

Calculating pH from ISFET pH Sensors

SeaFET V2, Shallow SeapHOx V2, Deep SeapHOx V2

Calculating ISFET pH

This application note provides formulas to calculate pH_{Total} from raw ISFET voltage ($V_{FET/REF}$) and CTD data. Formulas for calculating pH Internal and pH External from a Shallow SeaFET/SeapHOx V2, and pH External from a Deep SeapHOx V2 are listed below. More details can be found in the references cited.

Calculating pH Internal from the Shallow SeaFET/SeapHOx V2

The internal electrolyte gel electrochemical cell exhibits a Nernstian response to pH and has a negligible response to the chloride activity (Martz et al. 2010). Then

$$pH_{INT\ Cell} = \frac{V_{INT\ REF} - k_{0\ INT} - k_{2\ INT} * t}{S_{nernst}}$$

Calculating pH External from the Shallow SeaFET/SeapHOx V2

The solid state electrochemical cell exhibits a Nernstian response to pH but presents the added complexity of being sensitive to the chloride activity (Johnson et al. 2016). Then:

$$pH_{EXT\ Cell} = \frac{V_{EXT\ REF} - k_{0\ EXT} - k_{2\ EXT} * t}{S_{nernst}} + \log(Cl_T) + 2 * \log(\gamma_{HCl})_T - \log\left(1 + \frac{S_T}{K_S}\right) - \log\left(\frac{1000 - 1.005 * S}{1000}\right)$$

Where,

$$S_{nernst} = \frac{R * T * \ln(10)}{F}$$

Where,

- $V_{INT\ REF}$ and $V_{EXT\ REF}$ are the raw voltages from the internal cell and external cell, respectively
- $k_{0\ INT}$ and $k_{0\ EXT}$ are the cell standard potential offset for the internal reference and external reference, respectively
- $k_{2\ INT}$ and $k_{2\ EXT}$ are the temperature slope coefficient for the internal reference and external reference, respectively
- t is the temperature in °C
- R is the universal gas constant (8.3144621 J / (K mol))
- T is the temperature in K
- S is the Salinity in psu
- F is the Faraday constant (96485.365 C/mol)

Note: k_0 and k_2 are provided as part of the instrument calibration. The remaining derivation of pH involves salinity and temperature to derive the following:

- Cl_T is Total Chloride
- $\gamma_{\pm HCl}$ is the HCl activity coefficient
- S_T is Total Sulfate
- K_s is the Acid Dissociation Constant of HSO_4^-

These are outlined below.

Total chloride in seawater

Calculated as (Dickson et al. 2007):

$$Cl_T = \frac{0.99889}{35.453} * \frac{S}{1.80655} * \frac{1000}{1000 - 1.005 * S}$$

where S is salinity in psu.

Sample Ionic Strength

The sample ionic strength is calculated as (Dickson et al. 2007):

$$I = \frac{19.924 * S}{1000 - 1.005 * S}$$

where S is salinity in psu.

Debye-Huckel constant for activity of HCl

This constant is calculated as (Khoo et al. 1977):

$$A_{DH} = 0.0000034286 * t^2 + 0.00067524 * t + 0.49172143$$

where t is temperature in °C.

Logarithm of HCl activity coefficient

Calculated as (Khoo et al. 1977):

$$\log(\gamma_{\pm HCl})_T = \frac{-A_{DH} * \sqrt{I}}{1 + 1.394 * \sqrt{I}} + (0.08885 - 0.000111 * t) * I$$

where A_{DH} is the Debye-Huckel constant for activity of HCl, I is the ionic strength, and t is the temperature in °C.

Total sulfate in seawater

Calculated as (Dickson et al. 2007):

$$S_T = \frac{0.1400}{96.062} * \frac{S}{1.80655}$$

where S is salinity in psu.

Acid dissociation constant of HSO_4^-

Calculated as (Dickson et al. 2007):

$$K_s = (1 - 0.001005 * S) * e^{\frac{-4276.1}{T} + 141.328 - 23.093 * \ln(T) + \left(\frac{-13856}{T} + 324.57 - 47.986 * \ln(T)\right) * \sqrt{I} + \left(\frac{35474}{T} - 771.54 + 114.723 * \ln(T)\right) * I - \left(\frac{2698}{T}\right) * I^{1.5} + \left(\frac{1776}{T}\right) * I^2}$$

where S is salinity in psu, T is temperature in K, and I is the ionic strength.

Calculating pH External from the Deep SeapHOx V2

The solid state electrochemical cell exhibits a Nernstian response to pH but presents the added complexity of being sensitive to the chloride activity and pressure (Johnson et al. 2016). Then:

$$pH_{Cell} = \frac{V_{FET/REF} - k_0 - k_2 * t - f(P)}{S_{nernst}} + \log(Cl_T) + 2 * [\log(\gamma_{\pm HCl})_{T\&P}] - \log\left(1 + \frac{S_T}{K_{S,T\&P}}\right) - \log\left(\frac{1000 - 1.005 * S}{1000}\right)$$

Where,

$$S_{nernst} = \frac{R * T * \ln(10)}{F}$$

Where:

- R is the universal gas constant (8.3144621 J / (K mol))
- t is the temperature in °C
- T is the temperature in K
- S is the Salinity in psu
- P is the pressure in dbar
- p is the pressure in bar (*used in formulas below*)
- F is the Faraday constant (96485.365 C/mol)
- The constants k_0 and k_2 are the cell standard potential offset and temperature slope respectively
- $f(P)$ is the sensor pressure response function (6th order polynomial)

$$f(P) = f_1P + f_2P^2 + f_3P^3 + f_4P^4 + f_5P^5 + f_6P^6$$

f_0 is not used in pH calculations because it captured in the k_0 coefficient.

Note: k_0 , k_2 , and $f(P)$ are provided as part of the instrument calibration. The remaining derivation of pH involves salinity, temperature, and pressure to derive the following:

- Cl_T is Total Chloride
- $\gamma_{\pm HCl}$ is the HCl activity coefficient
- S_T is Total Sulfate
- $K_{S,T\&P}$ is the Acid Dissociation Constant of HSO_4^- T&P

Note: the term $[\log(\gamma_{\pm HCl})_{T\&P}]$ in the formula above is a value that represents the logarithm of HCl activity coefficient as a function of temperature and pressure. Do not take the logarithm of this value.

These are outlined below.

Total chloride in seawater

Calculated as (Dickson et al. 2007):

$$Cl_T = \frac{0.99889}{35.453} * \frac{S}{1.80655} * \frac{1000}{1000 - 1.005 * S}$$

Where S is salinity in psu.

Partial Molal Volume of HCl (for $\log(\gamma_{\pm HCl})_{T\&P}$)

Calculated as (Millero 1983):

$$\bar{V}_{HCl} = 17.85 + 0.1044 * t - 0.001316 * t^2$$

Where t is the temperature in °C.

Sample Ionic Strength (for $\log(\gamma_{\pm HCl})_T$)

The sample ionic strength is calculated as (Dickson et al. 2007):

$$I = \frac{19.924 * S}{1000 - 1.005 * S}$$

Where S is salinity in psu.

Debye-Huckel constant for activity of HCl (for $\log(\gamma_{\pm HCl})_T$)

This constant is calculated as (Khoo et al. 1977):

$$A_{DH} = 0.0000034286 * t^2 + 0.00067524 * t + 0.49172143$$

Where t is temperature in °C.

Logarithm of HCl activity coefficient as a function of temperature (for $\log(\gamma_{\pm HCl})_{T\&P}$)

Calculated as (Khoo et al. 1977):

$$\log(\gamma_{\pm HCl})_T = \frac{-A_{DH} * \sqrt{I}}{1 + 1.394 * \sqrt{I}} + (0.08885 - 0.000111 * t) * I$$

Where A_{DH} is the Debye-Huckel constant for activity of HCl, I is the ionic strength, and t is the temperature in °C.

Logarithm of HCl activity coefficient as a function of temperature and pressure

Calculated as (Johnson et al. 2017):

$$\log(\gamma_{\pm HCl})_{T\&P} = \log(\gamma_{\pm HCl})_T + \left(\frac{\bar{V}_{HCl} * p}{\ln(10) RT * 10} \right) / 2$$

Where $\log(\gamma_{\pm HCl})_T$ is the logarithm of HCl activity coefficient as a function of temperature, \bar{V}_{HCl} is partial molal volume of HCl in cm³/mol, T is temperature in K, p is the pressure in bar, and R is the universal gas constant (8.3144621 (m³ Pa)/(K mol)). $\bar{V}_{HCl} * p$ is divided by 10 to convert cm³ to m³ and bar to pascal.

Total sulfate in seawater

Calculated as (Dickson et al. 2007):

$$S_T = \frac{0.1400}{96.062} * \frac{S}{1.80655} \quad V_S = -18.03 + 0.0466 * t + 0.000316 * t^2$$

Where S is salinity in psu.

Acid dissociation constant of HSO_4^- (for $K_{S,T\&P}$)

Calculated as (Dickson et al. 2007):

$$K_S = (1 - 0.001005 * S) * e^{\frac{-4276.1}{T} + 141.328 - 23.093 * \ln(T) + \left(\frac{-13856}{T} + 324.57 - 47.986 * \ln(T)\right) * \sqrt{I} + \left(\frac{35474}{T} - 771.54 + 114.723 * \ln(T)\right) * I - \left(\frac{2698}{T}\right) * I^{1.5} + \left(\frac{1776}{T}\right) * I^2}$$

Where S is salinity in psu, T is temperature in K, and I is the ionic strength.

Partial Molal Volume of HSO_4^- (for $K_{S,T\&P}$)

Calculated as (Millero 1983):

$$\bar{V}_S = -18.03 + 0.0466 * t + 0.000316 * t^2$$

Where t is the temperature in °C.

Compressibility of HSO_4^- (for $K_{S,T\&P}$)

Calculated as (Millero 1983):

$$\bar{K}_S = \frac{(-4.53 + 0.09 * t)}{1000}$$

Where t is the temperature in °C.

Acid dissociation constant of HSO_4^- T&P

Calculated as (Millero 1982):

$$K_{S,T\&P} = K_S * e^{\frac{-\bar{V}_S * p + 0.5 * \bar{K}_S * p^2}{RT * 10}}$$

Where K_S is acid dissociation of HSO_4^- , \bar{K}_S is compressibility of HSO_4^- , \bar{V}_S is partial molal volume of HSO_4^- in cm^3/mol , T is temperature in K, p is the pressure in bar, and R is the universal gas constant ($8.3144621 \text{ (m}^3 \text{ Pa)/(K mol)}$).
 $-\bar{V}_S * p + 0.5 * \bar{K}_S * p^2$ is divided by 10 to convert cm^3 to m^3 and bar to pascal.

Example Values for Shallow SeaFET/SeapH0x V2 Test Calculations

With these test values, you should obtain the following pH values from the equation:

$$pH_{INT} = 7.8310 \text{ and } pH_{EXT} = 7.8454$$

- $R = 8.3144621 \text{ J/(K mol)}$
- $F = 9.6485365 * 10^4 \text{ C/mol}$
- $VIN_{INT \text{ FET/REF}} = -1.010404 \text{ Volts}$
- $VIN_{EXT \text{ FET/REF}} = -0.965858 \text{ Volts}$
- $k_{0 \text{ INT}} = -1.438788$
- $k_{2 \text{ INT}} = -1.304895 * 10^{-3}$
- $k_{0 \text{ EXT}} = -1.429278$
- $k_{2 \text{ EXT}} = -1.142026 * 10^{-3}$
- $t = 15.8735 \text{ }^\circ\text{C}$
- $S = 36.817 \text{ psu}$

Example Values for Deep SeapH0x V2 Test Calculations

With these test values, you should obtain the following pH values from the equation:

$$pH_{total} = 7.9394$$

- $R = 8.3144621 \text{ J/(K mol)}$
- $F = 9.6485365 * 10^4 \text{ C/mol}$
- $V_{FET/REF} = -0.885081 \text{ Volts}$
- $k_0 = -1.361736$
- $k_2 = -1.07686 * 10^{-3}$
- $t = 23.4169 \text{ }^\circ\text{C}$
- $P = 100 \text{ dbar}$
- $S = 34.812 \text{ psu}$
- $f(P) = (-8.31842 * 10^{-6}) \times P + (-7.47152 * 10^{-9}) \times P^2 + (1.91485 * 10^{-11}) \times P^3 + (-1.39273 * 10^{-14}) \times P^4 + (4.48185 * 10^{-18}) \times P^5 + (-5.42588 * 10^{-22}) \times P^6$

References

T. R. Martz, J. G. Connery, K. S. Johnson. Testing the Honeywell Durafet for seawater pH applications. *Limnol. Oceanogr.: Methods*, 8:172-184, 2010.

K. S. Johnson, H. W. Jannasch, L. J. Coletti, V. A. Elrod, T. R. Martz, Y. Takeshita, R. J. Carlson, and J. G. Connery. Deep-Sea DuraFET: A pressure tolerant pH sensor designed for global sensor networks. *Analytical Chemistry*, 88:3249-3256, 2016.

A. G. Dickson, C. L. Sabine, and J. R. Christian. IOCCP Report No. 8, 2007.

K. H. Khoo, R. W. Ramette, C. H. Culberson, and R. G. Bates. Determination of hydrogen ion concentrations in seawater from 5C to 40C: standard potentials at salinities 20 to 45%. *Analytical Chemistry*, 49:29-24, 1977.

F. J. Millero. In *Chemical Oceanography*; Riley, J. P., Chester, R., Eds.; Academic Press: London, 1983; Vol. 8, pp 1–88.

K. S. Johnson, J. N. Plant, T. L. Maurer. Processing BGC-Argo pH data at the DAC level. 2017

F. J. Millero. The effect of pressure on the solubility of minerals in water and seawater. *Geochimica et Cosmochimica Acta*, 46:11-22, 1982.