# Equação de Estado para a Atmosfera do Tipo Van der Waals <br> Van der Waals-like State Equation for Atmosphere 

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#### Abstract

Resumo Neste artigo, analisamos primeiro a atmosfera como uma mistura de gases por unidade de massa, que é governada pela equação de Van der Waals, considerando os principais componentes do ar e suas respectivas propriedades críticas (temperatura crítica $T_{C}$ e pressão crítica $p_{C}$ ). Depois de ajustar as constantes correspondentes e chamá-las de $I$ e $D$, encontramos a equação de estado de Van der Waals para a atmosfera neste contexto. Em seguida, analisamos a ordem de magnitude dos termos nessa equação e propomos uma equação de estado de forma semelhante a Van der Waals, dependendo apenas de $D$, que chamamos de equação de estado $W D$. Além disso, consideramos uma abordagem física para a equação de Van der Waals para a atmosfera, estudando os termos de pressão relativos às forças intermoleculares de repulsão e atração no ar, e mais uma vez encontramos a equação do estado anterior. Com esta nova proposta, verificamos que a temperatura potencial e a temperatura potencial equivalente são válidas para as mesmas expressões que as estabelecidas na termodinâmica atmosférica sob a análise da lei dos gases ideais. No entanto, descobrimos correções que dependem de $D$ tanto na forma alternativa da primeira lei da termodinâmica quanto na temperatura virtual.


Palavras-chave: Componentes do Ar; Temperatura; Termodinâmica


#### Abstract

In this paper, we first analyze the atmosphere as a gas mixture per unit mass, which is governed by Van der Waals equation, considering the main components of the air and their respective critical properties (critical temperature $T_{C}$ and critical pressure $p_{C}$ ). After adjusting the corresponding constants and calling them $I$ and $D$, we find Van der Waals state equation for the atmosphere in this context. Next, we analyze the order of magnitude of the terms in that equation and propose a Van der Waals-like form state equation depending only on $D$, which we call $W D$ state equation. Additionally, we consider a physical approach for Van der Waals equation for the atmosphere, studying the pressure terms concerning intermolecular forces of repulsion and attraction in the air, and once again we find the previous $W D$ state equation. With this new proposal, we verify that the potential temperature and the equivalent potential temperature hold for the same expressions as those set forth in atmospheric thermodynamics under the analysis of the ideal gas law. However, we discover corrections that depend on $D$ in both the alternative form of the first law of thermodynamics and the virtual temperature.


Keywords: Components of the Air; Temperature; Thermodynamics

## 1 Introduction

One of the main goals of thermodynamics is the search for the state equation of the system being studied (Luiz, 2007). A state of thermodynamic equilibrium in a homogeneous fluid is characterized by a state equation which depends on thermodynamic variables pressure $P$, volume $V$ and temperature $T$, through a function $f(P, V, T)=0$ (Young et al., 1989). Gases with the simplest possible thermodynamic behavior can therefore be treated satisfactorily as an ideal gas, obeying the equation $P V=m R T$, where $R$ is the constant of the ideal gases for 1 kg of the gas. In other words, the equation of the ideal gas is written as $p V=n R^{*} T$, where the number of moles $n$ is defined by the ratio between the mass $m$ and the molecular weight $M$ of the gas in grams, $n=m / M$, with the universal constant for one mole of the gas $R^{*}$. Considering the unitary mass of a gas and its specific volume $\alpha=V / m$, the equation of the ideal gas is also written as

$$
\begin{equation*}
p \alpha=R T \tag{1}
\end{equation*}
$$

The atmosphere is studied as an ideal gas, since the air is made up of gases, which individually obey the ideal gas law, and this process is a good approximation according to Wallace \& Hobbs (2006). Due to the fact that real gases do not strictly follow the equation of ideal gases, Van der Waals (1873) proposed a state equation in which he presented two constants that corrected the ideal gas equation. This equation is described as

$$
\begin{equation*}
\left[p+a\left(\frac{n}{V}\right)^{2}\right][V-n b]=n R^{*} T \tag{2}
\end{equation*}
$$

where constants $a$ and $b$ can be determined from the critical temperature and pressure (Smith et al., 2005), as will be shown in the Equation (5). In this case, the first correction in the pressure term has to do with intermolecular attractions, while the second correction refers to the volume of the molecules. For the unitary mass of a gas and its specific volume, the Van der Waals equation (Equation 2) is expressed as

$$
\begin{equation*}
\left[p+\frac{a}{\alpha^{2}}\right][\alpha-b]=R T \tag{3}
\end{equation*}
$$

In the pressure-volume function diagram for a Van der Waals gas there is a critical point where the three roots of Equation (2) coincide, which corre-
sponds to the change in concavity at that point with the critical temperature $T=T_{C}$, where one can see a second-order phase transition (Smith et al., 2005) that implies the following conditions:

$$
\begin{equation*}
\left(\frac{\partial p}{\partial V}\right)_{T_{c}}=0, \quad\left(\frac{\partial^{2} p}{\partial V^{2}}\right)_{T_{c}}=0 \tag{4}
\end{equation*}
$$

From Equation (3) and Equation (4), the constants $a$ and $b$ for a gas are determined by

$$
\begin{equation*}
a=\frac{27\left(R T_{C}\right)^{2}}{64 p_{C}}, \quad b=\frac{R T_{C}}{8 p_{C}} \tag{5}
\end{equation*}
$$

where $p=p_{C}$ is the critical pressure of the gas.
The determination of critical properties for mixtures represents some difficulty as to obtaining the experimental data, for each mixture in each one of its possible compositions. Although there is no theoretical basis for the extension of the generalized correlations for mixtures, many results can be obtained through group contribution methods, from pseudocritical parameters resulting from the simple rule of linear mixtures, known as Kay's Rule and described as (Kay, 1936; Joback \& Reid, 1983; Jalowka \& Daubert, 1986; Daubert \& Bartakovits, 1989)

$$
\begin{equation*}
C P_{j}=\sum_{i}^{\kappa} X_{i} C P_{i} \tag{6}
\end{equation*}
$$

In this equation, $C P_{j}$ represents the critical property of the mixture $j, C P_{i}$ and $X_{i}$ being the critical property and the fraction of the $i$-th component of this mixture, whereas $k$ is the number of components in $j$.

This paper first considers Van der Waals equation for the atmosphere, from the gases that compose air, using the critical temperature and the critical pressure of each constituent gas. In this sense, Van der Waals specific constants for the atmosphere are determined and denominated $I$ and $D$. From this equation, a mathematical approach is considered and another state equation for the atmosphere is calculated, called $W D$ state equation, which depends on only constant $D$. In a different approach, taking into account the terms of pressure related to the intermolecular interactions, the $W D$ state equation is once
again calculated. With this new formulation for the atmosphere, the alternative form of the first law of thermodynamics, virtual temperature, potential temperature and equivalent potential temperature are computed. Both the alternative form of the first law of thermodynamics and the virtual temperature present a correction term in relation to their equivalent expressions to the atmosphere as an ideal gas, which depend on the constant $D$. However, the equations for the potential temperature and the equivalent potential temperature remain unchanged when compared to the equations equivalent to the atmosphere as an ideal gas. Finally, when we consider $D=0$ in the expressions determined in this new proposal, the alternative form of the first law of thermodynamics and the virtual temperature, corresponding to the ideal gas law for the atmosphere, are retrieved.

## 2 Van der Waals Equation for Atmosphere

We analyzed the atmosphere as a mixture, whose components are described in Table 1, where the critical temperature $T_{c}$ and the critical pressure $p_{c}$ of the air are the critical properties determined by Kay's rule (Kay, 1936). The concentration of the gases for the main components come from the National Aeronautics and Space Administration (NASA, 2016), and the information about the gases with composition in the trace were provided by Manchester Metropolitan University (Trace Gases, 2010).

We varied the percentage of water content from $0.0 \%$ (dry air) up to $7.0 \%$ (extremely humid air), with an increment of $\Delta=0.1$ proportionally varying the gases of the atmosphere in order to include water vapor. Then, we obtained the values for $T_{c}$ and $p_{c}$ for the atmosphere, corresponding to each one of these variations in water content. After that, we used the solutions for Van der Waals equation (Equation 5) and calculated the corresponding values of $a$ and $b$. With these results, we applied subsequently the simple linear regression model to the values of $a$ and $b$ and found the relation

$$
\begin{equation*}
a=0.685830-15057.0 b \tag{7}
\end{equation*}
$$

that is shown in Figure 1. Here, the adjustment measure of the model is high $\left(R^{2}=0.9935\right)$.

| Compound | $T_{c}(K)$ | $P_{c}$ (Bar) | Concentration (\%) |
| :---: | :---: | :---: | :---: |
| Nitrogen* | 126.20 | 34.00 | 78.084 |
| Oxygen ${ }^{\text {* }}$ | 154.60 | 50.43 | 20.946 |
| Argon* | 150.90 | 48.98 | 0.934 |
| Carbon Dioxide * | 304.20 | 73.83 | 0.0314 |
| Neon' ${ }^{\text {c }}$ | 44.44 | 27.20 | 0.001818 |
| Methane ${ }^{\text {P }}$ | 190.60 | 45.99 | 0.0002 |
| Helium ${ }^{\text {* }}$ | 5.20 | 2.28 | 0.000524 |
| Krypton* | 209.40 | 55.02 | 0.000114 |
| Hydrogen* | 33.19 | 13.13 | 0.00005 |
| Ozone ${ }^{\dagger}$ | 261.05 | 55.32 | 0.000007 |
| Xenon* | 289.70 | 58.40 | 0.0000087 |
| Nitrous Oxide (N2O)* | 309.60 | 72.45 | 0.00003 |
| Nitrogen Dioxide* | 430.75 | 78.84 | 0.000002 |
| lodine ${ }^{\text {t }}$ | 819.15 | 117.00 | 0.000001 |
| Carbon Monoxide* | 132.90 | 34.99 | 0.00001 |
| Water* | 647.10 | 220.55 | From 0.0 to 7.0 |
| Air ( $79 \% \mathrm{~N} 2$ and $21 \%$ O2) ${ }^{*}$ | 132.2 | 37.45 | 99.9982 |

Table 1 Chemical species components of the air with their specific critical pressures and temperatures and mean concentration of the Earth's atmosphere. From *Smith et al. (2005), and **Guggenheim (1945), ${ }^{\dagger}$ Jenkins \& Birdsall (1952) and ${ }^{\dagger}$ Laird (1997).

As the variation of the $b$ values cover a small range from $3.47361 \times 10^{-5} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$ to $3.66103 \times 10^{-5}$ $m^{3} \mathrm{~mol}^{-1}$, we chose the mean value of $b$ and presented it as the constant $D$ for the atmosphere, that is,

$$
\begin{equation*}
D=3.55832 \times 10^{-5} \mathrm{~m}^{3} \mathrm{~mol}^{-1} \tag{8}
\end{equation*}
$$

We replaced $b$ in Equation (7) by the value of constant $D(8)$ found and computed the corresponding value of $a$, which we called constant $I$, i. e.,

$$
\begin{equation*}
I=1.50054 \times 10^{-1} \mathrm{Jm}^{3} \mathrm{~mol}^{-2} \tag{9}
\end{equation*}
$$

Therefore, we wrote an equation with these new constants $I$ and $D$ designated by

$$
\begin{equation*}
\left[p+I\left(\frac{n}{V}\right)^{2}\right][V-n D]=n R^{*} T \tag{10}
\end{equation*}
$$

and we established the Van der Waals equation for the atmosphere.


Figure 1
Simple linear regression of values $a$ and $b$.

## 3 Van der Waals-like State Equation

We considered the atmosphere as a system per unit mass and reproduced Van der Waals's equation for the atmosphere (Equation 10) in the form

$$
\begin{equation*}
p=R T\left(\frac{1}{\alpha}\right)+p D\left(\frac{1}{\alpha}\right)-I\left(\frac{1}{\alpha}\right)^{2}+I D\left(\frac{1}{\alpha}\right)^{3} \tag{11}
\end{equation*}
$$

in which we observed that the first term corresponds to the ideal gas, and that the corrections appear in the other three terms. Based on an analysis of the order of magnitude of pressure values for the atmosphere, as shown in Table 2, we neglected the last term, and rewrote Equation (11) as a quadratic function in $\alpha$,

$$
\begin{equation*}
\alpha^{2}-\left(D+\frac{R T}{p}\right) \alpha+\frac{I}{p}=0 \tag{12}
\end{equation*}
$$

It is verified in this equation that for atmosphere the order of magnitude for $D+(R T / p)$ is $10^{-1}$, whereas for $I / p$ it is $10^{-3}$. Therefore, the roots of Equation (12) are approximately the same as those in the quadratic function described below, that corresponds the Equation (12) in without the term $L / p$, i. e.,

$$
\begin{equation*}
\alpha^{2}-\left(D+\frac{R T}{p}\right) \alpha=0 \tag{13}
\end{equation*}
$$

| Pressure terms | $R T\left(\frac{1}{\alpha}\right)$ | $p D\left(\frac{1}{\alpha}\right)$ | $I\left(\frac{1}{\alpha}\right)^{2}$ | $I D\left(\frac{1}{\alpha}\right)^{3}$ |
| :---: | :---: | :---: | :---: | :---: |
| Order of Magnitude | $10^{5}$ | $10^{2}$ | $10^{2}$ | $10^{-1}$ |

Table 2 Order of magnitude of the terms in Van der Waals equation for the atmosphere.

For the solutions of Equation (13), we found root $\alpha=0$, which has no physical significance in our study, and root

$$
\begin{equation*}
\alpha=D+\frac{R T}{p} \tag{14}
\end{equation*}
$$

Then we rewrote the Equation (14) explicitly in terms of $p$, presenting a new state equation for the atmosphere that depends only on constant $D$ (Equation 8), which we named $W D$ state equation

$$
\begin{equation*}
p(\alpha-D)=R T \tag{15}
\end{equation*}
$$

On the other hand, we solved the Van der Waals equation (Equation 10) in terms of pressure
within the perspective of the molecular interactions and based on the specific volume $\alpha$, and found

$$
\begin{equation*}
p=\frac{R T}{\alpha-D}-\frac{I}{\alpha^{2}} \tag{16}
\end{equation*}
$$

In this equation, it is identified the pressures responsible for the intermolecular forces of repulsion and attraction between the particles that compose the air, in the first and second terms to the right of the equals sign, respectively. For the atmosphere, the pressure that represents repulsion is of order $10^{5}$, whereas the one which describes attraction is of order $10^{1}$, in such a way that, if we neglect the component of intermolecular attraction in Equation (16), we will again obtain the $W D$ state equation for the atmosphere (Equation 15). This later analysis is equivalent to ignoring the intermolecular attractions in Van der Waals equation for the atmosphere (Equation 10).

Thus, stemming from Van der Waals equation (Equation 10), we present a new state equation for the atmosphere, i. e., the Van der Waals-like state equation (15), which we named $W D$ state equation and depending only on one characteristic constant of atmosphere $D$ (Equation 8), where we have considered the gases that compose the air.

## 4 First Law of Thermodynamics

The first law of thermodynamics for the atmosphere as a closed system per unit mass is

$$
\begin{equation*}
d q-d w=d u \tag{17}
\end{equation*}
$$

where $d q$ is the differential increment of heat provided for the system, $d w$ is the differential increment of work done by the system and $d u$ is the differential increment of the internal energy of the system (Young et al., 1989).

Redefining volume $(\alpha-D) \equiv \alpha^{\prime}$ in $W D$ state equation (Equation 15) and analyze this system, we will find

$$
\begin{equation*}
p(\alpha-D)=p \alpha^{\prime}=R T \tag{18}
\end{equation*}
$$

such that $d \alpha^{\prime}=d(\alpha-D)=d \alpha$ and the work done by the system is given by

$$
\begin{equation*}
d w=p d \alpha^{\prime}=p d \alpha \tag{19}
\end{equation*}
$$

and, therefore, we combined this result with the first law of thermodynamics and found

$$
\begin{equation*}
d q=d u+p d \alpha \tag{20}
\end{equation*}
$$

Stemming from Joule's Law, we verified that the internal energy of an ideal gas depends only on temperature, regardless of the variation in the gas's volume. By comparing the ideal gas law (Equation 1) with the $W D$ state equation (Equation 15), we observed that both differ only by one constant subtracted from the volume, and this way we can still consider the internal energy as uniquely dependent only on temperature. For this reason, the specific heat at a constant volume can be written as

$$
\begin{equation*}
c_{v}=\left(\frac{d u}{d T}\right)_{v} \tag{21}
\end{equation*}
$$

regardless of the variations in volume. Thus, we used the total derivative for this system, governed by the Equation (15) and rewrote the first law of thermodynamics (Equation 20) as

$$
\begin{equation*}
d q=\left(c_{v}+R\right) d T-\alpha d p+D d p \tag{22}
\end{equation*}
$$

When we provide the system with heat with constant pressure, in such a way that it expands and the temperature rises, we define the specific heat as

$$
\begin{equation*}
c_{p}=\left(\frac{d q}{d T}\right)_{p} \tag{23}
\end{equation*}
$$

which, combined with the first law of thermodynamics, gives us the relation

$$
\begin{equation*}
c_{p}=c_{v}+R \tag{24}
\end{equation*}
$$

Finally, we used the Equation (22) and Equation (24) and obtained the alternative form of the first law of thermodynamics for the atmospheric system per unit mass governed by the $W D$ state equation (Equation 15), i. e.,

$$
\begin{equation*}
d q=c_{p} d T-\alpha d p+D d p \tag{25}
\end{equation*}
$$

In the last term of the Equation (25) we noted the dependence in relation to constant $D$. If we assume that $D=0$ in Equation (25), we recover the alternative form of the first law of thermodynamics for atmosphere as ideal gas.

## 5 Potential Temperature and Equivalent Potential Temperature

We studied here the atmosphere as a system per unit mass, considering a layer of air with pressure and temperature $T$, which could be adiabatically expanded or compressed to a new state of reference with pressure $p_{\mathrm{o}}$ and with temperature $\theta$, named potential temperature. In this case, we combined the $W D$ state equation (Equation 15) with the corresponding alternative form of the first law of thermodynamics (Equation 25), and found

$$
\begin{equation*}
\frac{c_{p}}{R} \frac{d T}{T}-\frac{d p}{p}=0 \tag{26}
\end{equation*}
$$

We integrated the above equation from the state of reference with temperature $\theta$ and pressure $p_{\mathrm{o}}$ up to the state with temperature $T$ and pressure $p$, and determined the potential temperature

$$
\begin{equation*}
\theta=T\left(\frac{p_{0}}{p}\right)^{\frac{R}{c_{p}}} \tag{27}
\end{equation*}
$$

Here, the potential temperature $\theta$ referent to the $W D$ state equation (Equation 15) is the same for the atmosphere as an ideal gas. We emphasize that Bolton (1980) found results similar, calculating the potential temperature in a very unconventional way, involving new empirical values of $R$ and $c p$ for dry air.

When we studied the ascending or descending processes of the saturated air, we found the equivalent potential temperature $\theta_{\mathrm{e}}$, describing how temperature varies under these conditions. For this purpose, we remembered that the quantity of rejected (or absorbed) heat $d q$ per unit mass of dry air, due to condensation (or evaporation) of water is given by

$$
\begin{equation*}
d q=-L_{v} d w_{s} \tag{28}
\end{equation*}
$$

where $L_{v}$ is the latent heat of condensation and $w_{s}$ is the saturation mixing ratio. Therefore, we differentiated the logarithm of the potential temperature $\theta$ (Equation 27), and combined it with the $W D$ state equation (Equation 15), first law of thermodynamics (Equation 25) and Equation (28), finding

$$
\begin{equation*}
\frac{-L_{v}}{c_{p} T_{L}} d w_{s}=\frac{d \theta}{\theta} \tag{29}
\end{equation*}
$$

where $T_{L}$ is the air temperature at the pressure level when air saturation occurs for the first time, i. e., at the Lifting Condensation Level.

Assuming that $L_{v} / c_{p}$ is independent from temperature $T_{L}$, we verified easily that

$$
\begin{equation*}
-d\left(\frac{L_{v} w_{s}}{c_{p} T_{L}}\right) \cong \frac{d \theta}{\theta} \tag{30}
\end{equation*}
$$

and, when we integrated the above expression, with the condition that the potential temperature tends to the equivalent potential temperature $\theta_{e}$ when $w_{s} / T_{L}$ $\rightarrow 0$, we found the equivalent potential temperature

$$
\begin{equation*}
\theta_{e} \cong \theta e^{\left(\frac{L_{L} w_{s}}{c_{p} T_{L}}\right)} \tag{31}
\end{equation*}
$$

which is the same expression in the context of an ideal gas for the atmosphere. We point out that Bolton (1980) proposed a new formula for computation of equivalent potential temperature for water-saturation pseudo-adiabatic process, considering the measuring errors by virtue of the variation of the specific heat of dry air.

When the saturation mixing ratio $w_{s}$ of a parcel of air is null, the equivalent potential temperature $\theta_{e}$ equals the potential temperature $\theta$. This happens when all the water vapor is condensed. Thus, we studied the air as a per unit mass system and verified that the potential temperature and the equivalent potential temperature for the atmosphere as a Van der Waals-type gas remained the same for the atmosphere as an ideal gas.

## 6 Virtual Temperature

The ideal gas constant for moist air depends on the portion of water vapor present in the air, since the amount of water in the atmosphere varies constantly. Therefore, it can be used the ideal gas constant for dry air and considered a fictitious temperature in the state equation for the atmosphere, named virtual temperature $T_{v}$.

In this sense, we initially treated a volume of moist air $V$ (dry air plus water vapor), with temperature $T$, pressure $p$ and the density of moist air $\rho=m / V=1 / \alpha$, and analyzed the atmosphere as a
system per unit mass, re-writing the $W D$ state equation (Equation 15) as

$$
\begin{equation*}
p\left(\frac{1}{\rho}-D\right)=R T \tag{32}
\end{equation*}
$$

We then found the partial pressures exerted by the water vapor $e$ and by the dry air $p_{d}$, respectively,

$$
\begin{equation*}
e\left(\frac{1}{\rho_{v}}-D\right)=R_{v} T \tag{33}
\end{equation*}
$$

and

$$
\begin{equation*}
p_{d}\left(\frac{1}{\rho_{d}}-D_{0}\right)=R_{d} T \tag{34}
\end{equation*}
$$

where $R_{v}=461.5 J^{-1} \mathrm{~kg}^{-1}$ is the constant for water vapor and $R_{\mathrm{d}}=287.0 \mathrm{JK}^{-1} \mathrm{~kg}^{-1}$ is the constant for dry air. Here, we used the value of $D$ (Equation 8) for the air and defined the value for the dry air $D_{0} \equiv 3.66103 \times 10^{-5} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$ (value of constant with $0.0 \%$ of water vapor), previously computed from the atmospheric gases.

Besides, we used the respective masses of dry air and water vapor, $m_{d}$ and $m_{v}$, and wrote

$$
\begin{equation*}
\rho=\rho_{d}+\rho_{v}=\frac{m_{d}+m_{v}}{V} \tag{35}
\end{equation*}
$$

where $\rho_{d}=m_{d} / V$ would be the density for the dry air mass, in case it occupied the total volume $V$ alone, and $\rho_{v}=m_{v} / V$ would be the density for the water vapor mass, in case it occupied the total volume $V$ alone.

Thus, we used Dalton's Law $p=e+p_{d}$ and the constant $\varepsilon=R_{d} / R_{v}=0.622$, and combined them with the Equation (33), Equation (34) and Equation (35), and obtained

$$
\begin{equation*}
p=\rho R_{d} \frac{T}{\left[\psi-\frac{e}{p}(\psi-\phi \varepsilon)\right]} \tag{36}
\end{equation*}
$$

where defined

$$
\begin{equation*}
\psi \equiv \frac{R_{d} T}{R_{d} T+D_{0}(p-e)}, \quad \phi \equiv \frac{R_{d} T}{R_{d} T+D e \varepsilon} \tag{37}
\end{equation*}
$$

We rewrote Equation (36) according to the $W D$ state equation for atmosphere (Equation 32),

$$
\begin{equation*}
p(1-\rho D)=\rho R_{d} T_{v} \tag{38}
\end{equation*}
$$

and found the virtual temperature in this new proposal

$$
\begin{equation*}
T_{v}=\left[\frac{1-\rho D}{\psi-\frac{e}{p}(\psi-\phi \varepsilon)}\right] T \tag{39}
\end{equation*}
$$

Here, we observed the dependence of the virtual temperature in relation to constant $D$, when we analyzed the atmospheric system per unit mass governed by the $W D$ state equation (Equation 15). If we consider $D=0$ and $D_{0}=0$ in Equation (33), Equation (34) and hence in Equation(37) and Equation (39), we will obtain $\psi=1, \phi=1$, as well as the partial pressure exerted by water vapor $e$, the partial pressure exerted by dry air $p_{d}$, and the virtual temperature $T_{v}$ corresponding to the atmosphere as an gas ideal.

## 7 Conclusions

Stemming from the mixture of gases which compose the air and from the order of magnitude of the interactions due to the pressures present in the atmospheric system, this paper developed a Van der Waals-like state equation for the atmosphere and analyzed some thermodynamic properties in this new formulation. To do that, we considered the air as a mixture and applied group contribution method through Kay's Rule. Then, we used the critical parameters for temperature and pressure of the gases that compose the air, and computed Van der Waals state equation for the atmosphere. Therefore, we established the two constants which are characteristic for the atmosphere in this relation, $D=3.55832 \times 10^{-5}$ $\mathrm{m}^{3} \mathrm{~mol}^{-1}$ and $I=1.50054 \times 10^{-1} \mathrm{Jm}^{3} \mathrm{~mol}^{-2}$.

We analyzed the atmosphere as a system per unit mass, carried out a study of the order of magnitude of the pressures involved in this environment and determined the relationship between the variables that describe the thermodynamic equilibrium of the system, described as $p(\alpha-D)=R T$, and which depends only on constant $D$. We named this relation $W D$ state equation. After an approach in which we evaluated the pressures responsible for intermolecular repulsion and attraction among the particles which compose the air, we neglected the latter and once again found the $W D$ state equation. Here, by considering $D=0$, we returned to the classical study of air as an ideal gas.
$W D$ state equation corresponded to a linear shift in the pressure-volume diagram, due to a subtraction in the volume, in such a way that we treated the internal energy of the atmosphere as depending only on temperature and used the specific heat at constant volume as the rate of the internal energy with respect to temperature. Therefore, we also defined the specific heat at constant pressure as being a rate of the heat with respect to temperature and obtained the alternative form of the first law of thermodynamics, whose relation presented a correction that depends on $D$. If a parcel of air with a fixed mass is moving about in a hydrostatic atmosphere, the first law of thermodynamics is used to show that the dry static energy is a constant provided the parcel neither gains nor loses heat. Therefore, the dry static energy is expected to depend on $D$ and to remain constant in this new proposal. When we assumed $D=0$, we retrieved the alternative form of this law for the atmosphere as an ideal gas.

In an adiabatic expansion and compression of a layer of air, in this scenario where the $W D$ state equation governs the atmosphere, we observed that the potential temperature had the same behavior for the ideal gas law. Furthermore, when heat was rejected or absorbed in the ascending or descending processes of saturated air, the equivalent potential temperature presented the same form in both scenarios of the state equation for the atmosphere.

Since the amount of water vapor in the atmosphere constantly varies, we calculated the virtual temperature that the air would have in a given pressure and in a determined density, according to $W D$ state equation and in complete absence of this vapor. Thus, the partial pressure exerted by the water vapor depended on $D$, whereas the partial pressure exerted by dry air depended on $D_{0}=3.66103 \times 10^{-5} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$, and the virtual temperature depended on both constants, $D$ and $D_{0}$, characterizing the atmosphere in this new state equation proposal. Once again, when we chose $D=0$, we retrieved the ideal gas law and the corresponding partial pressures exerted by water vapor and by dry air for the air.

We emphasize here that we can apply a method analogous to the one developed in this paper in
regions of the planet where the atmosphere has high variations in the concentration of a specific gas, such as carbon dioxide or ozone, determining the values corresponding to constants $D$ and $I$ for the air in these areas. In this case, we also need to measure the consequently variations of the other gases, such as the greenhouse gases. As an example, we could consider the worst-case scenario for the Earth's atmosphere in the next 100 years, if the greenhouse gases triple, to compute the constants $D$ and $I$, which would be about $D=3.55990 \times 10^{-5} \mathrm{~m}^{3} \mathrm{~mol}^{-1}$ and $I=1.50237 \times 10^{-1} \mathrm{Jm}^{3} \mathrm{~mol}^{-2}$, respectively.

An especially interesting issue is the use of the ideal gas law and of the $W D$ state equation to calculate the virtual temperature. Firstly, if we consider a tropical environment with a temperature of $35^{\circ} \mathrm{C}$ and water vapor mixing ratio of $w=0.03$, the virtual temperature is $T_{v}=40.6^{\circ} \mathrm{C}$ for atmosphere as ideal gas. Moreover, in the context of the WD state equation with water vapor pressure $e=57.60 \mathrm{hP} a$, dry air pressure $p_{d}=1107.19 \mathrm{hPa}$, the density of the dry air $\rho_{d}=1.250 \mathrm{kgm}^{-3}$, the density of the water vapor $\rho_{v}=0.0405 \mathrm{kgm}^{-3}$ and the values of and $D$ in $D_{0}$ in $\mathrm{m}^{3} \mathrm{~kg}^{-1}$, the new value of the virtual temperature is $T_{v}=40.9^{\circ} \mathrm{C}$, which corresponds to a small variation of $0.3^{\circ} \mathrm{C}$ in $T_{v}$. According to the Equations (32)(39), greater differences are expected when extreme climate events occur.

We further suggest that, if we get to know the components of the atmospheric system of another planet, it would be worthwhile to apply the group contribution method and Kay's Rule in order to study a new state equation and to analyze the thermodynamic properties in this environment.

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## 9 References

Bolton, D. 1980. The Computation of Equivalent Potential Temperature. Montly Weather Review, 108: 1046-1053.
Daubert, T.E. \& Bartakovits, R. 1989. Prediction of Critical Temperature and Pressure of Organic Compounds by Group Contribution. Industrial and Engineering Chemistry, 28: 638.
Guggenheim, E.A. 1945. The Principle of Corresponding States. The Journal of Chemical Physics, 13: 253.
Jalowka, J.W. \& Daubert, T.E. 1986. Group Contribution Method to Predict Critical Temperature and Pressure of Hydrocarbons. Industrial \& Engineering Chemistry Research, 25: 139.
Jenkins, A.C. \& Birdsall, C.M. 1952. The Vapor Pressures and Critical Constants of Pure Ozone, The Journal of Chemical Physics, 20: 1158-1161.
Joback K.G. \& Reid, R.C. 1983. Estimation of Pure-Component Properties from Group Contributions, Chemical Engineering Communications, 57: 233.
Kay, W.B. 1936. Density of Hydrocarbon Gases and Vapors, Industrial and Engineering Chemistry, 28 (9): 1014-1019.
Laird, T. 1996/1997. Ullmann's Encyclopedia of Industrial

Chemistry, Organic Process Research \& Development, 1 (5): 391-392.
Luiz, A.M. 2007. Física 2. Gravitação, Ondas e Termodinâmi$c a$. São Paulo, Editora Livraria da Física, 294p.
NASA. 2016. National Aeronautics and Space Administration, Earth Fact Sheet, Available in <http://nssdc.gsfc.nasa. gov/planetary/factsheet/earthfact.html>. Access in December 05, 2017.
Smith, J.M.; Van Ness, H.C. \& Abbott, M.M. 2005. Introduction to Chemical Engineering Thermodynamics. Boston, McGraw-Hill, 817p.
Trace Gases. Manchester Metropolitan University. 2010. Available in <https://web.archive.org/web/20101009044345/ http://www.ace.mmu.ac.uk/eae/atmosphere/older/ Trace_Gases.html>. Access in December 05, 2017.
Van der Waals, J.D. 1873. On the Continuity of the Gaseous and Liquid States. Doctoral Dissertation, Leiden University, Netherlands.
Wallace, J.M. \& Hobbs, P.V. 2006. Atmospheric Science: an introductory survey, San Diego, Elsevier, 504p.
Young, H.D.; Freedman, R.A.; Sandin, T.R. \& Lewis Ford A. 1989. Sears and Zemansky's University Physics. San Francisco, Addison-Wesley, 1280p.

