	
PREDEPLOYMENT_CALIB_COMMENT	Base current of pH sensor (in nanoampere).
PARAMETER	NB_SAMPLE_SFET
PREDEPLOYMENT_CALIB_EQUATION	
PREDEPLOYMENT_CALIB_COEFFICIENT	
PREDEPLOYMENT_CALIB_COMMENT	

6   Matlab code to compute pH

The function phcalc was used to produce the pH data shown in Table 5.

```
function [phfree,phtot]= phcalc(Vrs, Press, Temp, Salt, k0, k2, Pcoefs)
%
% INPUTS:
%   Vrs    = Voltage bewteen reference electrode and ISFET source
%   Press  = Pressures in decibars
%   Temp   = Temperature in degrees C
%   Salt   = Salinity (usually CTD salinity on the PSS)
%   k0     = Sensor reference potential (intercept at Temp = 0C)
%   k2     = constant or pressure dependant temperature response (slope)
%   Pcoefs = sensor dependent pressure coefficients


%*******************************************************************
% Check k2 dimensions
%*******************************************************************

if max(size(k2)) > 1
   disp('K2 input has pressure dependent terms!')
end

% *******************************************************************
%  SET SOME CONSTANTS
```

% ***

%Universal gas constant, (R) , http://physics.nist.gov/cgi-bin/cuu/Value?r
R   = 8.31446; % J/(mol K)
F   = 96485; %Faraday constant Coulomb / mol
Tk   = 273.15 + Temp; % degrees Kelvin
ln10 = log(10); % natural log of 10

% ***
% CALCULATE PHYSICAL AND THERMODYNAMIC DATA
% Dickson, A. G., Sabine, C. L., & Christian, J. R. (2007). Guide to best
% practices for ocean CO2 measurements.
% ***

% IONIC STRENGTH OF SEAWATER (mol / kg H2O)
% Varified units by comparing to Dickson et al. 2007: Chap 5, p10 Table 2
% Dickson et al. 2007: Chap 5, p13 Eq 34
IonS = 19.924 .* Salt ./ (1000 - 1.005 * Salt);

% MEAN SEAWATER SULFATE CONCENTRATION (mol / kg solution)
% This wants to be mol/kg-seawater as KHSO4 is on that scale
% Dickson et al. 2007: Chap 5, p10 Table 2
Stotal = (0.14 / 96.062) .* (Salt / 1.80655);

% MEAN SEAWATER CHLORIDE CONCENTRATION (mol / kg H20)
% this wants to be mol/kg H2O as activity is on mol/kg H2O scale
% Dickson et al. 2007: Chap 5, p10 Table 2
Cltotal = 0.99889 / 35.453 .* Salt / 1.80655; %(mol / kg solution)
Cltotal = Cltotal ./(1 - 0.001005 .* Salt); % (mol / kg H20)

% BISULFIDE DISSCIATION CONSTANT AT T,S AND IONIC STRENGTH(mol/kg solution)
% Dickson et al. 2007: Chap 5, p12 Eq 33
Khso4 = exp(-4276.1 ./ Tk + 141.328 - 23.093 .* log(Tk) + ...
    (-13856 ./ Tk + 324.57 - 47.986 .* log(Tk)) .* IonS .^ 0.5 + ...
    (35474 ./ Tk - 771.54 + 114.723 .* log(Tk)) .* IonS - ...
    2698 ./ Tk .* IonS .^ 1.5 + 1776 ./ Tk .* IonS .^ 2 + ...
    log(1 - 0.001005 .* Salt));

% Millero 1983 Chemical Oceanography vol 8
% partial molar volume and compressibility of HSO4 in seawater.
deltaVHSO4 = -18.03 + 0.0466 .* Temp + 0.000316 .* Temp .^ 2;
KappaHSO4 = (-4.53 + 0.09 .* Temp) / 1000;

%%%%%% Press changed from dbar to bar here by / 10
lnKhso4fac = (-deltaVHSO4 + 0.5 .* KappaHSO4 .* (Press / 10)) .* ...
        (Press / 10) ./ (R * 10 .* Tk);

% bisulfate association constant at T, S, P
Khso4TPS = Khso4 .* exp(lnKhso4fac);

% GAMMA +/- HCl, activity coefficient of HCl at T/S, P=1
% ADH is the Debye Huckel constant, calcualted as a polynomial
% fit to data in Khoo et al. 1977, doi:10.1021/ac50009a016
% See Martz et al. 2010, DOI 10.4319/lom.2010.8.172, p175
% Typo in paper 2nd term should be e-4 not e-6

```
%
ADH = (3.4286e-6 .* Temp .^ 2 + 6.7524e-4 .* Temp + 0.49172143);

log10gammaHCl = -ADH .* sqrt(IonS) ./ (1 + 1.394 .* sqrt(IonS)) + ...
         (0.08885 - 0.000111 .* Temp) .* IonS;
% Millero 1983 partial molar volume of HCl in seawater
deltaVHCl = 17.85 + 0.1044 .* Temp - 0.001316 .* Temp .^ 2;
```

% Effect of pressure on activity coefficient of HCl. %(Divide by 10 for units in the cm3 to F
% conversion. Additionally, the last term is divided by 2 following application of the power rule of
logs for the gammaHCL terms as listed in equation 10 of the Argo processing document.)

```
log10gammaHCLtP = log10gammaHCl + deltaVHCl.*(Press./10)./(R.*Tk.*ln10)./2./10;
```

%   Sensor reference potential

```
% *************************************************************************
% CHECK SIZE OF K2 VARIABLE
if max(size(k2)) == 1
   k0T = k0 + k2 * Temp; % Temp  in deg C
elseif max(size(k2)) > 1 % polynomial pressure dependance
%    k2pc = [flipud(Pcoefs);0]; TM: This was applying f(PRES) Pcoefs instead of k2??
   k2pc = [flipud(k2)];
   k0T  = k0 + polyval(k2pc,Press) .* Temp;
else
   disp('Max size should be >= 1 : Check k2 input!')
   return
end

% CALCULATE PRESSURE CORRECTION (POLYNOMIAL FUNCTION OF PRESSURE)
% ALL SENSORS HAVE A PRESSURE RESPONSE WHICH IS DETERMINED IN THE LAB
% AND CONTAINED IN THE POLYNOMIAL Pcoefs
pc   = [flipud(Pcoefs);0]; % Matlab wants descending powers & n+1 (add 0)
pcorr = polyval(pc,Press);
k0TP  = k0T + pcorr;


% pH on free scale then corrected to get to pH total on mol/kg-seawater scale
%    pHinsituFree = (Vrs - k0TP) / (R * Tk / F * ln10) + ...
%            log(Cltotal) / ln10 + 2 * log10gammaHCLtP
% this will be mol kg H2O  need to convert to mol/kg-seawater
phfree = (Vrs - k0TP) ./ (R .* Tk ./ F .* ln10) + ...
   log(Cltotal) ./ ln10 + 2 * log10gammaHCLtP; %mol/kg-H2O scale

% CONVERT TO mol/kg-seawater scale - JP 2/4/16
phfree = phfree - log10(1 - 0.001005 .* Salt); %mol/kg-seawater scale

% convert to total proton scale
phtot = phfree - log10(1 + Stotal ./ Khso4TPS);
%%%%%%%%%%%%%%%%%%%%%%%%%%%%


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
```

6.1 Check Values

Table 5 contains a test data set that was computed with the Matlab function pHcalc.m (Section 6). It lists the sensor calibration coefficients and a vertical profile of PRES/TEMP/PSAL values, the sensor VRS_PH, and the computed pH values at in situ conditions on the free and total proton scales (PH_IN_SITU_FREE, PH_IN_SITU_TOTAL).

Table 5. Check data for the calculation of pH. This data is from NAVIS float 1473 (WMO 2903465) and is a subsample of the values collected on cycle 4. Note that f(PRES) was fit to a 6th order polynomial and that k2(PRES) is a 3rd order polynomial in this example.

Calibration data					
k0		k2f0	k2f1	k2f2	k2f3
-1.321959		-0.0008682	1.6881e-08	-2.9158e-11	8.6709e-15
f1	f2	f3	f4	f5	f6
-8.453e-06	6.5885e-08	-1.1179e-10	8.713e-14	-3.2423e-17	4.6608e-21

Profile data					
PRES	TEMP	PSAL	VRS_PH	PH_INSITU_FREE	PH_IN_SITU_TOTAL
2.2	29.545	34.637	-0.82966	8.1104	7.9870
42.0	29.607	34.767	-0.83049	8.1022	7.9788
82.0	25.741	35.104	-0.83921	8.0204	7.9105
122.0	21.094	35.080	-0.85150	7.8788	7.7846
162.0	15.725	34.886	-0.85968	7.8102	7.7326
202.0	13.407	34.890	-0.86191	7.8016	7.7307
242.0	12.189	34.927	-0.86345	7.7884	7.7209
282.0	11.557	34.964	-0.86219	7.8157	7.7500
322.0	11.056	34.947	-0.86135	7.8326	7.7685
362.0	10.693	34.933	-0.86118	7.8357	7.7726
402.0	10.359	34.904	-0.86148	7.8297	7.7676
442.0	9.851	34.873	-0.86194	7.8235	7.7629
482.0	9.469	34.856	-0.86244	7.8155	7.7560
522.0	9.181	34.849	-0.86344	7.7976	7.7389
562.0	8.914	34.848	-0.86365	7.7939	7.7361
602.0	8.573	34.843	-0.86447	7.7808	7.7240
642.0	8.268	34.835	-0.86530	7.7674	7.7114
682.0	8.006	34.832	-0.86585	7.7589	7.7037
722.0	7.771	34.831	-0.86649	7.7488	7.6943
762.0	7.445	34.821	-0.86675	7.7472	7.6935
802.0	7.238	34.822	-0.86659	7.7518	7.6987
842.0	6.885	34.812	-0.86656	7.7564	7.7043
882.0	6.678	34.813	-0.86668	7.7566	7.7050
922.0	6.378	34.798	-0.86662	7.7612	7.7105
962.0	6.143	34.795	-0.86663	7.7639	7.7139

7 References

Campbell, D.M., Millero, F.J., Roy, R., Roy, L., Lawson, M., Vogel, K.M., Porter Moore, C., 1993. The standard potential for the hydrogen–silver, silver chloride electrode in synthetic seawater. Marine Chemistry, 44, 221–233.

Clayton, T. D. and R. H. Byrne. 1993. Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. Deep Sea Research, Part I, 40, 2115-2129.

Dickson, A. G. 1990. Standard potential of the reaction: $AgCl(s) + ½ H_2(g) = Ag(s) + HCl(aq)$, and the standard acidity constant of the ion HSO_4- in synthetic sea water from 273.15 to 318.15 K. Journal of Chemical Thermodynamics, 22, 113-127.

Dickson, A. G. 1993. The measurement of seawater pH. Marine Chemistry, 44, 131-142.

Dickson, A. G., C. L. Sabine, and J. R. Christian. 2007. Guide to best practices for ocean CO_2 measurements, PICES Special Publication 3 IOCCP Report No. 8. 191.

Johnson, Kenneth S., Hans. W. Jannasch, Luke J. Coletti, Virginia A. Elrod, Todd R. Martz, Yuichiro Takeshita, Robert J. Carlson, James G. Connery. 2016. Deep-Sea DuraFET: A pressure tolerant pH sensor designed for global sensor networks. Analytical Chemistry. 88, 3249-3256, DOI: 10.1021/acs.analchem.5b04653.

Johnson, K. S., J. N. Plant, L. J. Coletti, H. W. Jannasch, C. M. Sakamoto, S. C. Riser, D. D. Swift, N. L. Williams, E. Boss, N. Haëntjens, L. D. Talley, J. L Sarmiento. 2017. Biogeochemical sensor performance in the SOCCOM profiling float array. Journal of Geophysical Research Oceans, 122, doi:10.1002/2017JC012838.

Khoo, K. H.; Ramette, R. W.; Culberson, C. H.; Bates, R. G. 1977. Determination of Hydrogen Ion Concentrations in Seawater from 5 to 40 °C: Standard Potentials at Salinities from 20 to 45‰. Analytical Chemistry, 49, 29-34.

Liu, X.; Patsavas, M. C.; Byrne, R. H. 2011. Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements *Environ. Sci. Technol.* 45 (11) 4862– 4868 DOI: 10.1021/es200665d.

Marion, G. M., F. J. Millero, M. F. Camões, P. Spitzer, R. Feistel, and C.-T. A. Chen. 2011. pH of seawater. Marine Chemistry, 126, 89-96.

Martz, T. R., J. G. Connery and K. S. Johnson. 2010. Testing the Honeywell Durafet® for seawater pH applications. Limnology and Oceanography: Methods, 8, 172-184.

Maurer, T. L., Plant, J. N. and K. S. Johnson, K. S. 2021. Delayed-mode quality control of oxygen, nitrate, and pH data on SOCCOM biogeochemical profiling floats. Frontiers in Marine Science, 8, 683207. https://doi.org/10.3389/fmars.2021.683207

Millero, F. J. 1983. The influence of pressure on chemical processes in the sea. In, Chemical Oceanography, vol. 8, J.P. Riley and R. Chester (eds.), AcademicPress, pp. 1-88.

Rengel, Z. ed., 2002. Handbook of Plant Growth: pH as the Master Variable (Vol. 88). CRC Press, pp. iii.

Takeshita, Yuichiro, Todd R. Martz, Kenneth S. Johnson and Andrew G. Dickson. 2014. Characterization of an Ion Sensitive Field Effect Transistor and chloride ion selective electrodes for ph measurements in seawater. Analytical Chemistry, dx.doi.org/10.1021/ac502631z.

Waters, J. F., and F. J. Millero 2013. The free proton concentration scale for seawater pH. Marine Chemistry, 49, 8-22, http://dx.doi.org/10.1016/j.marchem.2012.11.003