

Method of Analysis for correcting dissolved CO₂ content for Specific Gravity and Alcohol variations in beer

“Creating a Dynamic Henry’s Law Equation”

Robert O’Leary,
Chief Technology Officer,
VitalSensors Technologies LLC. Acton, MA USA
email: bob.oleary@vitalsensortech.com

Abstract

This article will describe required updates to the ASBC Methods of Analysis to better match Henry’s Law calculations with Beer-Lambert’s Law used in spectroscopy and infrared instruments.

Dissolved carbon dioxide is a molecule that vibrates and has a mid infrared absorption band in the electromagnetic spectrum at 4.27 microns. Using Beer-Lambert’s Law, precise concentration measurements can be determined using reflective spectroscopy -specifically Attenuated Total Reflection (ATR).

This article will report results of studies showing flaws in the current Henry’s Law method for measuring concentration in beer and present updated formulas to make CO₂ content in beer consistent with stated instrument accuracies.

Introduction

The current Method of Analysis for measuring carbonation in beer uses a modified version of Henry’s Law, converting temperature and pressure measurements to concentration of CO₂.

$$\text{VolumesCO}_2 := \frac{4.85(\text{psi} + 14.7)}{\text{Fahrenheit} + 12.4}$$

Equation 1.0

Equation 1.0 is published in “A Handbook of Basic Brewing Calculations” by Stephen R. Holle. This method uses a single constant in Henry’s Law equation for solubility, an assumption of 1.01 specific gravity and no correction for atmospheric pressure making the method outdated and inaccurate.

The use of Henry’s Law to calculate CO₂ content is an indirect method which does not measure the concentration of any individual gas but the composite result of all dissolved gases. In recent years, changes in the beer industry product formulations have exacerbated these flaws. Out of necessity, density was introduced as a constant in the Henry’s Law equation because temperature/pressure instruments do not measure density at

all. Historically, this method evolved with the assumption that all beer had comparable density, a specific gravity of 1.015 and an alcohol content of 3.8% by weight.

Light beers, ales and low carbohydrate beers have made the assumption that all beers have comparable density incorrect. In fact, many beers now have a lower specific gravity than water. The use of nitrogen in many beers to give a richer head makes using temperature and pressure to measure dissolved gas inaccurate, both because of the lack of differentiation in the gases and because of the differences in the solubility coefficients. Beer with different alcohol contents has a different density. Additionally, the introduction of high speed bottling lines and dynamic tank changes in today’s modern breweries cause pressure spikes unrelated to carbonation, creating apparent concentration spikes in temperature/pressure based instruments.

This paper proposes an update to the Henry’s Law model that will make temperature/pressure lab methods better correlate to ATR based infrared online measurements that measure CO₂ content directly while removing the distortions of pressure spikes, membranes and instrument maintenance currently required and making comparisons to historical data more relevant.

Updating Henry’s Law Calculations

Henry’s Law equations for beer have not been significantly updated since they were introduced in “Methods of Analysis” American Society of Brewing Chemists 5th Edition-1949. At that time, charts were introduced based on empirical data that converted Henry’s Law equation for water to one for beer. Because of the unavailability of computers, constants were determined for many variables that today would be straight forward to keep as variables. These include alcohol content, specific gravity and atmospheric pressure.

The paper, “A compilation of Henry’s Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry” gives the relevant equation for determining solubility coefficients for gases in fluids.

$$k_{H,INV} = p_g / x_a = Q_{liq} / (M_{liq} x k_H)$$

Where: $k_{H,INV}$ = volatility

P_g = partial pressure gas phase

X_a = molar mixing ratio

Q_{liq} = Density of liquid

M_{liq} = Molar mass of liquid

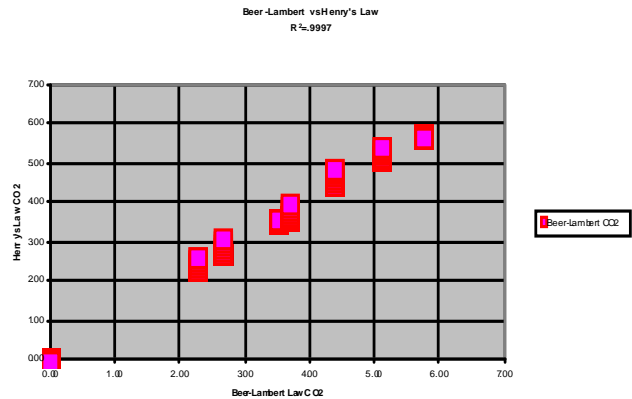
k_H = solubility of gas in liquid

Equation 2.0

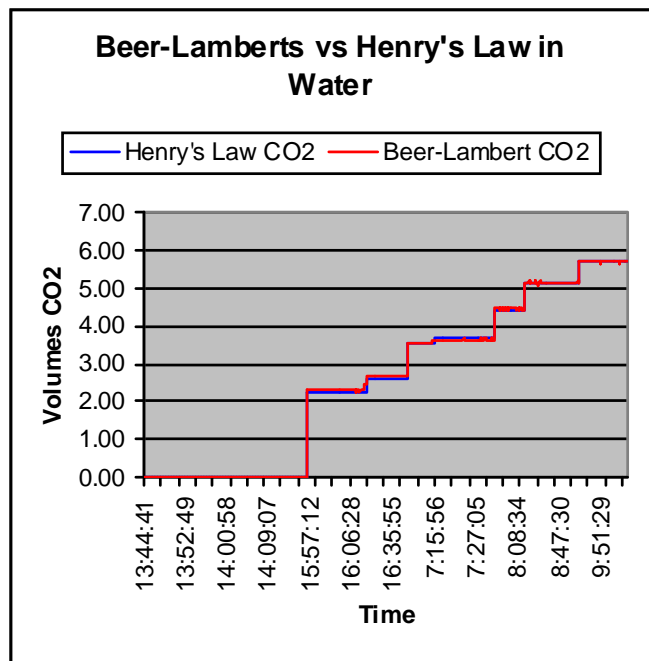
Equation 2.0 provide the basis for an important update to the Henry's law equation for CO₂ concentration. It states that Henry's Law constants are proportional to fluid density. To test Henry's Law a different method must be used. Beer-Lamberts law is used by infrared sensors which measure the vibrational spin of the CO₂ molecule.

Since there are specific Henry's Law constants for CO₂ concentration in water it makes sense to compare CO₂ concentration using both methods in water.

brand types makes the current implementation of Henry's Law by temperature/pressure instruments outdated.



Graph 2.0



Graph 1.0

For Graph 1.0 Henry's Law CO₂ concentration data was taken using absolute pressure and temperature. The Beer-Lamberts concentration was taken using a VS1000C inline infrared sensor. Graph 2.0 shows an X-Y scatter plot of actual data showing an R² regression of 0.9997 proving method equivalence.

At this point it should be understood that Henry's Law is applicable for Beer when the process environment is constant. This is to be expected. However, today's dynamic process environment with varying beer and

A Dynamic Henry's Law Equation

Today's modern instruments and systems make it possible to more accurately calculate and update Henry's Law for Beer. First we know that solubility is inversely proportional to density and ethyl alcohol has a density of .789 g/ml versus 1 g/ml for water. The second update is for specific gravity. The current ASBC method asks for a correction proportional to specific gravity. The current ASBC chart also suggests a correction for atmospheric pressure of 1PSI for every 2000 ft above sea level. If we take the current Henry's Law equation and add these as dynamic variables we get the following equation.

$$\text{Volumes_CO2} := \frac{5.16 \cdot (\text{psi} + \text{Baropressure})}{(\text{Fahrenheit} + 12.4) \cdot \text{SG} \cdot \left(1 + \frac{1}{.789} \text{ABW}\right)}$$

Where:

Volumes= CO2 volume/volume

PSI=Gauge pressure

Baropressure = Barometric Pressure PSIA

Fahrenheit= Fluid Temperature Fahrenheit

SG=Specific Gravity

ABW= Alcohol by weight ie: 3.6%=.036

Equation 3.0

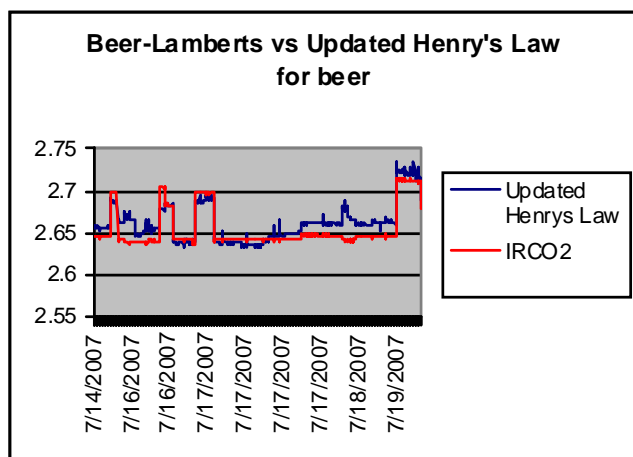
To make this equation easy to use VitalSensors Technologies has created a software calculator free of charge for the ASBC that uses this formula. To take current online pressure/temperature measurements and convert them to the updated Dynamic Henry's Law equation the following formula can be used.

$$\text{VolumesCO}_2 = \left[\frac{5.16}{4.85} \cdot (\text{PTCO}_2) \right] \cdot \text{SG} \cdot \left(1 + \frac{1}{.789} \text{ABW} \right)$$

Equation 4.0

Application

To determine if this formula is correct, data was collected over several days and several beer brands using a VS1000C dissolved CO₂ inline infrared instrument using Beer-Lamberts' Law and comparing it to an online pressure/temperature instrument using Equation 4.0. An online density meter was used to measure Alcohol and Specific Gravity. The data is shown on Graph 3.0



Graph 3.0

The data matches to the measurement accuracy of the pressure/temperature instrument. Note that data with pressure spikes was removed from the pressure/temperature instrument to improve its accuracy and repeatability. The Beer-Lamberts Law data is depicted as IR CO₂. The Updated Henry's Law data is depicted as Updated Henry's Law. A further improvement could be made if real time Barometric Pressure data were available. The pressure/temperature device was calibrated using a Haffman's Gehaltmeter with an absolute pressure meter to minimize this error. The graph shows that the Beer's Law infrared sensor data is more repeatable. Part of this remaining Henry's Law error could be due to changes in atmospheric pressure, using an absolute pressure sensor would solve this problem.

Conclusions

The current ASBC method for Henry's Law determination of CO₂ volumes in beer is inaccurate. This paper uses dynamic variables for specific gravity and alcohol to make the equation more accurate. When this is done Henry's Law method for CO₂ measurement in beer matches Beer-Lamberts Law method to the measurement accuracy of the pressure/temperature instrument over several beer brands with different specific gravity and alcohol

content.

Implementation of the Dynamic Henry's Law Equation allows breweries the potential to align and compare current and historical process temperature/pressure CO₂ data to inline infrared instruments.

References:

Volumes of CO₂ Gas Dissolved in Water, Zahm & Nagle Co.

Carbonation Volumes in Aqueous Systems, A.S. Medina, Coca-Cola USA

Attenuated Total Reflection Spectroscopy Method for Measuring Dissolved CO₂ in Beer, Robert K. O'Leary, Cerveza y Malta, pp 43-47

The In-Line Determination of Carbon Dioxide in Beer by Infrared Analysis, Paul A Wilks, MBAA Technical Quarterly, Vol. 25, No. 4 pp. 113-116

A Handbook of Basic Brewing Calculations, Stephen R. Holle; Master Brewers Association of the Americas, page 87

Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry, Rolf Sander, Max-Planck Institute of Chemistry, Version 3 (April 8, 1999)

Solubility of Carbon Dioxide in Beer Pressure-Temperature Relationships, Zahm & Nagle Co Novel On-line Sensor for Measuring Dissolved CO₂ Using Attenuated Total Reflectance Technology, F. M. Cash, G.P. Broski, and P.J. Slier, MBAA Technical Quarterly, Volume 44, Number 2, 2007, Pages 93-97.

On the Internet:

www.wikipedia.org
www.answers.com
www.webbook.nist.gov/chemistry