`Brain` of the Gasblender 1.0 program

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1 Intro

Here we intend to briefly explain how the `Gasblender` algorithms work. The game is to create a mixture of N_2, O_2 and He with wanted composition and pressure. You can either use an empty bottle or some initial mixture where gases just need to be added in the right amount. The program calculates how much He, O_2 and air (it can be also other mixture of N_2 and O_2, *i.e.* nitrox top–off gas) you have to put in your bottle to get the desired mixtures. For this there are two options you can use ideal gas model or real gas model. Ideal gas model does not give the correct values at high pressures, therefore it is wise to use the real gas model at higher pressures, both are implemented in the program.

2 Calculations using the Ideal Gas Model

The ideal gas model connects the pressure (P) of the gas mixture with its molar density ($\rho = \frac{n}{V}$ [mol/L]) and temperature (T):

$$P = \rho R T \,, \tag{1}$$

where R is the ideal gas constant $R = 8.314\ \frac{\mathrm{J}}{\mathrm{molK}}$. The equation is also valid for the partial pressures and densities *i.e.*:

$$P_i = \rho_i R T \,. \tag{2}$$

This means that is valid for every component i separately, where $P = \sum_i P_i$ and $\rho = \sum_i \rho_i$. From this it can be concluded that the molar composition of the mixture is directly connected to the partial pressure of each component:

$$P_i = X_i P \,, \tag{3}$$

where X_i represents the mole fraction of the component i and P is the total pressure of the mixture.

As program input we have the initial pressure P^{ini} of the mixture and the initial composition *i.e.* $X^{ini}_{O_2}$, X^{ini}_{He}, while $X^{ini}_{N_2} = 1 - X^{ini}_{O_2} - X^{ini}_{He}$. In the analogue way the final mixture parameters are defined: P^{final}, $X^{final}_{O_2}$, X^{final}_{He}, while $X^{final}_{N_2} = 1 - X^{final}_{O_2} - X^{final}_{He}$. These are all users inputs.

2.1 Mixing - Calculation of the Gas Pressures Needed to Create Final Mixture

The first option the program offers to the user is the usual mixing, where the calculation of pressures of gases that you need to add to create final mixture is done. The

`GasBlender::calculate` method calculates the result for the mixing regime. This is done through `do while` loop. First the amount of He that we have to add is calculated:

$$P_{He}^{add} = P^{final} X_{He}^{final} - P^{ini} X_{He}^{ini} \,. \tag{4}$$

If P_{He}^{add} is negative we have to reduce the initial pressure, P^{ini}, by the $P^{reduce} = \frac{P_{He}^{add}}{X_{He}^{ini}}$, because the partial pressure He is higher in the initial mixture than in the final mixture. The initial pressure is not reduced at this time, but P^{reduce} value is saved. Next the amount of N_2 to add is calculated:

$$P_{N_2}^{add} = P^{final} X_{N_2}^{final} - P^{ini} X_{N_2}^{ini} \,. \tag{5}$$

But as we are not filling the pure N_2 we have to calculate how much air/top off gas do we need:

$$P_{top-off}^{add} = \frac{P_{N_2}^{add}}{1 - X_{O_2}^{top-off}} \,, \tag{6}$$

where $X_{O_2}^{top-off}$ is the molar fraction of O_2 in the top–off gas, in the case of air $X_{O_2}^{top-off} = 0.21$. Again if the $P_{top-off}^{add}$ value is negative, we have to reduce the initial pressure of the mixture by $P^{reduce} = \frac{P_{N_2}^{add}}{X_{N_2}^{ini}}$, this is compared with the P^{reduce} value calculated for He, if this is more negative this value is saved, meaning that we have to reduce more due to the N_2 in comparison to He. The last thing is to calculate the amount of oxygen we need to add:

$$P_{O_2}^{add} = P^{final} X_{O_2}^{final} - P^{ini} X_{O_2}^{ini} - P_{top-off}^{add} X_{O_2}^{top-off} \,. \tag{7}$$

The last term in the previous equation $P_{top-off}^{add} X_{O_2}^{top-off}$ is there because we are adding some O_2 with air/top–off gas, therefore smaller amount of O_2 is needed. Combining the Eqns. 7, 6, 5, 4 we get the following equation, which is also used in the program for the calculation of O_2 to add:

$$P_{O_2}^{add} = \frac{P^{final}(X_{O_2}^{final} - X_{O_2}^{top-off}) + P^{ini}(X_{O_2}^{top-off} - X_{O_2}^{ini}) - P_{He}^{add} X_{O_2}^{top-off}}{1 - X_{O_2}^{top-off}} \,. \tag{8}$$

For the last time we need to check if the $P_{O_2}^{add}$ is negative, and if it is, then we need to calculate the $P^{reduce} = \frac{P_{O_2}^{add}}{X_{O_2}^{ini}}$ and if this is the lowest of all P^{reduce} values this one is saved. Now we are able to calculate the new initial pressure if the reduce of the initial pressure is needed:

$$P_{new}^{ini} = P^{ini} + P^{reduce} \,, \tag{9}$$

where we use the saved P^{reduce} value, note that P^{reduce} is added but as it is negative the new initial pressure is smaller. With this we are at the end of `do while` loop, and this loop is repeated until the $P^{reduce} = -0$, while P_{new}^{ini} must be positive. If P_{new}^{ini} during the looping becomes negative than the final mixture can not be created using selected top–off gas. When the `do while` loop ends you have your result as P_{He}^{add}, $P_{O_2}^{add}$, and $P_{top-off}^{add}$.

2.2 Best Mix - Calculation of the $He/O_2/N_2$ Gas Mixture Composition Needed to Create Final Mixture

This option calculates the composition of the $He/O_2/N_2$ mixture with which the user fills up the tank. The best mix is calculated with `GasBlender::bestmix` method. Here we again need the `do while` loop to calculate if we need to reduce the initial pressure to make the final mixture. The loop works in similar way than in previous example. First

the amount of He to add is calculated using the equation 4, and if the P_{He}^{add} is negative the $P^{reduce} = \frac{P_{He}^{add}}{X_{He}^{ini}}$ is calculated and saved, as already explained. Next the same thing is done for O_2, using the following equation:

$$P_{O_2}^{add} = P^{final} X_{O_2}^{final} - P^{ini} X_{O_2}^{ini} \,, \tag{10}$$

and if $P_{O_2}^{add}$ is negative the $P^{reduce} = \frac{P_{O_2}^{add}}{X_{O_2}^{ini}}$ is calculated – if this value is smaller than the one for He this one is saved. The last thing is the calculation of $P_{N_2}^{add}$ with equation 5 and off course if $P_{N_2}^{add}$ is negative $P^{reduce} = \frac{P_{N_2}^{add}}{X_{N_2}^{ini}}$ is again calculated. With the smallest P^{reduce} the new initial pressure is calculated using equation 9. This is the end of the `do while` loop which is repeated until the $P^{reduce} = -0$, while P_{new}^{ini} must be positive. When the loop ends the best mix composition is calculated:

$$X_{He}^{best-mix} = \frac{P_{He}^{add}}{P^{final} - P^{ini}} \tag{11}$$

$$X_{O_2}^{best-mix} = \frac{P_{O_2}^{add}}{P^{final} - P^{ini}} \tag{12}$$

$$X_{N_2}^{best-mix} = 1 - X_{O_2}^{best-mix} - X_{He}^{best-mix} \tag{13}$$

With this equations you get the composition of the best mix.

3 Real Gas Model: GERG2004

Why real gas model? The ideal gas model works fine for the pressure and temperatures around ambient. But as the bottles are filled with pressures of around 200 bars, the error made with the ideal gas model could be quite big. Therefore we decided to implement also the real gas model. The ideal gas equation is re-written with the use of compressibility factor which tells the difference between ideal and real gas:

$$P = Z\rho RT \,, \tag{14}$$

where Z is the compressibility factor. So actually what we need from our real gas model is the Z factor. Next we will explain the model used and how the Z is calculated and then it will be shown how it is applied in the GasBlender program.

One of the best real gas model was developed by European Gas Research Group (GERG). The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures is used for the Real Gas properties calculation[i]. In this model the Helmholtz free energy is fitted using huge amounts of experimental data for gases and gas mixtures. From the Helmholtz free energy all other thermodynamical properties are derived. The following two equations are the basis of the model. First the reduced Helmholtz free energy is divided to ideal and residual contributions:

$$\alpha(\delta, \tau, \bar{x}) = \alpha^o(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x}) \tag{15}$$

α ... reduced Helmholtz free energy
α^o ... ideal part of the reduced Helmholtz free energy

[i] O. Kunz et al., *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, Dsseldorf, 2007. `http://www.gerg.info/publications/tm/tm15_04.pdf`

α^r ... residual part of the reduced Helmholtz free energy
T ... temperature
ρ ... molar density
$\tau = \frac{T_r}{T}$ ... inverse reduced temperature
$\delta = \frac{\rho}{\rho_r}$ ... reduced density
$\bar{x}$ ... molar composition vector

What we only need from our real gas model is to calculate the pressures of the N_2, O_2, He gas mixture. This can be done by the calculation of the compressibility factor $Z = \frac{P}{\rho RT}$, where P is the pressure and R is the ideal gas constant. It does not depend on the ideal part of the reduced Helmholtz free energy, therefore we are only interested in the residual part:

$$\alpha^r(\delta, \tau, \bar{x}) = \sum_{i=1}^{N} x_i \left(\alpha^r_{oi}(\delta, \tau)\right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\alpha^r_{ij}(\delta, \tau)\right) \tag{16}$$

α^r_{oi} ... residual part of the reduced Helmholtz free energy of component i (of the pure substance)
α^r_{ij} ... part of the departure function developed for the binary mixtures using experimental mixture data
F_{ij} ... factor of the binary specific departure function

Class `Gerg2004` is used for the application of the real gas model GERG2004.

Z is calculated by `Gerg2004::Z_GERG2004` method by iteration. First Z is set to 1. Than density is calculated $\rho = \frac{P}{(ZRT)}$. Than Z is calculated using eq. 17. This is iterated to a preset accuracy ΔZ.

$$Z(\delta, \tau, \bar{x}) = 1 + \delta \alpha^r_\delta \tag{17}$$

Z ... compressibility factor
$\tau = \frac{T_r}{T}$ ... inverse reduced temperature
$\delta = \frac{\rho}{\rho_r}$ ... reduced density
$\bar{x}$ ... molar composition vector
α^r_δ ... derivative of the residual part of reduced Helmholtz free energy (α^r) with respect to reduced density δ

For calculating Z, τ and δ are needed. Thus we need to calculate T_r and ρ_r, as T is input temperature set by the user and ρ is calculated by iteration of Z.

T_r is calculated by `Gerg2004::temp_r` method using eq. 18.

$$T_r(\bar{x}) = \sum_{i=1}^{N} x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2 x_i x_j \beta_{T,ij} \gamma_{T,ij} \cdot \frac{x_i + x_j}{\beta^2_{T,ij} x_i + x_j} \cdot (T_{c,i} \cdot T_{c,j})^{0.5} \tag{18}$$

N ... number of components
x_i ... mole fraction of component i
$T_{c,i}$ ... critical temperature for component i (Table A3.5 of the GERG2004 monograph[i])
$\beta_{T,ij}$ and $\gamma_{T,ij}$ ... parameters fitted to data for binary mixtures (Table A3.8 of the GERG2004

monograph[i])

ρ_r is calculated by `Gerg2004::dens_r` method using eq. 19.

$$\frac{1}{\rho_r(\bar{x})} = \sum_{i=1}^{N} x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j \beta_{\nu,ij} \gamma_{\nu,ij} \cdot \frac{x_i + x_j}{\beta_{\nu,ij}^2 x_i + x_j} \cdot \frac{1}{8} \cdot \left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3 \quad (19)$$

$\rho_{c,i}$ ... critical density for component i (Table A3.5 of the GERG2004 monograph[i])
$\beta_{\nu,ij}$ and $\gamma_{\nu,ij}$ ... parameters fitted to data for binary mixtures (Table A3.8 of the GERG2004 monograph[i])

What is now left to do is to calculate α_δ^r, this is done by the `Gerg2004::dalphar_ddelta_mix` method using the following equation:

$$\alpha_\delta^r = \sum_{i=1}^{N} x_i \left(\frac{\partial \alpha_{oi}^r(\delta,\tau)}{\partial \delta} \right)_\tau + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial \alpha_{ij}^r(\delta,\tau)}{\partial \delta} \right)_\tau \quad (20)$$

α_{oi}^r ... residual part of the reduced Helmholtz free energy of component i (of the pure substance)
α_{ij}^r ... part of the departure function developed for the binary mixtures using experimental mixture data
F_{ij} ... factor of the binary specific departure function

No departure functions were developed for the N_2, O_2, He mixtures, therefore the F_{ij} coefficients for the N_2-O_2, N_2-He and He-O_2 are equal to 0. This means that the second part of eq. 20 is 0, and only derivative of the α_{oi}^r needs to be calculated. And this is done for the three components with the following methods: `Gerg2004::dalphar_ddelta_N2`, `Gerg2004::dalphar_ddelta_O2`, and `Gerg2004::dalphar_ddelta_He`. The derivatives are calculated by the following equation:

$$\left(\frac{\partial \alpha_{oi}^r(\delta,\tau)}{\partial \delta} \right)_\tau = \sum_{k=1}^{K_{Pol,i}} n_{oi,k} d_{oi,k} \delta^{d_{oi,k}-1} \tau^{t_{oi,k}} + \sum_{k=K_{Pol,i}+1}^{K_{Pol,i}+K_{Exp,i}} n_{oi,k} \delta^{d_{oi,k}-1} \left(d_{oi,k} - c_{oi,k} \delta^{c_{oi,k}} \right) \tau^{t_{oi,k}} e^{(-\delta^{c_{oi,k}})} \quad (21)$$

K_{Pol} ... number of polynomial terms used in the calculation of the derivative
K_{Exp} ... number of exponential terms used in the calculation of the derivative
n_{oi} ... coefficient
c_{oi} ... density exponent
d_{oi} ... density exponent
t_{oi} ... temperature exponent
The values of these exponents can be found in the GERG2004 monograph[i] in tables: O_2: Table A3.2, N_2: Table A3.3, He: Table A3.4.

So, now when GERG-2004 and calculation of Z is explained we can move on to its application in the program.

3.1 Mixing - Calculation of the Gas Pressures Needed to Create Final Mixture

The mixing calculation is in the first part similar to the calculation using the ideal gas model. In the ideal gas case we could directly use partial pressures for the calculation of the

composition, because in the ideal gas model the molar fraction is directly proportional to the partial pressure of the certain gas, see equation 3. In the real gas model this is not the case, due to the Z factor, which is a function of pressure, temperature, and composition. Therefore here we will directly use moles[ii] instead of pressure for the calculation of the compositions.

$$X_i = \frac{\rho_i}{\rho} \tag{22}$$

The above equation defines the molar fraction of the component i, X_i, which equals to the molar density of the gas i, ρ_i, divided by the molar density of all gases in the mixture, $\rho = \sum_i \rho_i$. Initial molar density in the initial mixture for the real gas is calculated by the following equation:

$$\rho^{ini} = \frac{P^{ini}}{ZRT}\,. \tag{23}$$

Z is off-course calculated by calling the `Gerg2004::Z_GERG2004`. In the same way the molar density of the final mixture is calculated:

$$\rho^{final} = \frac{P^{final}}{ZRT}\,. \tag{24}$$

Now we are ready to make the `do while` loop for calculating how much of each gas is needed and if the reduction of the initial pressure have to be done. The procedure is basically the same as in the case of ideal gas except that here we are using molar densities instead of pressures – this is also done by the `Gasblender:calculate` method if the real gas radio button is checked. First the molar density of He that have to be added is calculated:

$$\rho^{add}_{He} = \rho^{final} X^{final}_{He} - \rho^{ini} X^{ini}_{He} \tag{25}$$

The above equation is the analogue of the equation 4, just that the P is replaced with ρ. Check if the reduce of initial pressure is needed has to be done. If ρ^{add}_{He} is negative $\rho^{reduce} = \frac{\rho^{add}_{He}}{X^{ini}_{He}}$ is calculated and saved. In the analogue way to equation 5 we can rewrite equation for adding N_2:

$$\rho^{add}_{N_2} = \rho^{final} X^{final}_{N_2} - \rho^{ini} X^{ini}_{N_2}\,. \tag{26}$$

But as we are not filling the pure N_2 we have to calculate how much air/top off gas do we need:

$$\rho^{add}_{top-off} = \frac{\rho^{add}_{N_2}}{1 - X^{top-off}_{O_2}}\,, \tag{27}$$

Again if $\rho^{reduce} = \frac{\rho^{add}_{N_2}}{X^{ini}_{N_2}}$ is negative and smaller than previous one this one is saved. Next thing is to calculate how much more O_2 is needed, analogy with equation 8 pops out here[iii]:

$$\rho^{add}_{O_2} = \frac{\rho^{final}(X^{final}_{O_2} - X^{top-off}_{O_2}) + \rho^{ini}(X^{top-off}_{O_2} - X^{ini}_{O_2}) - \rho^{add}_{He} X^{top-off}_{O_2}}{1 - X^{top-off}_{O_2}}\,. \tag{28}$$

If $\rho^{add}_{O_2}$ is negative rho^{reduce} has to be recalculated $\rho^{reduce} = \frac{\rho^{add}_{O_2}}{X^{ini}_{O_2}}$ and compared to the previous two values, the smallest is than used for the new initial molar density calculation:

$$\rho^{ini}_{new} = \rho^{ini} + \rho^{reduce}\,. \tag{29}$$

[ii] Actually we will use molar density instead of number of moles, but as the volume of the tank is constant the number of moles can be replaced with molar density $\rho = \frac{n}{V}$, note that in the code ρ is replaced with n.

[iii] If you do not know how we got this equation look under the ideal gas model.

With this we are at the end of `do while` loop, and this loop is repeated until the $\rho^{reduce} = -0$, while ρ^{ini}_{new} must be positive. If ρ^{ini}_{new} during the looping becomes negative than the final mixture can not be created using selected top–off gas. When the `do while` loop ends you have ρ^{add}_{He}, $\rho^{add}_{O_2}$, and $\rho^{add}_{top-off}$. But oppositely to the ideal gas model our job is not totally finished here because we need to calculate the pressures to add from these molar density values. Furthermore because we are dealing with the real gases it is also important in which order are we filling our gas bottle. The user has two options *i*) to fill He first, then O_2 and at the end top-off gas or *ii*) to fill O_2 first, than He and top-off. If the `He first` checkbox is checked, than the *i*) is used otherwise *ii*) is taken, logically. So, we can now calculate this:

$$\rho^{add}_{He} = \rho^{final} X^{final}_{He} - \rho^{ini} X^{ini}_{He} \tag{30}$$

$$\rho^{add}_{O_2} = \rho^{final} X^{final}_{O_2} - \rho^{ini} X^{ini}_{O_2} \tag{31}$$

$$\rho^{add}_{N_2} = \rho^{final} X^{final}_{O_2} - \rho^{ini} X^{ini}_{N_2}\,, \tag{32}$$

which is how much of each gas in molar densities do we really need. If the reduction of initial pressure was needed we also have to calculate the new initial pressure by the iteration of $P^{ini} = Z\rho^{ini}RT$ and Z (the compressibility factor changes if the pressure changes). Now we will firs follow procedure *i*) – He first. So lets add He:

$$\rho^{i} = \rho^{ini} + \rho^{add}_{He}\,, \tag{33}$$

ρ^i is the molar density after He addition. Obviously after addition of He the composition of the mixture is changed and therefore we need to recalculate it for the use in the Z calculation:

$$X^{i}_{He} = \frac{\rho^{ini}_{He} + \rho^{add}_{He}}{\rho^{i}} \tag{34}$$

$$X^{i}_{O_2} = \frac{\rho^{ini}_{O_2}}{\rho^{i}} \tag{35}$$

$$X^{i}_{N_2} = 1 - X^{i}_{He} - X^{i}_{O_2}\,. \tag{36}$$

Now we can again iterate $P^i = Z\rho^i RT$ and Z to get the pressure after the He addition, and finally the pressure of He to add can be calculated:

$$P^{add}_{He} = P^{i} - P^{ini}\,. \tag{37}$$

Few more things and we are done – don't give up, be patient ;)
Next we have to calculate how much O_2 do we need from filling-in the pure oxygen:

$$\rho^{add-pure}_{O2} = \rho^{add}_{O_2} - \frac{\rho^{add}_{N_2}}{1 - X^{top-off}_{O_2}}\,, \tag{38}$$

the second part of this equation represents the O_2 added with top-off gas. So lets add this O_2:

$$\rho^{ii} = \rho^{i} + \rho^{add-pure}_{O_2}\,, \tag{39}$$

where ρ^{ii} is the molar density after addition of O_2. Composition has to be again recalculated and we again repeat the iteration procedure to get the P^{ii}, which is the pressure after addition of pure O_2, and now we are ready to calculate the pressure of O_2 to add:

$$P^{add}_{O_2} = P^{ii} - P^{i}\,. \tag{40}$$

Because we know the final pressure of the mixture we now just fill up the bottle to the final pressure with the top-off gas:

$$P_{top-off}^{add} = P^{final} - P^{ii}\,, \tag{41}$$

and we are finished, finally! But this was just the `He first` procedure. But fortunately the `oxygen first` procedure uses the same equations. We just have to first add the pure O_2 and recalculate the composition and the pressure after O_2 addition. And in the next step we add He and do the same for He, what is left is the top-off gas. Now we are really at the end just one more section to go!

3.2 Best Mix - Calculation of the $He/O_2/N_2$ Gas Mixture Composition Needed to Create Final Mixture

We will try to go fast through this, because now you are probably already an expert of gas mixing, and also you probably have a bit of a headache of all these equations. So here we try to do the best mixture, which is the mixture of $He/O_2/N_2$ with which you fill your bottle to the P^{final} and voila you have your final mixture. Off-course we use here the real gas model, for this `GasBlender::bestmix` method is used. We will start in the same way as in the previous section by calculating the molar density of our final and initial mixture using equations 23 and 24. Now when we have our molar densities, we can start we the `do while` loop to determine the amount of each gas that we need and if the initial pressure reduction is needed. The loop is basically the same as in the ideal gas best mix case, the difference is that in the equations the pressures (P) have to be replaced by the molar densities (ρ). The loop is solved by going through equations 31, 32, and 32 step by step, where at each step if the ρ^{add} values are negative we have to calculate the ρ^{reduce} value and the smallest of the reduce values is used for the new initial molar density calculation with equation 29. The `do while` loop is finished when the $\rho^{reduce} = -0$, while ρ_{new}^{ini} must be positive. If the the initial molar density needed to be reduce, we have to recalculate the initial pressure with $P^{ini} = Z\rho^{ini}RT$, Z iteration. What is left to do is to calculate the best mix composition:

$$X_{He}^{best-mix} = \frac{\rho_{He}^{add}}{\rho^{final} - \rho^{ini}} \tag{42}$$

$$X_{O_2}^{best-mix} = \frac{P_{O_2}^{add}}{\rho^{final} - \rho^{ini}} \tag{43}$$

$$X_{N_2}^{best-mix} = 1 - X_{O_2}^{best-mix} - X_{He}^{best-mix} \tag{44}$$

3.3 Conclusions

We have finally finished with all this equations. If you have any questions, improvements, or corrections regarding the GasBlender 1.0 program, its manual or this document you can contact the authors directly through e-mails: `alan.bizjak@gmail.com` or `gregor.trefalt@gmail.com`. The updates, new versions and other cool stuff is available on the website www.neki.com.

PS: We hope that your brain didn't suffer to much as you were getting to know GasBlender's `Brain`.