

CO₂ Volumes in Beer

1.0 Introduction

Tables have been published by the ASBC (Ref. 1) and others which give the number of volumes (at STP i.e. 0 °C and 1013.25 mBar) of CO₂ which are dissolved at equilibrium in a unit volume of beer. Given the ubiquity of programmable devices available to the brewer today it seems desirable to have a simple formula from which the tabulated values are readily obtained if such a simple formula is possible. It is indeed possible to find reasonably simple formulae which are reasonably accurate and such formulae are given here along with a somewhat more complicated algorithm for computing volumes with greater accuracy. The source of the ASBC data is not known and difficulty in coming up with more accurate formulas may derive from, for example, measurement, rounding or transcription errors in the table data. That such may be the case is suggested by deviations from what we would expect the basic physics of the problem to tell us. The ratio of the concentration of gas in the solution to the headspace pressure (the Henry coefficient) is easily determined from the tabular data. It should exhibit smooth dependence on temperature and little or no dependence on pressure. If there is any pressure dependence, it too should be smooth. As we will see the table data does show variation with pressure that is not smooth. This fact plus the basic nature of the data makes 2 dimensional polynomial fits to the data set difficult in the sense that a large number of terms are required.

The basic data in the ASBC table are summarized below in Figure 1.1. A few things need to be noted with respect to this figure and the table from which it is derived. First, it represents the situation at equilibrium. Equilibrium between beer and CO₂ takes a long time to establish - weeks or longer for a normal size 15.5 gallon keg. The ASBC's Method of Analysis (MOA) Beer - 13, from which the table is taken, requires the analyst to insure that beer and headspace are in equilibrium by vigorous shaking. This is not necessary, of course, if one merely wishes to know how many volumes will be in his beer after a period of weeks sitting under a given pressure which is the usual use to which these tables are put. As is well known, however, shaking under gas pressure will speed the rate at which the CO₂ dissolves. Second, we note that the data in the ASBC table are labeled as corresponding to beer of specific gravity 1.010. Solubility of CO₂ in beer will depend somewhat on what else is dissolved in it but we expect that this dependence is a weak one. Finally, a glance at the figure shows that only a subset of temperatures and pressures are represented, namely those that result in dissolved volumes of from 1.6 to 3.2. The reader may use some of the formulas given below outside the range indicated on Figure 1.1 but with others (polynomial fits) he should not.

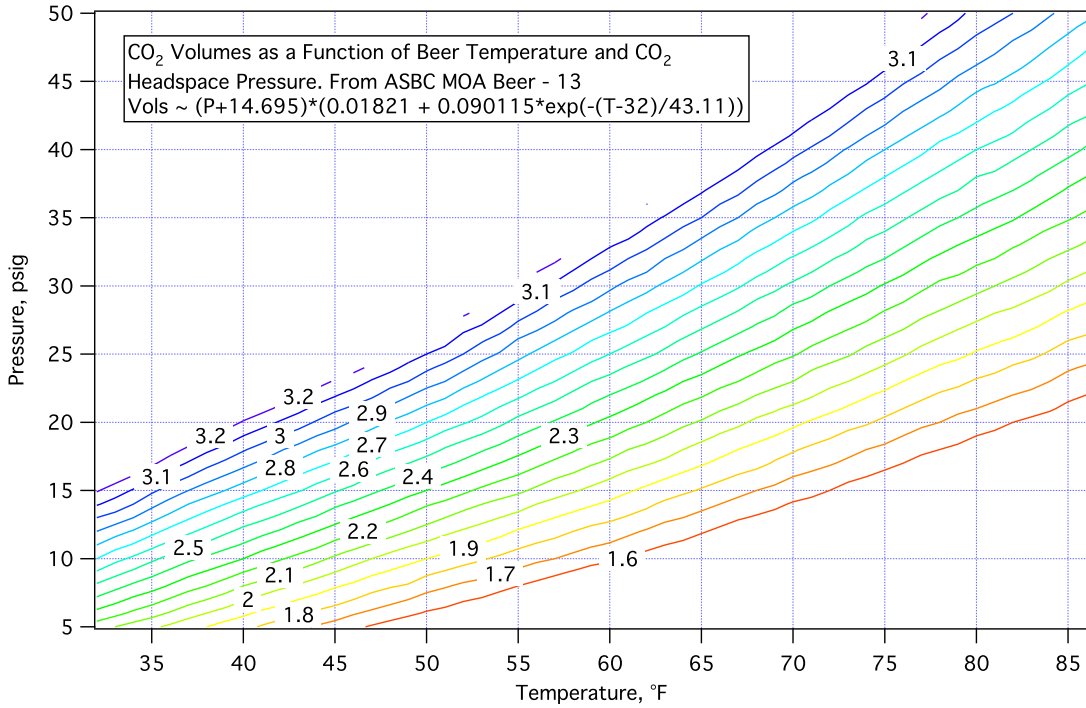


Figure 1.1 Graphic representation of ASBC CO₂ Table. Tables on curves denote volumes of CO₂ at STP in 1 volume of beer. Specific gravity of beer 1.01

In the section immediately following this one we will give the estimation formulas and an estimate of their accuracy. We defer derivation of these formulae to subsequent sections in anticipation that many if not most readers will be interested in the formulae themselves and not where they came from.

2.0 CO₂ Volume Estimation Formulas

In the following subsections we offer formulae which approximate the values in the ASBC tables

2.1 Constant Henry Coefficient

Equation (2.1) is a simple formula which expresses the volumes (STP) of CO_2 in a unit volume of beer at equilibrium with CO_2 gas at gauge pressure P (psig) at Fahrenheit temperature T :

$$V = (P + 14.695)(0.01821 + 0.090115e^{-(T-32)/43.11}) - 0.003342 \quad (2.1)$$

It is clear that the factor inside the first set of parentheses is the absolute pressure in psi and so the factor in the second set of parentheses is the Henry coefficient, the ratio between the equivalent volume of gas (at STP) dissolved to te pressure (absolute) which dissolves it. We assume this depends only on temperature. The formula was obtained by computing the ratio $V/(P + 14.695)$ for the tabulated data for each temperature and finding the parameters for the exponential which resulted in the best fit. The final constant has been added because the formula without it shows an average error of 0.003342 volumes. This constant can be omitted if desired. With the constant in place the rms disagreement between the table data and the formula is 0.01 volume with a peak error of -0.044 volumes (at 37 F and 19 psig where the dissolved level is 3.27 volumes). Figure 2.1 shows contours of disagreement level between this formula and the ASBC table. It is interesting and frustrating that the best agreement is seen at high temperatures and pressures (the right hand part of the figure) where few are going to be carbonating beer. Ratios as a function of pressure parametric in temperature can be seen on Figure 3.1 from which it is apparent that there is in fact pressure dependence except at the higher temperatures and pressures. This is why the errors associated with this model are best in that region.

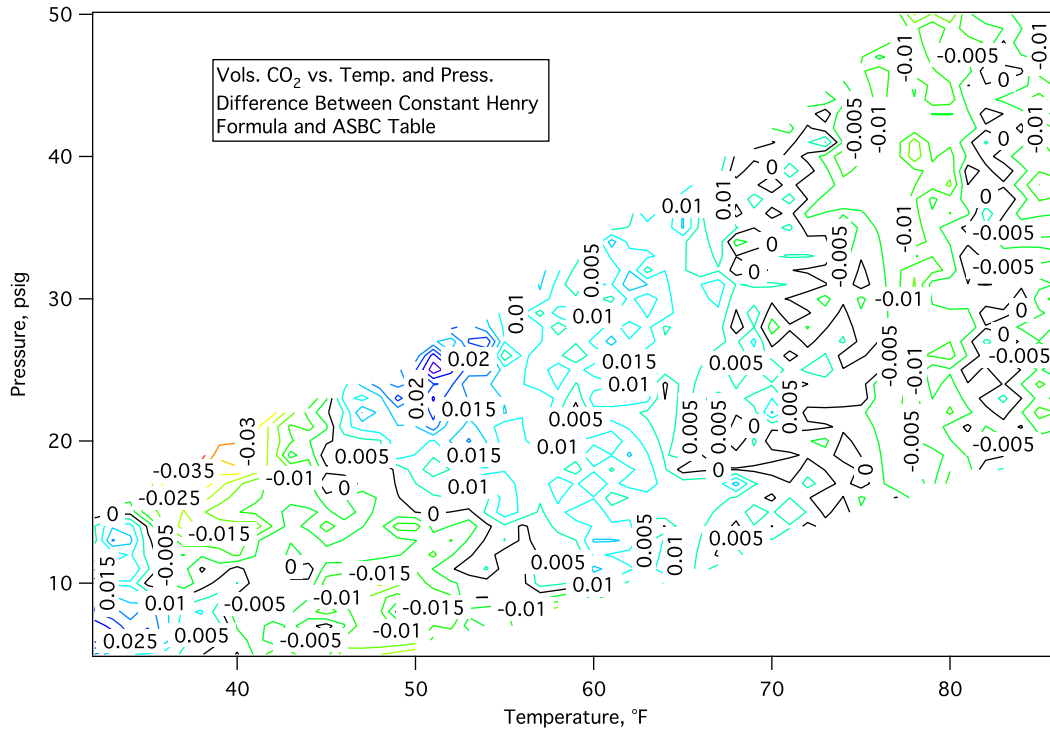


Figure 2.1 Map of disagreement between Equation (2.1) and ASBC table

One appealing aspect of this formula is that, because it models the Henry coefficient as a function of only temperature and the variation with temperature is smooth, it should be usable for pressures and temperatures outside the range of the ASBC table and Figure 1.1. For example, it predicts 3.54 volumes would be dissolved at 35 F and 20 psig but we have no data to verify this against.

2.2 Second Order Polynomial Fit

A second order polynomial fit is given by:

$$V = 3.4384 - 0.66441T + 0.12838P + 0.00040505T^2 - 0.0010092TP - 0.00001234P^2 \quad (2.2)$$

This formula is of approximately the same accuracy as Equation (2.1) i.e. its rms disagreement with the ASBC table is also about 0.01 volumes but its peak errors are somewhat larger reaching magnitudes of as much as 0.06 volumes at low pressure and temperature and high temperature and pressure (the lower left and upper right corners of Figure 2.2 which shows the differences between the polynomial and the ASBC table).

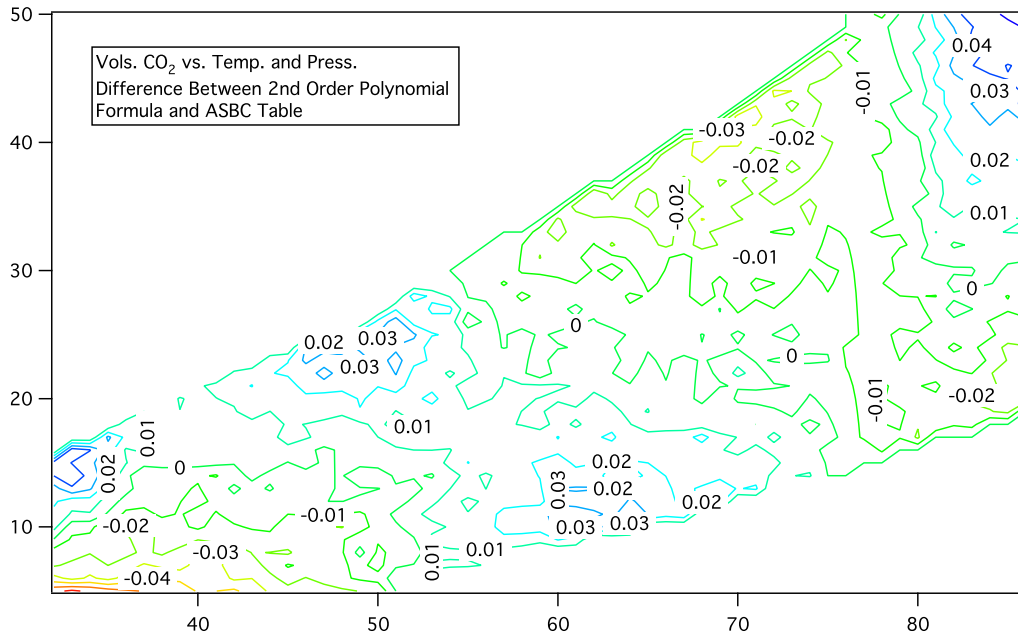


Figure 2.2 Disagreement between second order polynomial fit of Equation (2.2) and ASBC table.

Only a bold analyst uses a polynomial to extrapolate outside the bounds of the data from which the coefficients were derived unless he knows the model is valid and one should be cautious here too though as examination of Equation (2.2) shows dissolved volume is nearly linear with respect to both T and P (the constant and the coefficients of T and P are large relative to those for T^2 , P^2 and TP). Thus one may go outside the bounds somewhat but one is on firmer ground doing this with Equation (2.1). Equation (2.2) predicts 3.48 volumes for 35 F and 20 psig as compared to 3.54 from Equation (2.1). On the other hand Equation (2.2) gives 5.34 volumes for 35F and 40 psig whereas Equation (2.1) gives 5.59.

2.3 Third and Higher Order Polynomials

An obvious question is “If a second order fit gives a level of accuracy upon which we would like to improve, would a 3rd order fit do better?” The answer is “somewhat”. In a 3rd order fit the rms disagreement drops to 0.0055 volumes and the peak errors to magnitude 0.03. Equation (2.3) is a third order fit to the ASBC data.

$$V = 3.2788 - 0.071739T + 0.16885P + 0.00068873T^2 - 0.0021768TP - 0.00020031P^2 - 2.3653 \times 10^{-6}T^3 + 7.7244 \times 10^{-6}T^2P + 3.8693 \times 10^{-6}TP^2 - 1.108 \times 10^{-6}P^3 \quad (2.3)$$

Again, one might ask about a still higher order fit. A fourth order fit reduces the rms disagreement to 0.0046 volumes but the magnitude of the peak error remains at 0.03 volumes. Clearly we are achieving very little additional agreement for going to higher and higher order fits. This is a reflection on the underlying data as we will see in the next section.

2.4 Variable Henry Coefficient Model

A final model is one in which we look at the data in detail and try to model variations in the value of the Henry coefficient with pressure. As we are really more concerned with exposing the nature of the underlying table data than presenting a formula for practical use the model is the subject of its own section.

3.0 The ASBC table Data

Figure 1.1 summarizes the ASBC data. We wish to examine this data critically to see if it is consistent with our understanding of the physical chemistry of carbon dioxide solutions. We have alluded previously to characteristics of the data set which seem inconsistent in this regard.

3.1 Theory

The relationship between gas at equilibrium with a solution and the activity of the gas in the solution is given by

$$\{HCO_3^*\} = K_{Hy}P \quad (3.1)$$

where $\{HCO_3^*\}$ represents the chemical activity, which we shall assume here to be the concentration in moles per liter of solution (i.e. we will assume that the solution is ideal in the sense that the activity coefficient is 1). P represents the pressure in atmospheres (1 atm = 1013.25 mBar = 14.695 psia). Note that the pressures in the ASBC tables are gauge pressures i.e. pressures above the ambient 1 atmosphere. Absolute pressure (psia) is converted to gauge pressure (psig) by subtracting 14.695 psi and conversely.

Theory says that for low pressure (all the pressures we are dealing with here are low in this sense) that the Henry constant should be a constant indeed or at most a very weak function of pressure and should behave with temperature according to the van't Hoff equation:

$$\frac{\partial}{\partial T} \ln K_{Hy} = \frac{\Delta H}{RT^2} \quad (3.2)$$

where ΔH is the enthalpy change of the system per mole of CO₂ as it dissolves, $R = 8.314472$ J/(K-mol) is the universal gas constant and T is the temperature in Kelvins. The van't Hoff equation serves as a use full means of comparing beer as described by the ASBC table to pure water for which we have data on K_{Hy} (in fact on $pK_{Hy} = \log K_{Hy}$) from Ref. 3.)

As a “quality control” check on the ASBC table the first thing we did was to plot the ratio of tabulated volumes to absolute pressure (tabulated pressure +14.695 psi) for each temperature in Figure 3.1. While the ratios are calculated using the absolute pressure they are displayed in the figure against the corresponding gauge pressure. Recall that the volumes of CO₂ in the tables are the volumes that would be at hand if all the dissolved gas were removed from a unit of volume of beer, dried, cooled to 0 C and adjusted to pressure of 1 atmosphere. Since 1 liter of CO₂ at 0 C and 1 atmosphere weighs 1.9771 grams per liter, the number of volumes multiplied by this is the number of grams of CO₂ in a liter of beer and the molar concentration is thus

$$M = \frac{1.9771}{44.01} V(T', P') \quad (3.3)$$

where we have used primes to indicate the Fahrenheit temperature and psig pressures of the table, reserving P to represent pressure in atmospheres. It is clear that volumes are proportional to the molar concentration and that the ratios plotted in Figure 3.1

$$r(T', P') = \frac{V(T', P')}{(P' + 14.495)} \quad (3.4)$$

are proportional to the Henry coefficient at the temperature and pressure for which the volumes were taken out of the table:

$$\hat{K}_{Hy}(T', P') = \frac{M}{P} = \frac{1.9771}{44.01} \frac{V(T', P')}{(P'/14.495 + 1)} \quad (3.5)$$

Each of the horizontal line in Figure 3.1 plots the ratio of volumes to pressure for a particular temperature (as labeled on the plots) and, by the arguments just given should

1. Be a perfectly straight horizontal line
2. Have values (independent of pressure) which vary with temperature according to Equation (3.2)

It is clear from the figure that the first condition is not met as the low temperature line are neither horizontal nor of constant slope though the higher temperature lines are better behaved in this regard. We have no idea as to the provenance of the data which went into the ASBC table. It is quite clear that the irregularities in slope are due to measurement error as no physical law can explain such roughness.

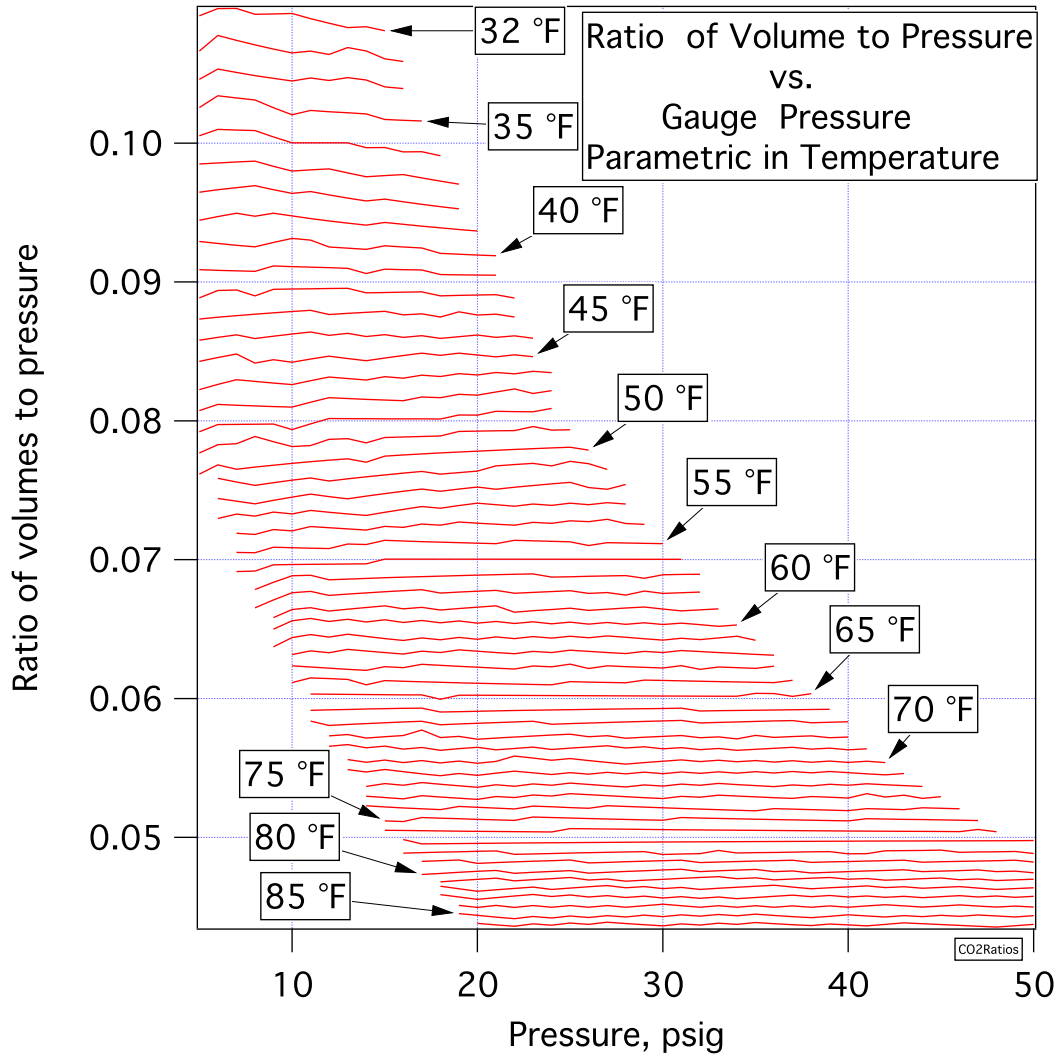


Figure 3.1 Ratio of dissolved volume to pressure at constant temperatures. Lines should be straight with constant small or 0 slope

Furthermore, the slopes, as determined by linear fits to each constant temperature ratio plot, do not vary smoothly with temperature as is shown in Figure 3.2. The solid line passing between the circles in this figure represents an approximation to the circle data set which approximation is used in an algorithm for reconstruction of ASBC table data which is to be described shortly.

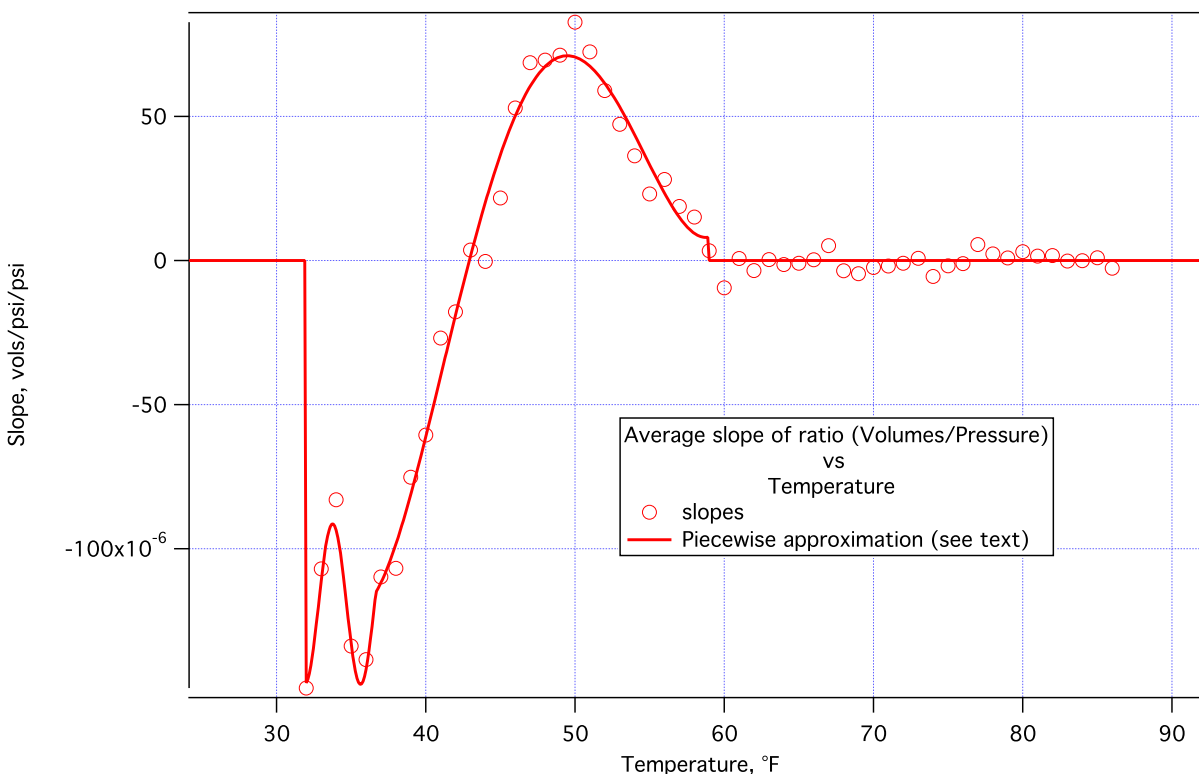


Figure 3.2 Slopes of constant temperature ratio (CO_2 Volumes/absolute pressure) plots vs. pressure

Certainly these irregularities prohibit good fitting of the data with low order polynomials and it is doubtless this fact that limits the accuracies of the formulae give in Section 2.

By taking the negative Briggs logarithm of Equation (3.5)

$$p\hat{K}_{Hy}(T', P') = -\log\left(\frac{M}{P'}\right) = -\log\left(\frac{1.9771}{44.01} \frac{V(T', P')}{(P'/14.495 + 1)}\right) \quad (3.6)$$

and averaging over all P' for each T' we obtain

$$p\hat{K}_{Hy}(T) = \langle p\hat{K}_{Hy}(T', P') \rangle_{P'} \quad (3.7)$$

which are directly comparable to the pK_{Hy} values for water from Ref. 3. Figure 3.3 shows these data and makes it clear, from this point of view at least, that beer, as described by the ASBC table, and water behave similarly. The slightly higher values of pK_{Hy} for all temperatures imply that CO_2 is slightly less soluble in beer than in water (0.02 pK_{Hy} units implies about 5% more dissolved for a given pressure).

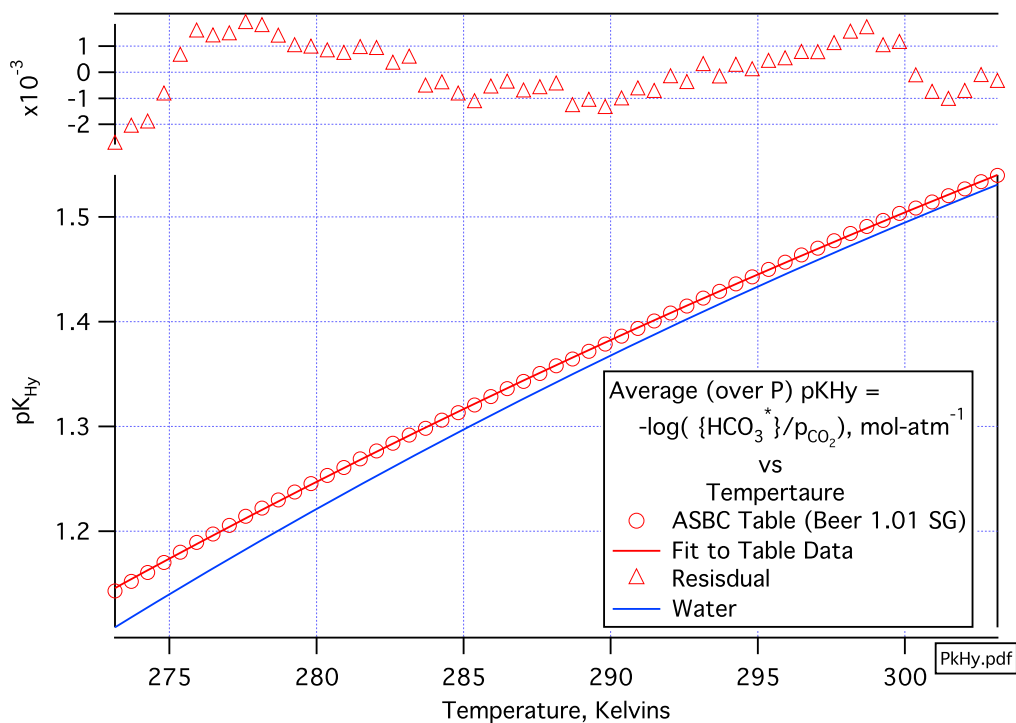


Figure 3.3 pK_{Hy} average values derived from ASBC tables compared to values for water from Ref. 3.

To use the van't Hoff equation we need the derivative of the natural logarithm of Henry coefficient with respect to temperature. The natural log of the Henry coefficient is easily obtained from pH_{Hy} by

$$\ln K_{Hy} = -\ln(10)pK_{Hy} \quad (3.8)$$

To get the derivative we fit the pK_{Hy} data with a polynomial such that it is approximated by

$$pK_{Hy}(T) = -1653.04T^{-1} + 9.06086 - 0.00682174T \quad (3.9)$$

where T is now the Kelvin temperature. This form was chosen because

1. It is the form chosen for representation of water data in Ref. 3.

2. It is trivial to compute the derivative of Equation (3.8) from it.

The values for pK_{Hy} for water in Ref. 3. are fit with this form by

$$pK_{Hy, Water}(T) = -2397.43T^{-1} + 13.9482 - 0.0148744T \quad (3.10)$$

from which it is clear that

$$\frac{\partial}{\partial T} \ln(K_{Hy, Water}) = \ln(10)(2397.43T^{-2} + 0.0148744) \quad (3.11)$$

Equation (3.9) gives the values for beer (per the table) as

$$\frac{\partial}{\partial T} \ln(K_{Hy, Beer}) = \ln(10)(1653.04T^{-2} + 0.00682174) \quad (3.12)$$

Inserting these values into Equation (3.2) and multiplying by RT^2 we get estimates of the enthalpy of solvation of carbon dioxide based on, respectively, the pK_{Hy} values published in Ref. 3. for pure water and calculated from the ASBC tables for beer (SG 1.010). These are shown, along with values of pK_{Hy} in

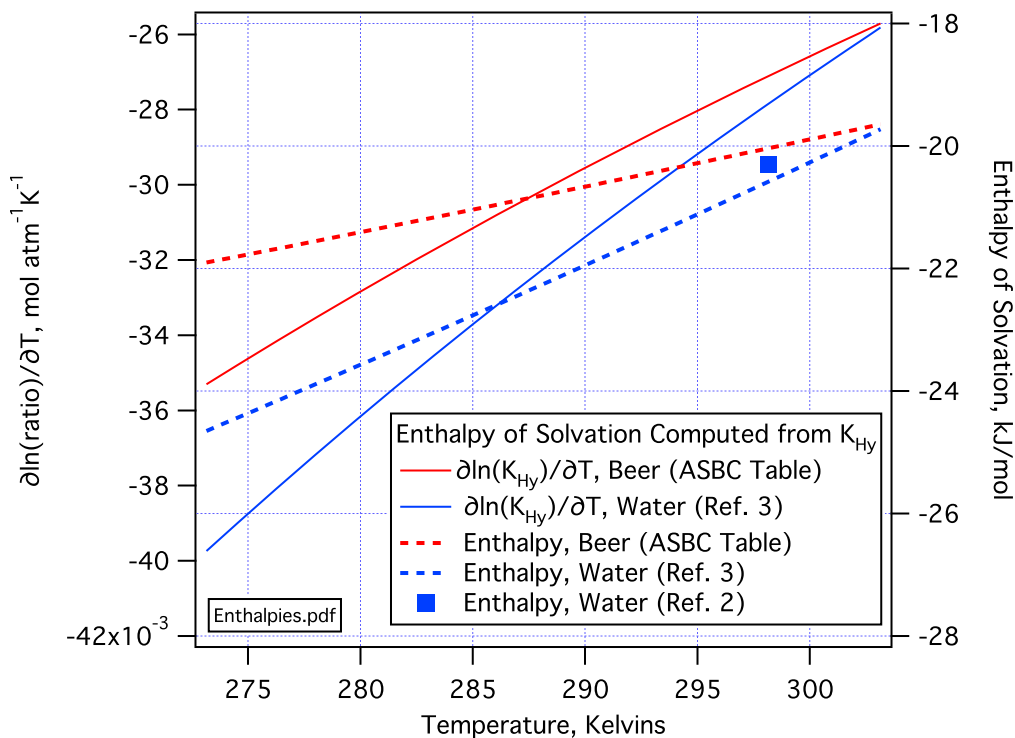
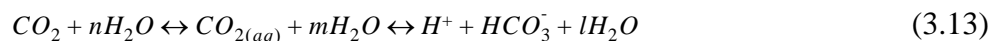


Figure 3.4 Derivatives of log of Henry coefficients and enthalpies of solvation calculated from them for both water and beer.



where $l < n < m$ are integers. Once ions come into the picture ideality departs and perhaps this explains the inconsistency of the enthalpy change derived from these data.

We note with interest that Ref. 2 lists the enthalpy of solution of CO_2 in water as -20.3 kJ/mol at 298.15 K/mol. Equation (3.10) gives a value of 20.04 kJ/mol. Thus we have the magnitude just about right but seem to have made a sign error. Ref. 2 definitely states that the reaction is exothermic. We also show on the figure enthalpy of solvation values calculated from Henry coefficient data taken from Ref. 3.

3.2 Fitting the Theoretical Model

The simple formula of Equation (2.1) models each of the lines of Figure 3.1 as a horizontal (0 slope) line with value of the ratio given by the average value of the data for the temperature associated with that line. Those ratio values are well fit by the exponential part of Equation (2.1). Given slope data for each line (Figure 3.2) it is clear that if we could model those slopes as a function of temperature and come up with a simple model for the intercepts of the lines also as a function of temperature we could determine the ratio of volume to pressure for any combination of temperature and pressure and easily calculate the volumes simply by multiplying by the absolute pressure. Intercepts are cooperative as is plain from Figure 3.5 below. Note that a double exponential fit is employed though it is not that much better than a single exponential. Given the complexity required of the slope model (to be described next) it seems little extra trouble to use a double exponential here. Fit coefficients are given in the legend box on the figure.

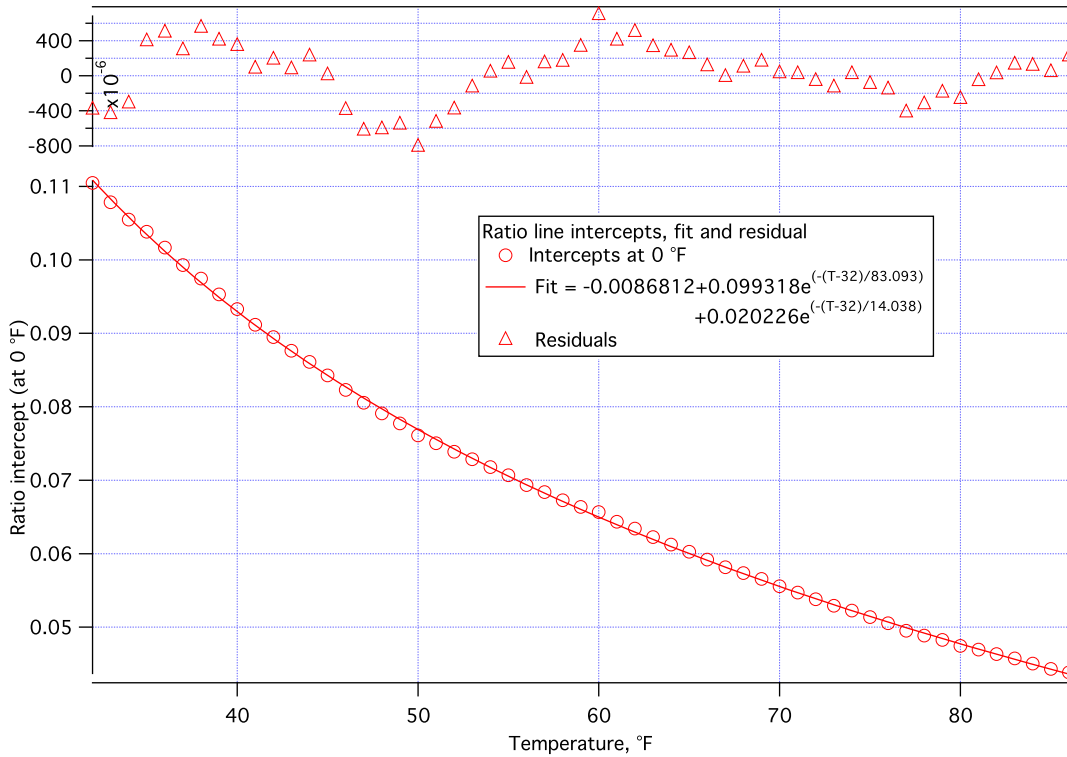


Figure 3.5 Ratio intercept values, double exponential fit and residuals.

Figure 3.2 makes it clear that no simple model exists for the slopes. Below 32 F we have no data and so model the

slope as 0. At temperatures above 59 F the slope is close to 0. Thus we can model the slope by

$$\begin{aligned} m &= (-0.00011919) + 2.7645 \times 10^{-5} \sin(1.6769T - 4.7745); (32 \leq T < 36.7) \\ &= 0.0283046 - 0.00262695T + 8.59711 \times 10^{-5}T^2 - 1.22132 \times 10^{-6}T^3 + 6.37612 \times 10^{-9}T^4; (36.7 \leq T < 59) \\ &= 0; OW \end{aligned} \quad (3.14)$$

Using this model for slope and the double exponential in Figure 3.5 for intercept

$$b = -8.6812 \times 10^{-3} + 0.099318 e^{-\frac{(T-32)}{83.093}} + 0.020225 e^{-\frac{(T-32)}{14.036}} \quad (3.15)$$

we can approximate the slope at temperature T (in Fahrenheit) and pressure P (psig) as $s = mP + b$ and thus the volumes by

$$V = (P + 14.695)(mP + b) \quad (3.16)$$

This model performs slightly better than the constant ratio model of Equation (2.1) with an rms disagreement of 0.01 volume but peak error magnitude of 0.03. This improvement is not worth the extra complexity of this model.

4.0 Summary and Conclusions

Several methods for modeling the data contained in the ASBC carbon dioxide table have been explored and found to deliver accuracy which seems to be limited at about 0.03 volumes peak disagreement with rms disagreement between 0.0055 and 0.01 volumes. The peak errors are believed to be caused by deviations of the table data from the gas laws and exemplified by the “jaggy” nature of Henry coefficient plots at constant temperature. Based on this we conclude that it would be impossible to come up with better fits to this data other than spline or other interpolators.

The simplest model appears to be the most robust in terms of being able to extrapolate beyond the temperature and pressure limits of the ASBC table. Though its peak error at 0.044 volumes (within the temperature and pressure range covered by the ASBC table) is larger than the peak error of other fits it is not appreciably so (compare to 0.03 for the best fits). This should not be significant in practical applications and it is this model, Equation (2.1), that we therefore recommend.

5.0 References

1. Beer -13 Dissolved Carbon Dioxide, Methods of Analysis of the American Society of Brewing Chemists, Eighth Revised Edition, American Society of Brewing Chemists, 3340 Pilot Knob Road, St. Paul, MN 55121, 1975
2. Lyman, Joel F., Some thoughts on the solubility of carbon dioxide and silicon dioxide in water, Structured Chemistry Vol. 8, No. 5 1997
3. Stumm, Werner and James J, Morgan “Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibrium in Natural Waters”, Wiley, NY 1981 p 204