Applications of the Partial Molar Volume Concept in Whisky and Gin Dilutions with Water

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KEYWORDS

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The meaning of the partial molar volume, the analytical methods for finding the partial molar volumes and the additivity theorem of the partial molar volumes are explained. The additivity theorem of the partial molar volume is used for whisky alcohol strength dilutions and for single shot or multi-shots for gin in both flavor dilution with GNS and alcohol strength dilution.

INTRODUCTION

Whisky, rum, gin, and other spirits are projected to contribute up to $507,465 million in global revenue in 2021, and the market is expected to grow annually by 5.49%[2] [1]. Bourbon and other whiskies are made from the aging of barrel-filled grain alcohol which is often 100-150 proof[3] (50-75% ABV (Alcohol by Volume)). The final bottled spirit products are often 76-90 US degrees of proof (38-45% ABV). For a spirit sensory test, the spirit is then served at bottle strength or often diluted to around 20% ABV. In making gins [2], whether it is made via a single-shot, or multi-shot process, the botanical compounds, extracted via maceration and distillation or via vapor infusion through a gin basket, may first be mixed with a large amount of neutral spirit approximately at 96% with water then added to attain a final alcohol content of 40% ABV (gins maybe bottled at between 37.5 and up to 55% ABV). In all three examples, barrel to whisky, whisky diluted to samples for sensory tests, or in the process of making gins, ethanol is mixed with water to obtain a desired final ABV. In all those processes, the questions pertaining to the distillery are: (1) How much water should be added for dilution to obtain a desired ABV? (2) What is the final product volume? (3) If a fixed amount of water and neutral spirit of 96% ABV are mixed, what is the final ABV, and how much water should the distillery add to obtain the final and accurate 40% ABV?

Both the U.S. Gauging Manual Method [3] and Travagli's method [4-5] are the available math-oriented methods used in the distilling industry. In this paper, we offer another approach based on the partial molar volume concept to solve those problems.

Partial Molar Volume is a thermodynamic definition [6]. In a two-component system (e.g., ethanol and water) at constant temperature T and pressure P, the partial molar volume of water (component 1) is usually denoted as[4]

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2,T,P} \quad \text{[Equation 1]}$$

Partial molar volume is additive. In a two-component system (e.g., water and ethanol) at constant temperature *T* and pressure *p*, we have

2 According to the Distilled Spirit Council of the United States, in 2020 spirits gained the largest share of the US beverage alcohol market. The 1.3% increase was more than double the average share gain over the past four years. https://www.just-drinks.com/analysis/has-the-spirits-category-emerged-stronger-from-covid-19-fight-analysis_id132749.aspx

3 Proof here refers to US proof, which is two times alcohol by volume. A vodka that is 40 percent ABV is 80 proof and one that is 45 percent ABV is 90 proof

4 Throughout the paper, the subscript "1" implies the water phase, while superscript "2" implies the ethanol phase. Thus n_1 means number of moles of water, $\bar{V}_2$ means the partial molar volume of ethanol. In addition, when mole fraction "x" is referred to, it means the mole fraction of ethanol

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 \quad \text{[Equation 2]}$$

Likewise, in a three-component system (e.g. water, ethanol, and sugar) at constant temperature T and pressure p, we have

$$V = n_1 \bar{V}_1 + n_2 \bar{V}_2 + n_3 \bar{V}_3 \quad \text{[Equation 3]}$$

Equation [3] is exact and its proof can be seen in many physical chemistry textbooks [7]. In the context of this paper we focus only on the water-ethanol system. The partial molar volume is different from the molar volume because of the formation of the hydrogen bonds between the solute and the solvent [8-10].

MATERIALS AND METHODS

Ethyl alcohol is 200 U.S. Proof from Pharmco (Cottrellville, MI). Water is a distilled water prepared from the UW-Green Bay double distilled facility. The density meter used is a DMA 4500 Density Meter, Anton Paar. (Ashland, Virginia)

To produce a spreadsheet for data analysis, it is usual to prepare approximately 10 binary mixtures of ethanol and water gravimetrically, with ethanol weight percentage ranging from 0% to 100% with a 5% interval. The density for each mixture is then determined by a density meter at 20 °C. The data tables published by the legal metrology organization known as the OIML tables [10] are consulted for data analysis. Once spreadsheets are prepared, calculation of the partial molar volumes are made using the following procedures:

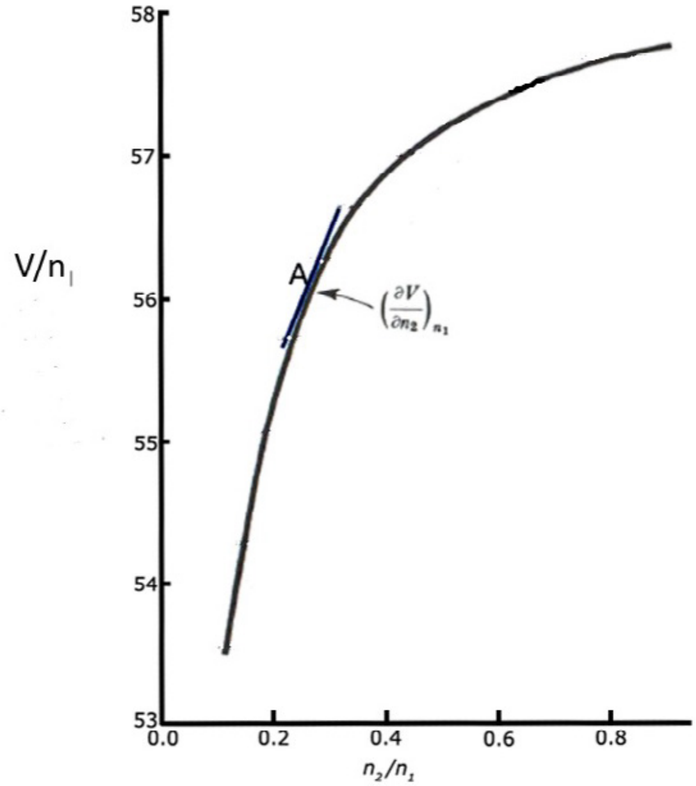

FIGURE 1 Finding the Partial Molar Volume of the Solute by the Graphical Method [11].

(1) GRAPHICAL APPROACH

We will start with a binary solution of n_1 moles of the solvent (water), and n_2 moles of the solute (ethanol), and the volume of the solution V. If we are interested in finding the partial molar volume of ethanol, the first step is to plot V/n_1 against n_2/n_1. An example of the plot is shown in Figure 1. The partial molar volume of ethanol at a specific n_2, say point A in the graph, is determined by the slope of the curve at point A.

Alternately, we can construct an Excel spreadsheet starting with a set of density and weight percentages. Such a data table exists in the Table V_b of the legal metrology tables known as the OIML tables [11]. Figure 2 shows the plot of density of ethanol-water mixtures against ABW (alcohol by weight) from two different data sets: one from the OIML table and the other from the UW-Green Bay. Both data sets agree within 0.5% of error tolerance.

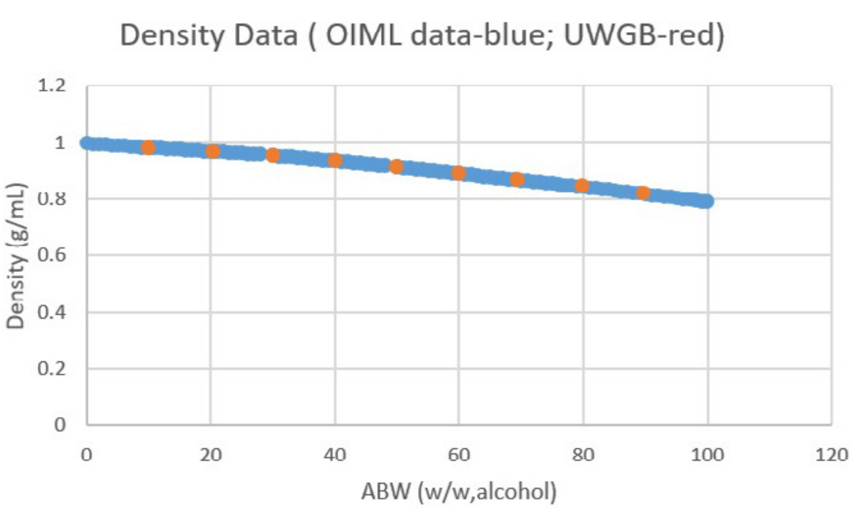

FIGURE 2 Density data from the OIML table (blue) and from UW-Green Bay (red).

TABLE 1 An example set of data illustrating how the partial molar volumes of ethanol are calculated.

	A	B	C	D	E	F	G	H	I	J	K
1	ABW	Density (g/mL)	n1 (moles of water)	n2(moles of ethanol)	V (total), mL	x (mole fraction of ethanol)	V/n1	n2/n1	Vp (ethanol), mL/mol	Vp (water), mL/mol	Additivity test
2	93.02	0.8097	0.387454899	2.01918902	123.5025	0.839006138	318.7533	5.211417	58.23687635	15.2566666	123.5025
3	92	0.8125	0.444074382	1.99704784	123.0769	0.81808597	277.1538	4.497102	58.20140771	15.4161727	123.0769
4	91	0.8152	0.49958368	1.9753408	122.6693	0.798141849	245.543	3.953974	58.17362566	15.5260222	122.6693
5	89.99	0.8179	0.555648071	1.95341669	122.2643	0.778543751	220.0392	3.515565	58.14779807	15.6168208	122.2643
6	89.01	0.8205	0.610047183	1.93214379	121.8769	0.760030938	199.7828	3.167204	58.11506324	15.7204987	121.8769
7	88.02	0.8231	0.665001388	1.91065382	121.4919	0.741812729	182.6942	2.873158	58.08022087	15.8206063	121.4919
8	87.02	0.8257	0.720510686	1.88894677	121.1094	0.72388487	168.0882	2.621678	64.11475612	15.9172624	132.5779

Table 1 presents an example set of data values illustrating how the partial molar volumes of water are calculated.

For an example, the cell A3 has ABW=92%, which stands for 92g of ethanol and 8g of water in a 100g of ethanol-water mixture. The solution volume in column E is weight/density, or 100g over the density value in column B. The cell E3 value is obtained as $100\,g \Big/ \left(0.8125\ {}^{g}\!/_{mL}\right) = 123.0769\ {}^{g}\!/_{mL}$

Cell values in column C are obtained by dividing the water mass by the molar mass of water, which is 18.015g/mol. Cell values in column D are obtained by dividing the ethanol mass by the molar mass of ethanol, which is 46.068g/mol. The mole fraction of ethanol is then defined as

$$x = \frac{n_2}{n_1+n_2} \qquad \text{[Equation 4]}$$

Mole fraction values of ethanol for each ABW are shown in column F of Table 1.

If we are interested in calculating the partial molar volume of ethanol (the second component in our illustration), everything has to be normalized by the number of moles of water (the first component in our illustration). This includes V (total)/n_1, and n_2/n_1 shown in columns G and H of Table 1.

The partial molar volume of ethanol can then be calculated as:

$$\left(\frac{\Delta V_{total}}{\Delta n_2}\right)_{n_1} = \left(\frac{\Delta\left(\frac{V_{total}}{n_1}\right)}{\Delta\left(\frac{n_2}{n_1}\right)}\right) \qquad \text{[Equation 5]}$$

Considering the first two data rows (Rows 2 and 3 in Table 1):

$$\left(\frac{\Delta V_{total}}{\Delta n_2}\right)_{n_1} = \left(\frac{277.1538-318.7533}{4.4971-5.2114}\right) = 58.2369\ \left(\frac{ml}{mol}\right) \qquad \text{[Equation 6]}$$

Where ΔV_{total} is the difference of two cell values G3 and G2, and Δn_2 is the difference of two cell values H3 and H2 in Table 1. The resulting value is shown in cell I2. The cell values in I3 to I8 are calculated using a similar equation.

This is the numerical value shown on cell I3 of Table 1. Using the same procedures, we can also calculate the partial molar volumes of water which are shown as cell values between J2 and J8.

The values shown in column K in Table 1 are the additivity tests for the partial molar volumes of water and ethanol using the procedures seen through the application of equations 5 and 6. For the additivity test, it implies equation 2 must be strictly followed. The values in column K should exactly match the values in column E in Table 1. This is indeed the case, except we have an outlier, K8 with a value of *132.5779 mL* while the value of E8 is *121.1094 mL*. This is because the spreadsheet is truncated on row 8. In this limited set of data, we are not able to carry out ΔV_{total} and Δn_2 calculations for Equations 5 and 6 on Row 8 and beyond.

This problem can, however, be overcome by plotting partial molar volumes of either ethanol (column I) or water (column J) against the mole fraction of ethanol (column D). This is shown in Figure 3, plotting partial molar volume of ethanol and water against the mole fraction of ethanol; and Table 2 which expresses the regression equations of the partial molar volumes of both ethanol and water as a function of ethanol mole fraction.

Regression equations are obtained from the two plots of partial molar volumes shown in Figure 3 and Table 2:

TABLE 2 Regression Equation Expressions of the Partial Molar Volumes of Ethanol and Water as a Function of Mole Fraction of Ethanol from Table 1.

PARTIAL MOLAR VOLUME AS A FUNCTION OF ETHANOL MOLE FRACTION (*x*)	R^2
Water $\bar{V}_1 = -10.57\,x^2 + 11.076\,x + 13.414$	0.9971
Ethanol $\bar{V}_2 = -2.1002\,x^2 + 4.8896\,x + 55.611$	0.9976

In row 8 of Table 1, the mole fraction of ethanol is *0.7239*. Using the two regression equations from the plots, we have the new partial molar volumes of ethanol and water: *58.05* and *15.89 mL/mol*. The additivity test would be *(0.7205) (15.89) +(1.889) (58.05) =121.105 mL/mol*, which differs from *121.109 mL/mol* (cell E8) within *0.003%*.

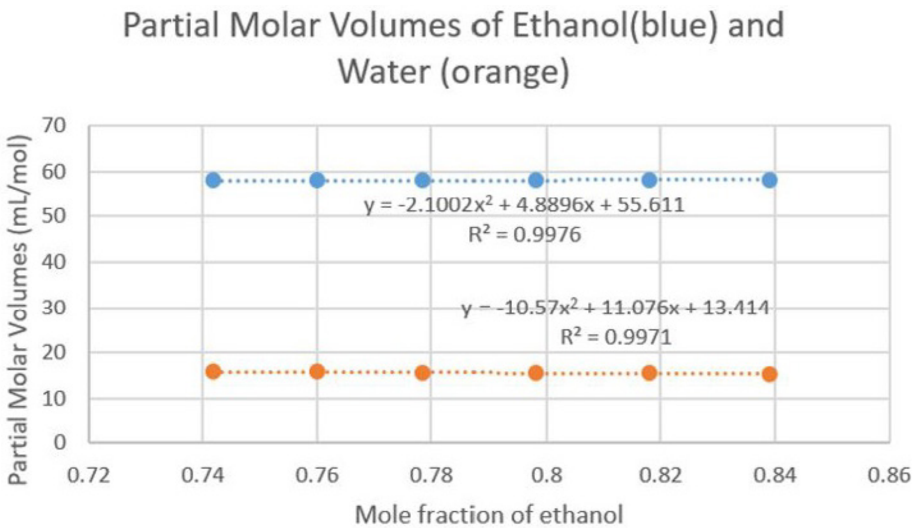

FIGURE 3 Plotting of Partial Molar Volumes of Ethanol and Water as a Function of Mole Fraction of Ethanol from Table 1.

Note that the example we provide in Table 1 has a very limited data set with mole fractions of ethanol ranging only from 0.7239 to 0.8390. The OIML table provides us alcohol density data with ethanol ranging from 0% to 100% with 0.1 ABW incremental intervals. Regression formulas for finding partial molar volumes of ethanol and water are useful. The regression equations[5] for ethanol and water from the OIML table are:

$$\bar{V}_2 = 23.967\,x^3 - 48.407\,x^2 + 32.826\,x + 50.414\,;$$

$$\bar{V}_1 = -2.1713\,x^2 - 1.8511\,x + 18.138$$

[Equation 7]

In solving all the distillery and the brewery problems, we will all use Equations 2, 4, and 7. Equation 2 is simply the additivity property of the partial molar volume. Equation 4 allows us to find the mole fraction of the ethanol so that we can use Equation 7 to calculate the partial molar volumes of both ethanol and water.

All data presented in the OIML tables were obtained at 20 °C. For temperatures other than 20 °C, such as 60 °F (15.56 °C) which is used in the U.S, then the investigators must generate zdata tables similar to the OIML table which can be a formidable task. The U.S. Gauging Manual published in 1918 [3] presents an extensive data set on specific gravity of ethanol-water mixtures at 60 °F. Since specific gravity and density values are related, in the absence of any new data source, this latter reference can be used for spirit dilution practices in both the brewing and distilling industries [5, 13].

(3) SPOT-CHECKING APPROACH

Our lab has also adopted a technique used by Trandum et al. [14] which can be used to find partial molar volumes at a specific molecular composition without establishing an extensive data table. This is illustrated in the following:

According to the definition of the partial molar volume from Equation 1, we have

$$\bar{V}_1 = \left(\frac{\delta V}{\delta n_1}\right)_{n_{i,i\neq 1}}$$

$$\delta V = \left(\frac{mass\ of\ the\ mixture}{d}\right)_{after} - \left(\frac{mass\ of\ the\ mixture}{d}\right)_{before}$$

[Equation 8]

In our studies, when $\delta n_1 = 0.06$ mol, and $\delta n_2 = 0.02$ mol, the partial molar volumes obtained from Equation 8 agree with data calculated from Equation 7 within 4%. The agreements can be improved if we tweak both the δn_1 and the δn_2 values.

RESULTS AND DISCUSSION

(1) PARTIAL MOLAR VOLUMES ARE DIFFERENT FROM THE MOLAR VOLUMES

There are a few comments to be made regarding partial molar volumes. First, the partial molar volumes are functions of compositions. As the composition changes, so do partial molar volumes. Second, the partial molar volumes of ethanol are close to, but not the same as, the actual molar volume of ethanol which is $\frac{46.068\left(g/mol\right)}{0.7893\left(g/mL\right)} = 58.37\left(mL/mol\right)$

In fact, all the partial molar volumes calculated for ethanol range from 52.59 mL/mol to 58.37 mL/mol and are lower than the molar volume of the ethanol. Similarly, the partial molar volumes of water ranging from 13.82 to

5 Supplemental Excel Spreadsheet -1

18.05 mL/mol are different from the molar volume of water which is 18.05 mL/mol. The differences between the partial molar volumes and the molar volumes of both water and ethanol are the origins of the volume contractions that are also composition dependent. The origin of the difference between the partial molar volume and the molar volume is the hydrogen bond formation between the ethanol and water [8-10].

The difference between the molar volume and partial molar volume is relevant for the distillery industry and is a well known volume-contraction phenomena where ethanol and water are mixed. We shall explore this volume contraction phenomenon in the following application examples.

(2) APPLICATIONS OF THE PARTIAL MOLAR VOLUMES ON ALCOHOL DILUTIONS IN WHISKY

Bourbon and other whiskies are made by aging grain alcohol at strengths ranging from 100-125 proof (50-62.5% ABV) in charred or toasted oak barrels [15]. The Alcohol and Tobacco Tax and Trade Bureau (TTB) specifies that the alcohol strength in the barrel is 125 proof (62.5% ABV) or less [16]. The spirits undergo reduction in strength with water prior to bottling. The final strength of the bottled products is often found in the 76-90 proof (38-45% ABV) range, in many cases 40% ABV [15, 16]. For a spirit sensory test, the spirit is then often served undiluted (bottle strength) or often diluted to around 20% ABV (20-23%) depending on the investigators [17-20].

For this presentation, we will work on three dilution problems: 65% ABV to 40% ABV, 40% ABV to 23% ABV, and lastly 65% ABV to 23% ABV. We are interested in answering the following questions: (1) How much water (mass and volume) are required for each stage of the dilution? (2) What are the final solution volumes for each stage of the dilution? (3) What is the volume contraction for each stage of the dilution?

It is noted that the mathematical procedures for diluting 40% ABV to 23% ABV and for 65% ABV to 23% ABV are the same as those for 65% ABV to 40%. Therefore, we will just simply explain the dilution for 65% ABV to 40% ABV in the details here. We then set up an Excel spreadsheet and use the algorithm in the sheet to find the answers for the other two dilutions.

Mathematical Procedures for 65% ABV to 40% ABV Dilution

The procedures require the use of Tables IV_a and IV_b of the OIML data [10]. Let us start with 100 mL of 65% ABV which is equivalent to 57.15% ABW (OIML, Table IV_b) and has a density of 0.89765 g/mL (OIML, Table IV_a). The mass of ethanol in 65% ABV is calculated as follows:

$$100\ mL \times 0.89765\ \frac{g}{mL} \times 0.5715 = 51.30070g$$

[Equation 9]

Note that the ethanol mass is conserved which implies this mass does not change after the dilution.

For a 40% ABV, the density is 0.94805 g/mL (OIML, Table IV_a) and is equivalent to 33.3 % ABW (OIML, Table IV_b). The total mass of the final diluted solution is calculated as:

$$51.30070\ g/_{0.333} = 154.056\ g$$ [Equation 10]

The water mass of the final solution is

$$154.056\ g - 51.3007\ g = 102.756\ g$$ [Equation 11]

The number of moles of water (n_1) and ethanol (n_2) are then calculated as follows:

$$n_1 = 102.756\ g \Big/ \left(18.015\ g/_{mol}\right) = 5.704\ mol$$

$$n_2 = 51.3007\ g \Big/ \left(46.07\ g/_{mol}\right) = 1.114\ mol$$

[Equation 12]

Note that the molar masses of water and ethanol are 18.015 g/mol and 46.07 g/mol respectively.

The mole fraction (x) of ethanol is calculated as follows:

$$x = 1.114/_{(5.704 + 1.114)} = 0.163$$ [Equation 13]

Using Equation 7, the partial molar volumes of ethanol and water are then calculated. The answers are:

$$\bar{V}_1 = 17.78\ \frac{ml}{mol} \quad \bar{V}_2 = 54.58\ \frac{ml}{mol}$$ [Equation 14]

Using the data generated from Eqs. 12-14, the final volume as calculated from the additivity theorem of partial molar volumes in Equation 2 is then

$$n_1 \bar{V}_1 + n_2 \bar{V}_2 = 162.19\ mL$$ [Equation 15]

To calculate the mass of water needed to be added to achieve a final 162.1886 mL 40% ABV, we need to find the difference of the water masses before and after the dilution. This is calculated as follows:

$$0.94805\ g/_{mL} \times 162.19\ mL \times (1 - 0.333) - 0.89765\ g/_{mL} \times 100\ mL \times (1 - 0.5715) = 64.096\ g$$

[Equation 16]

The density of water at 20 °C is 0.99820 g/mL. The volume

TABLE 3 Summary of Whisky Dilution—Comparison of the Results between This Work and Travagli's Method.

DILUTION	INITIAL VOLUME (mL)	FINAL VOLUME (mL)		VOLUME (mL) OF WATER ADDED FOR DILUTION		VOLUME CONTRACTION	
		THIS WORK	TRAVAGLI METHOD [4]	THIS WORK	TRAVAGLI METHOD [4]	THIS WORK	TRAVAGLI METHOD [4]
65%ABV to 40% ABV	100	162.19	162.5	64.21	64.29	2.02	1.79
40%ABV to 23% ABV	100	173.01	173.90	73.36	73.93	0.35	0.03
65%ABV to 23% ABV	100	281.14	282.60	183.62	184.44	2.48	1.84

of water to be added for this dilution is then

$$64.096\ {}^{g}\!/_{(0.99820\ {}^{g}/_{mL})} = 64.212\ mL$$ [Equation 17]

The volume contraction in this dilution is

$$(100 + 64.212)mL - 162.19\ mL = 2.02\ mL$$ [Equation 18]

This lengthy mathematical manipulation can be streamlined with an Excel spreadsheet. Such a spreadsheet is provided as a supplemental material[6] in this paper.

Table 3 provides the summary of the work that includes 65% ABV to 40% ABV, 40% ABV to 23% ABV and 65% ABV to 23 % ABV. Included in the table are the mass and volume of the water to be added, the final solution volume and the extent of volume contraction. Also included are the results obtained from Travagli's method of solving ethanol solution dilutions [4].

The agreement between this partial molar volume-based dilution method and the Travagli method [4] are within 0.5% in final volume, and 0.7% in the volume to be added. The trend of volume contraction of various dilution processes between the two algorithms is also in agreement with each other. It is therefore concluded that both methods are valid for the applications for distillery dilution applications. Also, it is noted that volume contraction depends both on the starting ABV and the difference between starting ABV and final ABV. The contraction is the largest for 65% ABV to 23% ABV (2.48 mL) and the smallest for 40% ABV to 23% ABV (0.35 mL). This is explored further below.

(3) APPLICATIONS OF THE PARTIAL MOLAR VOLUMES ON GIN MULTI-SHOT FLAVOR DILUTION AND ALCOHOL DILUTION

Distilled gin production [2], does not require aging in charred or toasted barrels, though some innovative producers do this. A gin product must contain juniper. A distiller will also select other materials (botanicals) to give the final product additional flavor and character. These botanicals are used in carefully determined quantities, so that they complement the juniper. Organic compounds in juniper and the supporting botanicals (terpenes) provide the key flavor components through distillation, generally either via maceration or vapor infusion. Distillation tools and techniques include pot stills, continuous stills, low-pressure vacuum stills, and rotary evaporation [21-24]

The botanical loads (in weight per unit volume) influence how a distiller may choose to reduce the concentration of the terpenes in the gin by mixing in "shots" of neutral spirits at ~ 192-194 proof (96.0%-96.2% ABV), in known quantities. These quantities are called liquid alcohol liters (LALs) or proof gallons. If the distiller does not do this, then the product is a single shot gin. If the distiller chooses to do this, then the product is called a multi-shot gin. Increasing the amounts of botanicals in the distillation operation, and then diluting the terpenes and other flavor volatiles extracted via alcohol addition, and then diluting to bottle strength, increases the amount of final gin to be bottled. The number of shots the distiller chooses is often a risk management response to 'louching'.[7] The final bottle strength of gin products, taken globally, is often found in the 75-110 proof (37.5% - 55% ABV) range. That said, there are some products in the 115 proof (57.7% ABV) and above range which are called Navy Strength gins. These too, may be single shot or multi-shot [25].

For the purpose of the mathematical procedure in this problem, we will initially set up blending 100 mL of gin (hypothetically dealing with an extreme 25 times multi-shot botanical load) with 2500 mL of GNS with 96% ABV. We would like to ask the following questions: (1) What is the final volume of the mixture and the volume contraction due to such a mixing? (2) What is the resulting ABV after

6 Supplemental Excel spreadsheet -2
7 Louching means the forming of colloidal particles in the ethanol-water mixture due to the presence of botanical compounds.

the mixing? (3) How much water to be added to the mixture to reach a 40% ABV, and finally what are the volume contractions on this step?

In order to find the final volume using the additivity theorem (Eq.2] of the partial molar volumes, we need to find the number of moles of water and ethanol. 96% ABV is equivalent to 93.84% ABW (OIML, Table IV_b) and has a density of 0.80742 g/mL (OIML, Table Iv_a). The ethanol mass of the mixture can be calculated as:

$$0.80742\ {}^{g}/_{mL} \times 2500\, mL \times 0.9384 = 1894.20\, g$$

[Equation 19]

The water mass is calculated as follows:

$$0.99820\ {}^{g}/_{mL} \times 100\, mL + 0.80742\ {}^{g}/_{mL} \times 2500\, mL \times (1 - 0.9384) = 224.16\, g$$

[Equation 20]

Moles of ethanol (n_2) and water (n_1) are then calculated as,

$$n_1 = {}^{224.16\, g}\Big/\left(18.015\ {}^{g}/_{mL}\right) = 12.44\, mole$$

$$n_2 = {}^{1894.20\, g}\Big/\left(46.07\ {}^{g}/_{mol}\right) = 41.12\, mol$$

[Equation 21]

Mole fraction of ethanol, x, is calculated as,

$$x = \frac{41.12}{41.12+12.44} = 0.768$$

[Equation 22].

Now, we invoke Eq.7 to calculate partial molar volume of both water and ethanol,

$$\bar{V}_1 = 15.44\ \frac{ml}{mol},\ \bar{V}_2 = 57.93\ \frac{ml}{mol}$$

[Equation 23]

The final volume is then calculated as:

$$n_1\, \bar{V}_1 + n_2\, \bar{V}_2 = 2573.90\, mL$$

[Equation 24]

The volume contraction of adding *2500 mL* of *96% ABV* to *100 mL* of the original volume of the distilled botanical compounds is then,

$$\Delta V = (2500 + 100)\, mL - 2573.90\, mL = 26.1\, mL$$

[Equation 25]

Percentage of volume contraction for stage-1 (flavor strength dilution) is calculated as follows:

$$\%\ volume\ shrinkage = \left({}^{26.1}/_{2600}\right) \times 100\ \% = 1.0\ \%$$

[Equation 26]

The ABW of the final mixture is calculated as ethanol mass divided by the total mass, which is

$$1894.2\, g\Big/\left(1894.2\, g + 224.16\, g\right) = 0.894$$

[Equation 27]

This is equivalent to 89.42% ABW. The OIML Table IIIb indicates that *89.42%* ABW is equivalent to *92.84%* ABV.

This is the answer to the part 1 question: For *1:25* addition of botanical dilution ethanol with a concentration of *96%* ABV, the final volume is *2573.9 mL* with *92.84%* ABV.

TABLE 4[8] Summary of Single Shot and Multi-Shot Gin Processes Which Include both Flavor- dilution with GNS (96% ABV) and Alcohol Strength Dilution with Water. Volume unit is in mL. The volume of the starting flavor stock is 100 mL. The final alcohol strength is 40% ABV.

VOLUME RATIO Flavor stock to GNS	ABV after flavor neutralization	VOLUME (mL) after initial flavor dilution	VOLUME CONTRACTION (mL, %) in Stage-1 (flavor dilution)	VOLUME (mL) OF WATER to be added for alcohol strength dilution	FINAL 40% ABV VOLUME (mL) before bottling	VOLUME CONTRACTION in final stage alcohol strength dilution (mL, %)
1:25	92.84	2573.9	26.1 (1.0%)	3560.9	5974	160.8 (2.6%)
1:20	92.06	2076.8	23.2 (1.1%)	2828.5	4779	126.7 (2.6%)
1:15	90.79	1580.3	19.7 (1.2%)	2098.1	3587	91.5 (2.5%)
1:10	88.33	1084.4	15.6 (1.4%)	1367.3	2394	57.4 (2.3%)
1:5	82.19	590.7	9.3 (1.6%)	647.9	1214	24.9 (2.0%)
1:2	66.46	292.9	7.1 (2.4%)	199.6	487	5.9 (1.2%)
1:1	49.50	193.9	6.1 (3.1%)	47.0	240	1.0 (0.4%)

8 Supplemental Excel spreadsheet-3

In the second part, the questions to be addressed are: (1) How much volume of pure water is needed to be added to dilute 2573.9 mL with 92.84% ABV to 40% ABV? (2) What is the final volume of the finished ready to bottle gin? (3) What is the volume contraction on the post-stage dilution?

These questions are the same as those discussed in the whisky dilution problems. The calculations are provided in the Excel spreadsheet as a supplemental material. The answers are: (1) *3560.9 mL* of water to be added, and (2) The final volume is *5962.6 mL*. The extent of volume contraction is *160.8 mL*.

Table 4 summarizes the results of both single shot and multi-shot processes which include (1) What are the ABV values after GNS initial dilution of the flavor? (2) What are the volumes after GNS initial dilution of the flavor? (3) How much water is needed to bring the alcohol ABV to 40% ABV for each process? (4) How much volume of 40% ABV is required for a subsequent bottling? (5) What are the volume contractions for each scenario? For the examples shown volumes are in mL but may be scaled up to production volumes in liters, hectoliters etc.

The results indicate that multi-shot gin processes can yield more bottles of gin than the single-shot gin process. Also, in the multi-shot process, the operators may encounter more volume contraction issues in multi-shot versus the single-shot process[9], especially at stage two with the alcohol strength dilution with water. Interestingly, the multi-shot process sees less percentage of volume contraction than the single-shot situation at stage one when the flavor is diluted with 96% ABV of alcohol.

CONCLUSION

In all three examples discussed in this paper — barrel-to-whisky, whisky diluted to prepare samples for sensory testing, or in the process of making gins — ethanol is mixed with water to obtain a desired final ABV. Thus, the additivity theorem of the partial molar volumes can be successfully applied to both whisky dilution, gin multi-shot flavor programs, and alcohol strength dilution processes. It also demonstrates that in alcohol dilution, volume contraction occurs. Because of volume contraction, one cannot rely on the conventional additive algebra process, but such distillation issues need to call upon more sophisticated math equations such as the use of the partial molar volume concept.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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SUPPLEMENTAL MATERIALS

Three Excel spreadsheets are provided to allow interested readers to explore partial molar volumes calculations, whisky alcohol strength dilution and single shot versus multi-shot gin process calculations: http://artisanspirit-mag.com/journalds/jds_v1n1/