Real gas – the real deal

by David de Marneffe, December 2007

Introduction

The purpose of this article is to lay the foundations for sound state-of-the-art real gas blending calculations (as opposed to ideal gas). This is directed not only to software and spreadsheet programmers, but also meant to increase the awareness of the blenders when they shop for real gas software. This may also appeal to anybody in the diving community interested in more knowledge about a thermophysical phenomenon directly related to the sport, which, for decades, scientists have been and still are working at solving.

The need for such an article may be questioned, considering that information on the subject has already been published in the internet diving community and that software and spreadsheets geared towards real gas blending are already quite widely available. However, erroneous information on this topic has spread around in the community and has been reproduced in software and spreadsheets that base their calculations on this information. A well-known example is the article about real gases published on the Atomox website, which, to put it mildly, takes serious liberties with the laws of thermophysics. In other cases, programmers have correctly applied well-known real gas laws to pure gases, but have made errors in the way these laws apply to mixtures of pure gases. This article will give easy means to programmers to correct such mistakes.

I would like to stress that I have no quarrel whatsoever with Atomox or any software programmer around. Atomox has been contacted privately about this issue well before this article was published. I received a response asking for more precisions, which I provided, but have not heard from them since then. Some software programmers have also been contacted. Some have been showing concern about the issues with their programs and keenness about solving them (GUE's Gas Management Program), and some of them have already released corrected versions of their software (GASMIX, PP Mixer) based on the information in this article. Some others have refused to discuss "their" formulas or have not responded.

The article briefly presents real gas models as opposed to the ideal gas model and introduces a uniform and easy formulation suitable for all real gas models, which effectively allows splitting the problem in two parts which can then be solved separately. Solutions for each problem are then presented, and free open source code is offered to calculate gas mixtures compressibility according to a modern state-of-the-art model. Finally, some of the common mistakes made when performing real gas calculations are looked into.

Ideal gas

Most of us are familiar with the ideal gas model. It simply says:

$$PV = nRT$$

with P the pressure of the gas, V the volume in which the gas is contained, n the number of molecules of gas, R the universal gas constant and T the temperature.

Notice how the ideal gas model applies to all gases in the exact same manner. It doesn't matter if we are compressing helium or oxygen or a mixture of both. If we believe the ideal gas model, the results will be the same. The ideal gas model also empowers the partial pressure concept to be used for all our blending calculations, since pressure and number of molecules are simply proportional. Why bother with moles and molecules when one can simply use partial pressures, which can be read almost directly off one's pressure gauge?

Now, the ideal gas model is a close enough description of reality at low pressures and at temperatures high above the absolute zero, but as pressure increases and/or temperature decreases, the ideal gas model fails to appropriately describe the actual pressure-volume-temperature (PVT) relationship within a gas. This is because in the ideal gas model, nor the actual size and shape of the molecules of the gas, neither the interactions between these molecules (attractive and repulsive molecular forces, non elastic collisions, polarity, etc) are taken into account. And the higher the pressure or the lower the temperature, the more these effects become important, so causing the ideal gas model to fail.

Enter the "real" gas models

Over the decades, a myriad of models have been and still currently are introduced, attempting to better describe the actual PVT relationship within a gas. The wonderful thing about all these models is that they can all be written in a really simple and unique manner, which is going to make our life much easier:

$$PV = znRT$$

A simple extra factor, called z-factor or compressibility, is introduced into the ideal gas law. If the z-factor is very close to 1, then the ideal gas model can reasonably be applied. The further away z is from 1 (it can be more or less than 1), the less the behavior of the gas follows the behavior of an ideal gas. In our blending process, when blending to pressures as high as 300 atmospheres, the z-factor can be as high as 1.25! This makes for a very significant 25% difference compared to the ideal gas model, and if a blender attempts to strictly apply ideal gas calculations in such a situation, the final analysis of the mix will most of the time reveal a significant discrepancy with what was expected.

So the z-factor is our friend, but life is not that easy. Trouble is, the z-factor is not just a constant. It is actually a function of pressure and temperature. And it is a different function of P and T for each different gas. To be exact and make it clear that z is a function of these three parameters, we should always write:

$$PV = z(gas, P, T) * nRT$$

To keep the formulas short, we won't do it but we should always keep that fact in the back of our minds.

Mixing rules

It's getting worse: <u>the z-function of a mixture of pure gases cannot easily be obtained from the z-functions of the pure gases composing the mixture</u>. For example, the z-function of a mixture can generally <u>not</u> be obtained from a simple linear combination of the z-functions of the pure gases, which is something that is seen a lot in current blending software (see *common misconceptions* paragraph). The real gas models actually need to have the constants in their formulas redefined for each possible gas mixture composition. For pure gases these constants are generally obtained from experimental data. But it would be a daunting task to obtain constants in this manner for all the possible mixtures of even only three pure gases. Fortunately, along with their models, scientists have developed sets of <u>mixing rules</u>, allowing the calculation of their models' constants for a mixture from the constants of the pure gases composing the mixture. In the more advanced models, they also use in these mixing rules binary interaction coefficients or departure functions, further characterizing the interaction between the molecules of a pair of pure gases.

So the various real gas models differ from one another in the way they define the z-functions of pure gases and formulate the mixing rules allowing the calculation of the z-functions of mixtures of pure gases.

All this seems to be bad news for our trimix and nitrox blending, because along the blending process, the pressure, temperature and composition of the gas mixture all change together.

The plan…

We are now facing quite a complex challenge. The way to go with that kind of animal is to cut it in smaller, more manageable problems. Let's forget all about having to obtain the z-function. Let's assume that we do have a reliable way of obtaining a good approximation of the actual z-factor of any trimix gas mixture at a particular pressure and temperature. Relieved? Wait. Now we have to forget all about our gas blender training. Forget about partial pressures. The concept still exists, but is useless for real gas calculations. From now on, moles are our friends.

Moles?

One mole of any substance is (approximately) 6.022E23 molecules of that substance. The only reason we don't use directly the actual number of molecules in our equations is that numbers with 20 zeroes are not practical to handle. So from hereon, we use moles. If it helps, in the text below, just replace the word "moles" with "6.022E23 molecules".

Molar blending

Ever thought of what 50% nitrox really means? Yes, of course: 50% nitrox has 50% oxygen and 50% nitrogen… but percent of what? Volume? Weight? Pressure? No! It actually means that 50% of the <u>molecules</u> in the mix are O_2 and the other 50% are N_2. So we are actually talking about <u>molar percentages </u> or molar fractions. In the ideal gas world, because of the simple linear relationship between moles, volume and

pressure, 50% molar is equivalent to 50% volume or 50% pressure, which is why partial pressures can conveniently be used directly for blending. Not so in the real gas world, where the relationship is much complicated by the z-function. And that will be the name of the game in the next paragraph: we will be giving up partial pressure blending, to take on molar fraction blending. Of course, because we don't have molar density gauges, we will also have to translate back and forth into pressures.

Molar fraction blending - calculations

We will work in bar and metric units. These can easily be translated to other units using a website such as unitconversion.org.

Before we get started, let's mind the following points:

- The value of a constant such as R depends on which units are used.

- All the calculations, whether for ideal or real gas, are volume independent. It does not matter whether we blend into an 11 liters or 24 liters volume: everything else being equal, we will still have to go to the exact same intermediate pressures when adding the different gases. So we will always assume a unit volume (V=1) to simplify the equations.

- Also mind that the equations used here take absolute temperatures (in degrees Kelvin) and <u>absolute</u> pressures (bar-a), not <u>gauge</u> pressures (bar-g). More details can be found on this in the *common misconceptions* paragraph.

- Unlike ideal gas calculations, the order in which the gases are added does matter.

- Ambient temperature also matters, because the compressibility factors vary quite steeply with temperature. Hence a software user should be able to input the ambient temperature at which he is working. More on temperature and thermal effects later.

OK, there is no better way to do this than with a simple example:

"Hi! I am Joe-the-Blender and I want to blend 50% heliox to 250 bar. To make your life easy, my gauge reads in bar-a and I will vacuum my cylinder completely before I start so it will be at 0 bar-a. I want to add the helium to the empty cylinder first, then the O2. The ambient temperature is 25 degC. How should I do that in terms of real gas?"

1) Let's focus on the target mix and figure how many moles are contained into a unit volume (one liter) of 50% heliox gas at 250 bar-a and 25 degC (298.15 degK):

$$n = P / (zRT) = 250 / (1.1295 * 0.08314472 * 298.15) = 8.9286 \text{ moles}$$

(we got the 1.1295 z-factor for 50% heliox at 250 bar-a and 25 degC using our reliable method, remember?)

2) In 50% heliox, half of the above moles are O2 and the other half He. So that is 4.4643 moles of each.

3) We now take the empty (vacuumed) unit volume and want to add 4.4643 moles of He to it. At which pressure should we stop adding He to achieve that?

$$P = znRT$$

Trouble is, we need z to calculate P, but z depends on P, so what now? We got ourselves an egg and chicken problem here. No worry: let's take z = 1 as a first estimate. This gives us

$$P = znRT = 1 * 4.4643 * 0.08314472 * 298.15 = 110.67 \text{ bar-a}$$

We can now look up the z-factor of pure helium for these values of P and T: 1.0524, and re-inject it into the equation to calculate a more accurate P:

$$P = znRT = 1.0524 * 4.4643 * 0.08314472 * 298.15 = 116.47 \text{bar-a}$$

Repeating the same process for a few iterations to achieve sufficient convergence, we finally get P = 116.77 bar-a (with z = 1.0552)

4) So we now have 116.77 bar-a of helium in our unit volume and all we have to do to obtain our target mix is to top up with O2 to 250bar-a.

In this example, had we strictly followed the ideal gas model, we would have added 125 bar of He, then 125 bar of O2 and we could calculate that this would have given us approximately a 46/54 heliox rather than the desired 50/50. A significant difference.

At the end of this article is example 2, a full blown real-life example of trimix blending over a left over from a previous dive.

Obtaining the z-factor of a gas mixture

From the original van der Waals to the modern GERG-2004, numerous models and their associated mixing rules have been proposed to calculate the z-factors as functions of gas mixture composition, pressure and temperature. All of them have their advantages and limitations, usually on valid pressure and temperature ranges. Lots of these models have been developed for the oil & gas industry, so it can be quite difficult to locate their parameters for the gas mixtures we are interested in.

The purpose here is to offer some guidance as of how adequate some of these models are for real gas blending calculations, but not to review the details of the models, which can be done with some internet or library research.

After many hours of programming and testing, and comparing results to reliable experimental data, the van der Waals and Peng-Robinson models did yield unsatisfying results at the pressures and temperatures of interest. Although the errors on the z-factors are quite large, van der Waals yielded decent results in many practical blending cases because the errors on the z-factors tend to cancel out during blending calculations.

The Beattie-Bridgeman model, when employed with the proper mixing rule, yields satisfying results up to 150-200 bar at 25degC but at higher pressures and/or lower temperatures, the errors on the z-factors increase quite rapidly to less acceptable levels. Still, considering the simplicity of the equations, this is quite a feat and to be honest, it does not make a massive difference for practical blending, maybe 1 or 2 % on the final helium content and less than 1% on the O2 content. This is again because errors on the z-factors tend to cancel out during the blending process. Many people

have based their spreadsheets or software on the Beattie-Bridgeman equation, but many also got the mixing rules and / or molar calculations wrong. Programmers who wish to fix this (please do!) can find attached here a document stating the correct mixing rule for the Beattie-Bridgeman equation and an Excel spreadsheet with Visual Basic open source code that implements these equations. But read on, because there is another top notch solution available right off the shelf.

The Benedict-Webb-Rubin (BWR) model would surely do a very adequate job, given that it is a refinement of Beattie-Bridgeman. I could not test it extensively because I do not have values of its parameters for helium, neither do I have the binary interaction coefficients for the O2-N2, O2-He and N2-He pairs required for the mixing rule. This data may exist somewhere in the literature, although I doubt it, and I gave up my research when I came across GERG-2004.

GERG-2004 is (currently) the holy grail of equations of state. GERG stands for "Groupe Européen de Recherche Gazière" (European Gas Research Group), a joint effort by the main gas companies of Europe. The model has been developed by a team of German engineers and thermodynamicians and has been fully published in 2007. The model is meant for much more than just calculating z-factors, such as calculating the state and thermal properties of a mixture over a very wide range of temperature and pressure conditions and remaining valid across phases. The parameters, including binary interaction coefficients and departure functions for the mixing rules, have been fine tuned using a phenomenal amount of high quality experimental data and are currently available for 18 pure components, including oxygen, helium and nitrogen. The full details of the model can be obtained as a 555 pages pdf document at this address: http://www.gerg.info/publications/tm/tm15_04.pdf . When comparing the GERG-2004 z-factors to the best experimental data I could obtain, the differences were plainly negligible for our purpose. The only downside for the programmer is to have to find his way through the 555 pages and program lengthy equations.

GERG-2004 for trimix compressibility - open source code

To spare you the trouble, please find attached an Excel spreadsheet with Visual Basic open source code of a partial GERG-2004 implementation for the calculation of the compressibility factors of O2, He, N2 and their mixtures. The code can easily be adapted to any common programming language. The outputs of this code have been verified against the ones of the software written by the very team who developed the model and they are a perfect match. Mind however that this is a (very) partial implementation and that as such, unlike the full-blown model, it is limited to O2, He and N2 well into the gas phase. Outside or on the edge of the gas phase, the routines will fail to converge to a valid physical solution. Hence, please prevent users to use them for temperatures below 250degK or pressures above 400bar.

If you decide to use GERG-2004 in your spreadsheets or software, please give credit to the scientists who developed it as follows, in the about tab and user manual:

Kunz, O.; Klimeck, R.; Wagner, W.; Jaeschke, M. (2007): The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures: GERG Technical Monograph 15 (2007) and Fortschr.-Ber. VDI, Reihe 6, Nr. 557, VDI Verlag, Düsseldorf, 2007.

If you decide to use the code, feel free to give me credit for writing it and doing the leg work of deciphering the GERG-2004 Monograph. But you don't have to. If you have questions or need any help with GERG-2004 or the molar calculations, feel free to ask. However I will not support Beattie-Bridgeman or other equations of state, given that a better solution is readily available. You can give me credit as follows:

The partial GERG-2004 implementation used to calculate the compressibility factors of oxygen, helium, nitrogen and their mixtures in the gas phase was inspired by open source code written by David de Marneffe in December 2007. David can be contacted at daviddemarneffe@yahoo.com

Thermal effects and instruments accuracy

What we forgot to mention to Joe Blender in the example above is that all our efforts to improve the accuracy of his blending by using a real gas model could well be totally wasted and may even actually have a detrimental effect. That is because thermal effects do introduce errors of the same order of magnitude as the ones made by using the ideal gas model. And in some circumstances, thermal and ideal gas errors almost cancel each other. In the above example, we assumed that all the gases involved and their containers were and stayed at the same temperature during the whole process. In reality, this is not true. Generally (not always), heat is produced during the compression of a gas, and absorbed during the decompression. Let's say for example that just after decanting the prescribed 116.77 bar-a of helium, the gas in Joe's target cylinder has warmed to 40 degC (313.15 degK) instead of having stayed at the assumed 25 degC. Well instead of having decanted the desired 4.4643 moles of helium, Joe would now have this much helium in his unit volume:

$$n = P / (z\,RT) = 116.77 / (1.0522 * 0.08314472 * 313.15) = 4.2623 \text{ moles}$$

and the final mix would have too little helium in it. Joe would probably have been better off using the ideal gas model in this case, because after a while the normally excessive 125 bar-a of helium would have cooled down to approximately the required 116.77 bar-a.

The trouble with thermal effects is that they are a whole lot of hassle to model properly. We would need to know the exact transfer rate of the gas, the exact amount of heat dissipation through the wall of the cylinder over time, and/or we would have to ask the blenders to measure the exact temperature of the gas in their cylinders after adding gas to them. Not practical. The way to go is to take it easy and/or… fudge. If Joe has time, he just adds the first gas, then lets it rest and cool down to ambient temperature. Then he adjusts the pressure to the target pressure and repeats after adding each gas. If he doesn't have time… he fudges! He just knows that he has to go "a little over" because the gas will cool down and the pressure will drop. With experience, he can get it pretty much spot on.

Of course, lots will argue that with experience, a good blender does not need a real gas model at all… Maybe, but still, it may be good to have only one parameter to fudge on. The rest is taken care of by good real gas calculations.

There is also the issue of the accuracy of the instruments used to measure pressure and gas composition, which furthers the arguments of those who say they don't need a real gas model. These are perfectly valid arguments. However I am not the one who

decided in the first place to put real gas software and information on the diving marketplace. My purpose is only to address issues with such software and information, not to discuss their pertinence or necessity.

Common misconceptions

The following addresses a few misconceptions that have been published on some diving websites and/or implemented in blending software. Let's use the traditional trimix notation for the gas, such as 10/70 for 10% O2 and 70% He, the balance being nitrogen.

Atomox "mixing rule"

The z-factor of a gas mixture at pressure P is a weighted average of the z-factors of the pure constituents of the mixture <u>at the partial pressure of the pure constituent</u>, the weights being the fractions of each constituent:

$$z(50/50, P, T) = 0.5 * z(O2, 0.5*P, T) + 0.5 * z(He, 0.5*P, T)$$

This has been published on the Atomox website, and reproduced on numerous diving websites, and is the base of many spreadsheets and software. Unfortunately, this is completely wrong. To demonstrate this, remember that the z-factors of reasonably light gases at atmospheric pressure are very close to 1, because at atmospheric pressure, the molecules in the gas don't interact much with each other. Now consider the above equation for a mixture at 100 bar-a of 100 light gases g1, g2, …, g100. We would have:

$$z(mix, 100 \text{ bar-a}, T) = 0.01 * z(g1, 1 \text{ bar-a}, T) + … + 0.01* z(g100, 1 \text{ bar-a}, T)$$

but since the z-factor of each gas at 1 bar-a is very close to 1, according to the above equation, the z-factor of the mixture at 100 bar-a would also be very close to 1. This surely fails to reflect the fact that at 100 bar-a, the molecules in the mixture do interact with each other much more than at 1 bar-a. The Atomox equation also would have us believe that the more the pure constituents in a gas mixture, the more the mixture behaves like an ideal gas. Why would that be???

Other "mixing rule"

Others have been tempted by another wrong approach, which actually, by chance, works quite well with air or nitrox, but not anymore at all once helium is present. This writes, for example for heliox 50:

$$z(50/50, P, T) = 0.5 * z(O2, P, T) + 0.5 * z(He, P, T)$$

This is also a weighted average, but this time of the z-factors of the pure constituents <u>at the total pressure of the mixture</u>. The problem is that this fails to account for the fact that a molecule of O2 and a molecule of He do not interact in the same manner as two molecules of O2 or two molecules of He. The above equation in effect says that O2-He molecules interactions are an average of O2-O2 molecules interactions and He-He molecules interactions. Physically, this does not make sense. One of the reasons this equation works relatively well for air or nitrox is that N2 and O2 molecules are similar in size and weight.

Absolute pressure, gauge pressure and "empty" cylinders

What blending users want in software for input and output is <u>gauge</u> pressures, because that is what they read off their gauges. The equations we use for the calculations, however, take <u>absolute</u> pressures. So it is important not to forget to translate back and forth. Simply put, at atmospheric pressure a gauge reads zero (bar-g) but the actual absolute pressure (at sea level on a fair day) is 1.01325 bar-a. If we zero a digital gauge at 5000m of altitude it will also read zero, although the atmospheric pressure is less than 1.01325 bar-a, so if we really want to be fancy, we can allow the user to adjust for local atmospheric pressure. So bar-g = bar-a – atmospheric pressure. To avoid confusion, we also have to let the users know that what they are entering in and obtaining from the software is gauge pressures. This is actually one of the small problems seen a lot in software, when it says "starting from empty cylinders"!? Unless we vacuum them, they are not empty. If we bleed them to atmosphere, there are still molecules of gas at atmospheric pressure in there and strictly speaking, these molecules should be taken into account in our calculations. Not that the above considerations will change the results very much. But keep in mind that what we are doing here is to apply rather small corrections to the ideal gas model. Accumulating small errors when calculating a small correction can make the small correction very wrong.

Conclusion

This article has presented a uniform notation for all real gas models along with its correct application to molar blending calculations. Guidelines have been proposed for the choice of suitable models for the purpose of closely approximating the actual compressibility factors of trimix gas mixtures. Open source code implementing these models has been offered.

My only hope and purpose for writing this article and offering my code is that it will entice webmasters to publish technically correct information on the topic and help software programmers to check whether their code correctly applies molar calculations and correctly calculates the z-factor of gas mixtures.

Example 2

Joe has 80 bar-g of 10/70 left over from his last dive and wants to turn it into 18/45 at 240 bar-g. He wants to add O2 first, then helium and finally top up with air. Ambient temperature is 25 degC and atmospheric pressure is 1.01 bar-a.

1) Pressures in bar-a:
   a. 80 bar-g -> 81.01 bar-a
   b. 240 bar-g -> 241.01 bar-a
2) Initial mix:
   a. Total number of moles in a unit volume of trimix 10/70 at 25 degC and 81.01 bar-a: the z-factor from GERG-2004 is 1.0467 and so the total number of moles n_i is 3.1223
   b. $n_iO_2 = n_i * 0.1 = 0.3122$
   c. $n_iHe = n_i * 0.7 = 2.1856$
   d. $n_iN_2 = n_i * 0.2 = 0.6244$

Feel free to reproduce this document or link to it, but please notify me you did so at daviddemarneffe@yahoo.com

3) Similarly, for the target mix:
   a. $z = 1.1390$
   b. $nt = 8.536$
   c. $ntO2 = 1.5365$
   d. $ntHe = 3.8412$
   e. $ntN2 = 3.1583$
4) Hence, in moles, Joe has to add:
   a. $dnO2 = ntO2 - niO2 = 1.2243$
   b. $dnHe = 1.6556$
   c. $dnN2 = 2.5339$
5) Since air is the only source of N2, let's figure how many moles of air need to be added in order to add the dnN2 moles of N2, and how many moles of O2 are added in the process, and so how many moles need to be added from the pure O2 bank?
   a. $dnAir = dnN2 / 0.791 = 3.2034$
   b. $dnO2\_from\_air = dnAir * 0.209 = 0.6695$
   c. $dnO2\_from\_O2\_bank = dnO2 - dnO2\_from\ air = 0.5548$
6) Step 1: after adding pure O2 to initial mix:
   a. $n1 = ni + dnO2\_from\_O2\_bank = 3.6771$ (total moles of mix)
   b. $n1O2 = niO2 + dnO2\_from\_O2\_bank = 0.867$
   c. $n1He = niHe = 2.1856$
   d. $f1O2 = n1O2 / n1 = 0.2358$ (fraction of O2 in the mix)
   e. $f1He = n1He / n1 = 0.5943$ (fraction of He in the mix)
7) Knowing the gas composition and total number of moles from step 6, we can calculate the pressure and z-factor using the same iterative process as in example 1:
   a. Pressure after step 1: $P1 = 95.9$ bar-a ($= 94.89$ bar-g)
   b. O2 added at step 1: $PO2 = 94.89$ bar-g $- 80$ bar-g $= 14.89$ bar
   c. So Joe has to add 14.89 bar of pure O2 to a total of 94.89 bar-g on his gauge.
8) Step 2: add helium
   a. $n2 = n1 + dnHe = 5.3327$ (total moles of mix)
   b. $n2O2 = n1O2 = 0.867$
   c. $n2He = n1He + dnHe = ntHe = 3.8412$
   d. $f2O2 = n2O2 / n2 = 0.1626$ (fraction of O2 in the mix)
   e. $f2He = n2He / n2 = 0.72031$ (fraction of He in the mix)
9) Knowing the gas composition and total number of moles from step 8, we can calculate the pressure and z-factor using the same iterative process as in example 1:
   a. Pressure after step 2: $P2 = 143.06$ bar-a ($= 142.05$ bar-g)
   b. $PHe = P2 - P1 = 142.05$ bar-g $- 94.89$ bar-g $= 47.16$ bar
   c. So Joe has to add 47.16 bar of helium to a total of 142.05 bar-g on his gauge.
10) And don't let Joe forget to top up with air to 240 bar-g…