pH Compensation of Free ISE to Determine Total ISE

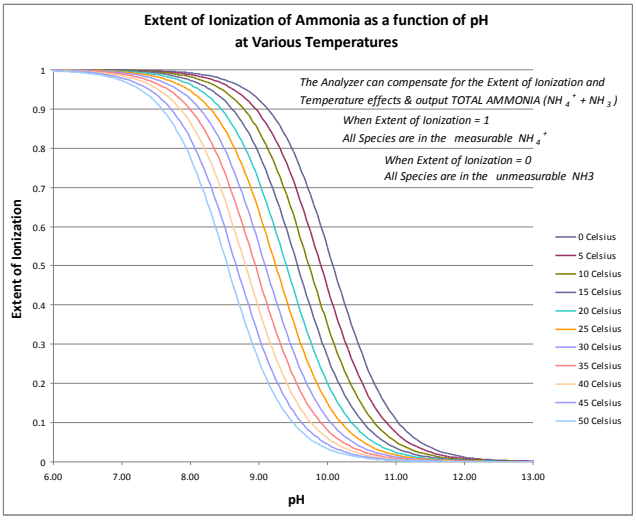
This document will detail the following frequently asked questions about pH compensation of free ISE (such as free ammonia, free fluoride, free cyanide and free sulfide) to find total ISE (total ammonia, total fluoride, total cyanide and total sulfide). The topics that will be discussed below are as follows:

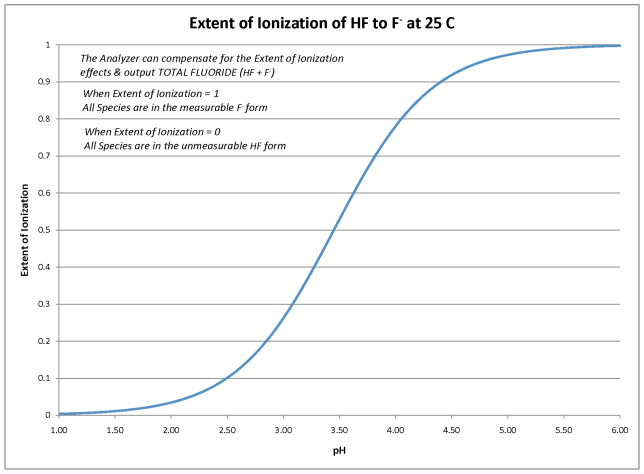
- What is the difference between free ISE and total ISE?
- What exactly does pH compensation do?
- When do I need to perform pH compensation?

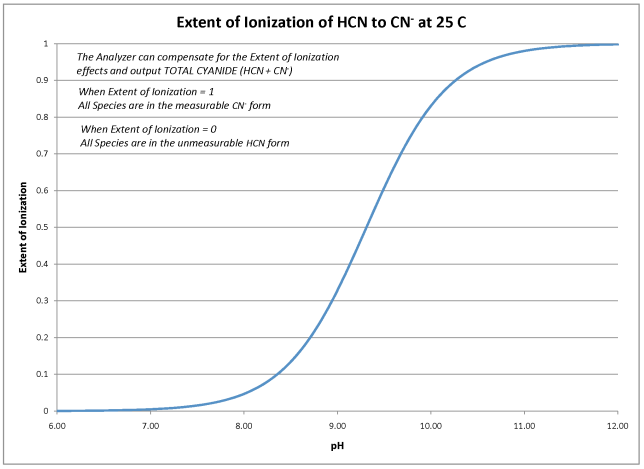
The top graph to the right shows the effects of pH and temperature on the extent of ionization for the weak base, ammonia. The dissolved ammonia gas is converted into the ionized ammonium ion, which is measured by the ISE sensor. The extent of ionization reveals the percent of the weak base which can be measured. When the extent of ionization is 1.00, then 100% is in the measurable form. When the extent of ionization is 0.00, then 0% is in the measurable form. The preconfigured easy to use 3TX-TOT module is able to compute, display and transmit what would be 100% of the weak acid or base activity, even if only a small fraction is actually in the measurable form.

The bottom graphs to the right show the impact of pH on the extent of ionization of various weak acids as a function of pH. Unlike the top graph on the right for the conversion of the weak base ammonia to ammonium ion as function of pH shown at various temperatures, the two bottom graphs to the right are shown at a single temperature for a more simple visualization of these effects at the common 25 degrees Celsius condition. As short explanation of the chemistry behind the pH compensation to compute total ISE is below to understand the conditions under which such pH compensation should be performed to obtain the total system ISE as a real-time process parameter.

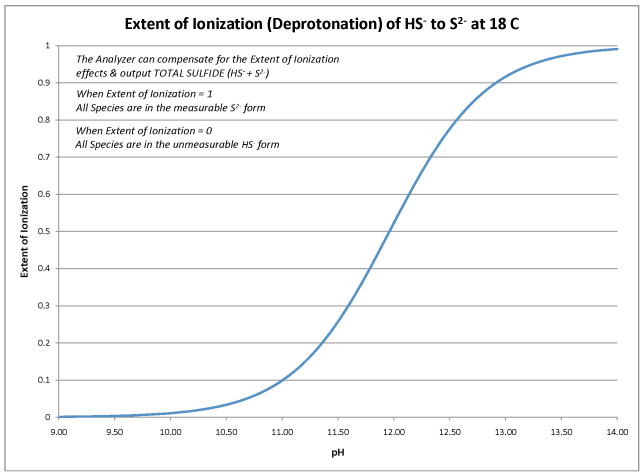
The extent of ionization defines the percent of the species of interest for the weak base (typically ammonia) or the weak acid (typically HF, HCN or HS^-) is converted into the form which te ion selective sensor can detect, which is the free ionized species. On the vertical axes this extent of ionization is 0.00 when none of the species is in the measurable form for the ion selective sensor. In cases where the extent of ionization is at or near 0.00, it is not posssible to use pH compensation since none of the Free ISE species can be measured by the ISE sensor at all.







When the extent of ionization is 1.00 then all of the weak base or weak acid is in the ionized form that can be detected by the ISE sensor and so not pH compensation is required. For example, all of the NH_3 gas is in the NH_4^+ ion form, all of the HF gas is in the F- ion form, all of the HCN gas is in the CN^- ion form and all of the HS^- ions is in the measurable S^{2-} ion form. The portion which is in the measurable form at that given pH and temperature (the extent of ionization) is called the "Free ISE". The "Total ISE" computed by pH compensation is the value computed as though all 100% of the species were in the measurable form. An pair of selected simple examples are given below for total ammonia and total fluoride the purposes of illustration of the concepts described above.



EXAMPLE 1: TOTAL AMMONIA: *See Top Graph on Page 1*

Samples conditions are Temp: 40.0 °C, pH: 8.50

The extent of Ionization at this pH and temperature for the NH_3/NH_4^+ system is 0.67

Free ISE: 1.25 ppm Ammonium (NH_4^+), Computed Total ISE: 1.89 ppm Ammonia/Ammonium (NH_3/NH_4^+)

EXAMPLE 2: TOTAL FLUORIDE: *See Middle Graph on Page 1*

Samples conditions are Temp: 25.0 °C, pH: 3.45

The extent of Ionization at this pH and temperature for the HF/F^- system is 0.50

Free ISE: 35.0 ppm Fluoride (F^-), Computed Total ISE: 70.0 ppm HF/Fluoride (HF/F^-)

The 3TX-TOT pH compensation module for Total ISE in conjunction with the 3TX-ISE and 3TX-pH measurement modules (which serve as the inputs for the 3TX-TOT module) use built-in ASTI programmed algorithms to compute the extent of ionization for the system of interest (NH_3, HF, HF or HS) at the current pH and temperature. The Total ISE is then determined (computed) by by the 3TX by simply taking the Free ISE and diving it by this computed extent of ionization. The resulting Total ISE shows what would be the ion activity detected if all of the species where at a condition such that they were in the measurable form.

When the appropriate 3TX transmitter assembly is used (such as the model 3TX-4M-ISE-A-pH-A-TOT-PS for example), both the free ISE and total ISE can be output via a scalable 4-20mA analog outputs and MODbus digital outputs as well as the pH and temperature process parameters. A fourth input can also be accepted by the 3TX-TOT module and dispatched via both analog and digital outputs. This fourth input is commonly a related measurement such as ORP, conductivity or another ISE that does not required pH compensation.

If the 3TX dual ISE/pH with TOT pH compenation module transmitter assembly was purchased complete at time of commissioning including sufficient details about the total ISE requirements, then most all parameters will have been preconfigured at the ASTI factory in the must suitable manner possible based upon the information provided. As such, quite often very few of the parameters may need to be modified to begin viewing and sending the total ISE to SCADA or other data acquisition systems for further analysis or control. If no data acquisition system is in place for the installation location of interest, real-time monitoring, graphing and datalogging capabilities are possible via the free of charge Windows 3TX MODbus interface software.